International Workshop

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

Final Programme

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10 & 11
December 2009
Paris
UNESCO

Based 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.

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.

Expected outcomes

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

Thursday 10 December 2009 Scientific state of the art dedicated to classical and most innovative approaches of nitrate monitoring	
12h30	Registration
13h30 13h45	Welcome and opening, Alice Aureli, UNESCO; David Widory, BRGM 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 Valued of isotope approache: 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

Detailed agenda of Thursday 10 December 2009

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

Detailed agenda of Friday 11 December

Alternative methods to support water stakeholders in managing nitrate pollution	
09h00	**Introduction of day II** **David Widory, BRGM** **Nitrate Pollution Management: the transboundary challenge** **Daniel Valensuela, INBO**
09h15	**Session 3: Added Valued of isotope approache: demonstration of ISONITRATE case studies** **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	**Discussion**
10h25	**Coffee break – Posters session**
10h55	**Session 4: How to implement multi-isotope approach?** **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***	**Discussion**
12h30	**Closing remarks** ▪ **'Take home messages', Jeroen Casaer, DG Environment** ▪ **Conclusion and next steps, David Widory, BRGM**
13h00	**End of the workshop**

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[1] and the Urban Waste Water Directive[2]. Both directives form an integral part of the Water Framework Directive[3] 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.

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

[1] Directive 91/676/EEC concerning the protection of waters against pollution caused by nitrates from agricultural sources; OJ L375 – 31/12/1991
[2] 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
[3] Directive 2000/60/EC concerning the establishment of a framework for Community action in the field of water policy; OJ L327 - 22/12/2000

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[4] 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, 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 though means of the life instrument[5].

Session 1: Current nitrate pollution monitoring and management

Classical surface and groundwater monitoring for NO3: 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 it's 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

[4] Commission Staff Working Document SEC(2009) 1114 final, 3.8.2009

[5] More info about LIFE: http://ec.europa.eu/environment/life/index.htm

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 it's 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 campaigns. Regional differences are related to physico-chemical boundary conditions in combination with source-related pressures. A clear link the 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 was 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

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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 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^2) 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

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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 ^{15}N, ^{18}O and ^{11}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: ^{14}N, ^{16}O and ^{10}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 ^{15}N and ^{18}O natural abundance in nitrate (NO_3^-) and the ^{11}B abundance in boron (B^-) have been used and are denoted as: $\delta^{15}N\text{-}NO_3^-$, $\delta^{18}O\text{-}NO_3^-$ and $\delta^{11}B$, respectively. The isotopic composition of NO_3^- and B can be measured using dedicated sample preparation techniques to remove interfering compounds and state of the art mass spectrometry. For $\delta^{15}N\text{-}NO_3^-$ and $\delta^{18}O\text{-}NO_3^-$tree sample preparation techniques can be used: the so called “$AgNO_3$”, “bacterial denitrification” and “Cd-reduction” method. For analyses an Isotope Ratio Mass Spectrometer (IRMS) coupled to a high temperature elemental analyzer ($AgNO_3$ method) or a trace gas unit (bacterial denitrification and Cd-reduction) is needed. For $\delta^{11}B$ 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. ^{15}N, ^{18}O and ^{11}B. This implies that unidirectional reactions with 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 (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 ($\delta^{15}N$ and $\delta^{18}O$) and associated dissolved species ($\delta^{11}B$) 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 NO_3 levels in water (i.e. samples with higher NO_3 are considered polluted). The measured low 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 NO_3 budget in water.

d) Complex case: sampling sites where 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

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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 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 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 Valued of isotope approache: 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 $mg.L^{-1}$. 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 $mg.L^{-1}$.

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 ($\delta^{15}N-NO_3$, $\delta^{11}B$) 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 NO3- 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 NO_3 levels in water (i.e. samples with higher 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 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 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 ?

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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 rule 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

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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
- 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.

Posters summaries

Posters session on Thursday 10 December

Use of $\delta^{15}N$ and $\delta^{18}O-NO_3$ isotopes as indicators of nitrate sources in the quaternary sand aquifer of Thiaroye (Dakar, Senegal)

S. Cissé Faye[6]; V. Re[7]; M. Diedhiou[6]; O. C. Diouf[6]; S. Faye[6]; C.B. Gaye[6]; S. Wohnlich[8]

Ten years of monitoring groundwater has shown that nitrate was and still is the major groundwater pollutant in the Thiaroye Quaternary sand aquifer. Hydrogeological and environmental context of the study area reveals that potential sources and fate of nitrate may be widely diversified; they can derive from mixing of nitrate from different contamination sources – precipitations - individual septic tanks – effluent spread on soil and leached fertilizers into the aquifer during recharge periods.

The objectives of this research were to study the distribution of NO_3^- in the aquifer and to establish the effectiveness and applicability of nitrogen and oxygen isotopes contents in dissolved nitrates as useful technique to help identifying sources and fates of nitrate in groundwater. The most recent samples collected in July 2009 showed excessive elevated NO_3^- levels between 400 – 700 mg/l, where 60% of the wells exhibit NO_3^- concentration higher than the WHO standards of 50 mg/l.

The isotopes approach regarding ^{15}N and $^{18}O-NO_3$ based on the distinct isotopic composition that characterized nitrate of different origin are used to discriminate origins and geochemical process in the groundwater system.

The $\delta^{15}N$ of NO_3^- ranged between +8.2 and +22.2 ‰ where 65% of the wells exhibit values greater than +10‰. These occur in the unsewered suburban areas where is located the pumping field (F17; F19; F21; F22; P3-2) or in the rural areas with domestic wells (Pts. 202, Pts.02, Pts.234). Highly enriched nitrates with $\delta^{15}N$ (NO_3) compositions greater than +10‰ are generally interpreted as representing local pollution by animal or sewage waste. The nitrate concentrations of these groundwater samples are high as 100 - 700 mg/l. Given the urban development and the lack of sanitation system in the fast growing suburban areas, point-source anthropogenic pollutants from septic or sewer effluents or non-point source with effluents spread on soils are more probable origin of high nitrate level in the Thiaroye unconfined sand aquifer.

Wells P2-10; P2-7, and P3-2 contain groundwater nitrate which $\delta^{15}N$ (NO_3) values are greater than +10‰ (+11.25; +15.15 and +19.26‰ respectively) and reflect a similar source but at a much lower concentration (NO_3^- content are 14.5; 41.29 and 11.76 mg/l) which could be interpreted as a minor denitrification process.

No groundwater samples had $\delta^{15}N-NO_3^-$ values within the range of fertilizers (-2 to 0‰); this support the view that fertilizers which was one of the suspected nitrate sources did not represent a significant contributor of nitrate contamination.

Fourth values lie within the range +4 - +10‰ suggesting that nitrate is probably derived by mineralization and nitrification of soil organic nitrogen, however $\delta^{15}N$

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values between +8 and +10‰ are probably derived from a mixture of animal or sewage waste and soil organic NO_3^-.

The $\delta^{18}O$- NO_3^- of groundwater NO_3^- ranged between +8.52 and +15.59‰ (SMOW), lie within the range of NO_3^- produced by nitrification of NH_4 from manure and sewer and from mineralized organic nitrogen of the soil. The plot of $\delta^{18}O$ versus $\delta^{15}N$ reveals values shift in positive direction with an isotopic enrichment during the denitrification process which taking place in the system.

The $\delta^{15}N$- NO_3^- and $\delta^{18}O$- NO_3^- confirmed that nitrate in the Thiaroye unconfined sand aquifer was predominantly derived from septic or sewer effluent, non-point source with effluents spread on soils and the soil organic nitrogen flushed into the aquifer during fall recharge. The nitrogen contamination in the aquifer is less extent from synthetic fertilizers. The $\delta^{18}O$- NO_3^- data further suggested the nitrification process occurred with ammonium from the soil organic nitrogen, manure and sewer. The $\delta^{15}N$- NO_3^- and $\delta^{18}O$- NO_3^- data conclusively indicated that denitrification is taking place in the Thiaroye aquifer.

Nitrate occurrence in natural springs: origin and background concentration in the Osana region (NE Spain)

A. Menció, M. Boy[9], J. Mas-Pla[9]

Natural springs usually reflect the hydrological processes that occur at the upper subsurface layers. They are valuable indicators of the water cycle dynamics at the subsoil as well as of the response to fertilizer application to crops. In this study, we evaluate nitrate concentration in 131 natural springs of the Osona region (NE Spain) for a sampling period of 5 years. We seek a relationship between nitrate pollution, geological setting and land use.

The Osona region (1260 km2) has intensive livestock and agriculture activities, and manure production is used as fertilizer. Consequently, high values of nitrate are found in groundwater. Natural springs have been classified according to their geological setting: crystalline rocks, prequaternary sedimentary rocks, quaternary sedimentary rocks, and regional fault zones. Land uses (agricultural, forested, and urban) in the recharge areas have been considered, as well as meteorological data.

Results show that nitrate concentration in spring waters ranges from <1 mg/L to 256 mg/L, with an average of 75.7 ± 67.1 mg/L. More than half of the collected samples have average nitrate concentrations higher than 50 mg/L. The highest nitrate concentrations are found in springs located in agricultural areas on prequaternary and quaternary sedimentary rocks. Flow paths through fractures or coarse-grained alluvial layers permit an effective transport from manure application areas to springs. In addition, springs in crystalline rocks drain surface weathered formations as well as the underlying fractured material. As manure is seldom applied in these areas, springs are less affected by nitrate pollution.

In average, nitrate concentrations decrease after drought periods, and they are particularly high when rainfall has been intense in the preceding months. This indicates that water storage on the soil plays a significant role on the spring water chemistry. High nitrate levels point out a complete transformation of organic nitrogen to nitrate, suggesting some time delay between the rainfall event and the spring response. A nitrate background concentration lower than 10 mg NO_3^-/L has been calculated using statistics methods This threshold value indicates that larger nitrate concentrations are due to anthropogenic sources.

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This project reveals the importance of spring hydrochemistry long-term databases to evaluate the effects of anthropogenic activities on groundwater quality, and the vulnerability level at specific locations. New policies on nitrate management and land-use control can be inferred to prevent spring water as well as groundwater pollution.

This study has been funded by Spanish Government Project CICYT CGL2008-06373-C03-03, and by the Consell Comarcal d'Osona through a grant for regional studies.

Agriculture and nitrate contamination of groundwater in the irrigated perimeter of Beni Amir,Tadla, Morocco: water balance and mass balance method.

Houria DAKAK[10] [11], Aicha BENMOHAMMADI[11], Brahim SOUDI[12]3, Ahmed DOUAIK[10], Mohamed BADRAOUI[10], Mouanis Lahlou[12], Mohamed Kobry[13]

This work presents the problem of diffuse agricultural pollution and its impact on the degradation of groundwater quality used for irrigation. He traces the objective the qualitative and quantitative study in terms of nitrate contamination of aquifer water in the irrigated area of Beni Amir, Tadla - Morocco,for assessing the effect of intensive agriculture on the physico-chemical quality of groundwater and appreciate the different ways to use these water resources. An approach has been followed with the realisation the water balance and the nitrogen apparent mass balance across a hydrological unit of 2060ha located in this area. A diagnosis of the current quality of groundwater nitrate was carried out by setting up a network of 50 water points. The results show a relative deterioration of the water, the water wells tested show nitrate levels below 50 mg/l with a maximum of 52mg/l. The observed situation is not alarming as that of the whole area of Beni Amir, which can reach 150mg/l with 53% of wells tested exceed the maximum allowable for drinking water. Thus the results of the water balance approach for the years 2006-2007, showed that the water level has decreased due to drought and development of agricultural pumping, and this decline has resulted in a destocking the order of 630m3/ha/an. An attempt to establish mass balance for the determination of nitrate reaching the water allowed to quantify an average rate of nitrate nitrogen of 32.65 kg/ha/year, this shows the potential problem of nitrate pollution of waters groundwater in this region.

Keywords: Water quality, nitrate ,agriculture, mass balance, nitrogen mass balance.

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Environmental and dietary exposure to nitrate in central Lebanon

Talal Darwish[14], Therese Atallah[15], Safa Baydoun[16]

Agriculture in Lebanon is concentrated mainly in the fertile Bekaa plain, where intensive agricultural practices prevail. Due to weakness of policies and extension service, farmers apply excessive chemical fertilizers notably nitrogen. Consequently, ecological and health problems are suspected due to nitrate accumulation in the soil-groundwater-food chain. We have monitored the status of soil and GW quality in Terbol area located in Central Bekaa Plain. Soil and water samples were collected between July 2007 and July 2009. The aim was to assess current agricultural practices, soil vulnerability to nitrate leaching and to study soil and groundwater exposure to nitrate pollution. Nitrate dietary exposure from the consumption of main vegetable was evaluated. After excluding extreme cases, the estimation of nitrates and nitrites daily dietary exposure was based on food frequency study of 419 individuals from the same region. Soil samples were taken in four representatives plots under four different existing agriculture practices (leafy vegetable monoculture, potato-lettuce rotation, wheat-potato rotation and grape fields). GW samples were systematically taken from 25 wells water is used for irrigation, industrial and domestic purposes. Analytical water results show alarming levels of nitrate concentration in a number of wells mainly in the central part of the plain reaching 517.7 mg NO_3 L^{-1}. Soil data show large accumulation of nitrates towards the end of the cropping season in the topsoil layer reaching 102 mg Kg^{-1} soil. Due to nitrate leaching by intensive irrigation, higher amounts of nitrates are found at deeper layers which could not be detected from the root zone after one winter season. Results were confirmed using Cl tracer technique.

A GIS soil model based on soil properties affecting soil infiltration, like soil depth, soil texture, soil structure type and strength, organic matter content, pore abundance and size, was elaborated to assess soil vulnerability to leaching. Results show medium and high vulnerability in the larger area of the Central Bekaa plain, with very high vulnerability in the foot slope due to larger porosity and infiltration rates. The drawn soil and GW maps are useful tools for decision makers and local stakeholders including consumers delineating critical areas where special care must be applied to control N input and balance in the soil-GW system and food chain.

Our results show an average intake of 3363.6 Calories/day and daily intakes of potatoes, tomatoes, lettuce, spinach and parsley to be 140.78, 50.45, 37.07, 20.13 and 40.12 g/day, respectively. The consumption of only these vegetables showed an exposure of 3.32 mg/kg bw/day of nitrates. This dose is on the upper boarder line of the Acceptable Daily Intake (ADI) of 0-3.7 mg/kg bw/day evaluated by the Joint FAO/WHO Expert Committee on Food Additives (JECFA). Ecological and health risks imply further assessment studies and the implementation of tools and strategies to control agricultural practices and the excessive use of fertilizes in Lebanon.

Key words: Soil, Groundwater, Nitrate accumulation, Nitrate leaching, nitrate exposure

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Agricultural nitrate pollution in heterogeneous fissure hydrogeosystems (Brittany, France)

Jean Pierre Faillat[17]

This paper is focused on agricultural nitrate (mainly organic) and denitrification (synthesis by Mariotti, J. Hydrol.,1986; Heaton, Chem. Geol., 1986 and Korom, Water Resour. Res.,1992). Structural geology (faults and fracturation), geophysics (electrical and electro-magnetic), drillings, hydrogeochemistry and hydrodynamic have been used.

The Kerharo river basin (50 km^2) was chosen for a study on two scales (Faillat and Somlette, IAH Coll., Avignon, 1995; Somlette, UBO Thesis, 1998; Faillat et al., Bull. Soc. Géol. Fr., 1999): river basin and experimental perimeter. The Kerveldréac'h experimental perimeter (0.35 km^2), here presented, is a mixed farming area on a 4 to 5 % average slope; pigs, cows and maize, wheat and grazing land are above Brioverian sandstone schist.

Eight boreholes from 35 to 55 m deep (diameter 140 mm), 10 piezometers from 10 to 22 m deep (120 mm) and 8 auger borings from 1.2 to 2.3 m deep were executed in two steps. They complemented 2 existing wells, 1 borehole, 23 drains (depth 0.5 to 1 meter) installed by farmers and a spring. Auger borings, piezometers and boreholes were laid out in sets of three so that each of them covered topsoil, weathered rock or fissured rock. The boreholes were grouted only in the weathered layer and the deeper parts were not cased. The piezometers were grouted in the topsoil layer. The total flow intake to the boreholes was graduated from 4 to 25 $m^3.h^{-1}$. There were 43 fissures with 3 to 9 m intervals in the 8 boreholes. All these boreholes were located at three sites 300 to 400 m apart: base, middle and near the top of the slope. Boreholes and piezometers were 5 to 60 m apart at the same site.

Pumping tests indicate the presence of a semi-captive fissured aquifer with T= 1.10^{-5} to 1.10^{-3} $m^2.s^{-1}$ and S = 1.10^{-4} to 1.10^{-3} and a leakage effect. The continuous recording of water level variations in 4 boreholes coupled with rainfall in 3 rain gauges revealed short reaction times and varying sensitivity and amplitude after rainfall according to the morphological position and the depth of the piezometric level. A NW-SE oriented threshold less than 10 m wide divides the site into two compartments of different piezometric levels (4-5 m).

The results show that the structure of the Kerveldréac'h experimental perimeter consists of a generalized, more of less connected fissured aquifer in the Brioverian sandstone schist. Alternate of sandstone or clayey levels, schistosity and fracture orientation dominates aquifer geometry, resulting in anisotropy, heterogeneity and compartmentation of the aquifer. The surface formations have a storage function and the fissures have a drain function. They constitute a double layer drain-storage system.

In a four years period of observation, several variations have been observed in the chemical characteristics of the water from high nitrate and low sulphate concentrations to low nitrate and high sulphate concentrations with the appearance of iron and a decrease in electrical conductivity (EC). These changes have been correlated with an inversion of the hydraulic head, indicating a flow reversal between fissures with different hydraulic heads, as illustrated by electrical conductivity logs. Under undisturbed conditions, the EC_{20} varied between 280 and 320 $\mu S.cm^{-1}$ with nitrate concentrations of 60 to 90 $mg.l^{-1}$. During low water periods, a decrease of 20 to 40 $\mu S.cm^{-1}$ in EC and nitrate concentrations of less than 10 $mg.l^{-1}$ has been observed. A one-year test with a permanent packer

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in a borehole, situated between reduced fissures (lower) and oxided fissures (upper) show the reality of different hydraulic heads and of permanent vertical oxido-reducing levels (Goujon, Poitiers Thesis, 2005). Under pumping conditions, EC and nitrate concentrations result of the mixing of waters.

The pattern deduced from these experiments consists of the superposition of two levels. The upper level less than 30 m thick, oxidized with nitrate, is separated by an oxido-reduction barrier (concept by Edmunds, Proc. Tokyo Symp.,1970), horizontal and very thin here, from a reduced level where organic matter, ferrous iron and sulphide (essentially pyrite) are oxidized and nitrate is biologically reduced. The denitrified level nearly outcrops in the intermediate site where artesian flow has been observed. Field data have shown the two-hydrochemical poles in deep boreholes and in piezometers.

The superposition of two different redox levels in the experimental perimeter is now demonstrated. Moreover, observations in the experimental perimeter of Maupertuis, near Saint-Brieuc (Côte d'Armor), with fissured granite rocks, shows the same functioning, with a oxidized level less than 50 m thick (Marjolet et al., Interceltic Symp. Aberrystwyth, 2000). So, this hydrochemical vertical zoning might extend to all the Brioverian and the other formations of the Armorican bedrock. In the same way, this might be true in all countries with similar hydrogeological characteristics, where water supplies without nitrate are systematically possible if water resources are accessible more than 30-50 m depth. In an other way, it appears that study of hydrochemical phenomenons in heterogeneous aquifer are of a reduced interest if representative sampling is not done, that require the use of packers or a set of pumps and boreholes carefully located and equipped (Faillat et al., Coll. ADEME, Paris, 2002).

Natural Attenuation of Nitrate in the Pétrola Basin groundwater's (SE Spain)

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Groundwater nitrate contamination can cause serious health problems in both humans and domestic animals, and contributes to the eutrophication of surface water bodies. Furthermore, this problem affects all countries in the world, independently of their development level. Denitrification is the only effective process that irreversibly eliminates nitrate from groundwater environments. In natural systems, denitrification is limited by the availability of electron donors such as organic carbon, sulphides and Fe^{+2} that leads to nitrate elimination throughout NO_3^- conversion into harmless N_2.

The unconfined sandy aquifer of the Endorreic Pétrola lake Basin (Segura River Basin, Spain), which sustains a saline wetland, is located in a region declared as "vulnerable area to nitrate pollution" (Resolution 07/08/1998 and 10/02/2003 of the JCCM). In fact, the lake is classified as a heavily modified water body. Groundwater is contaminated by nitrate, whose concentration can reach values of up to 133 mg/l. There are, however, water points in the area in which nitrate contents are below the detection limit. The fluid-rock mechanism leading to nitrate attenuation in the groundwater

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occurs in a buried lower Cretaceous organic and sulphide rich sandy-clayey unit (ARMO). Thus, one of the objectives of the research was to understand the role of ARMO in the reduction of NO_3^- input to the aquatic system. Recovered material from four drill holes showed that organic matter from vegetal remains and secondary sulphide minerals are common in ARMO deposits. Total organic carbon contents in organic rich clayey sediments range from 0.28 to 0.76%.

A microcosm scale experiment using ARMO sediment has been carried out to understand the natural attenuation processes and to quantify denitrification by means of a multi-isotopic analysis. The microcosm experiment consisted in a flow-trough column filled with ARMO sediment. The flow rate was controlled by a peristaltic pump and ranged form 0.1 to 0.01 ml/min. The experiment was carried under anaerobic conditions in an Ar chamber. The outlet of the column has been sampled and analyzed regularly during 8 months. Results showed a complete attenuation of nitrate concentration after 2000 hours. The rate of attenuation is controlled by the water residence time in the ARMO sediment. During denitrification, as nitrate concentration decreases, residual nitrate becomes enriched in heavy isotopes ^{15}N and ^{18}O with a εN/εO ratio that ranges from 1.3 (Fukada et al., 2003) to 2.1 (Böttcher et al., 1990).The isotopic data in the present study indicated that attenuation is due to denitrification that is probably driven by dissolved organic matter oxidation.

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Behaviors of the basic elements compared to the modifications of the nitrate: Concentrations in subterranean water of Mitidja

Ouahiba Hadjoudj[22]

Within the framework of a study relating to “pollution of subterranean water of Mitidja by nitrates”, a complete physicochemical analysis using standardized analytical methods related to eight hundred and sixty taking away of water which were the subject of the analysis physicochemical of ten parameters besides nitrates namely: pH, Conductivity, Bicarbonates, Calcium, Magnesium, Chlorides, Sulfates, hardness, Sodium, Potassium.

A statistical analysis (Software SPSS version 12.0) was applied to more than nine thousand four hundred results on the whole, which enabled us to understand the existing correlations between variations of the nitrate concentrations related to pollution and all ten parameter analyzed simultaneously. It is primarily come out from it a very significant correlation

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between nitrates and the ions calcium, chlorides, conductivity and hardness ($p<0,01$) and a significant correlation between nitrates and Magnesium ($p<0,05$)) and between nitrates and the sulfates ($p<0,05$). However the nitrates are not correlated with sodium, bicarbonates, potassium and the pH.

Key words: Nitrate, correlations, pollution.

Modelling the influence of climate change on N-Leaching and the water balance: a regional study of farmland in Denmark

Jensen, N.H. & Veihe, A.[23]

Climate change and the associated changes in land-use are expected to affect thehydrological processes and the water quality. In this study the dynamic agro-ecosystems model 'Daisy' (Hansen et *al.*1991) was used for assesing changes in nitrate leaching and the water balance as a result of climate change predicted by IPCC's scenario A2 for 2070-2100. The Daisy-model was set up for a number of representative soil types and crop managements for the island of Zealand in Denmark. Three scenarios were modelled. In the first scenario, the present situation was modelled providing the basis for an assessment of future changes. In the second scenario, climate was changed as indicated in table 1 (see annexe p49). In the last scenario, sowing dates of the crops were changed to 1 month earlier and maize was introduced into the crop rotation. It was found that evapotranspiration increased while percolation and drainage remained at the same level as at present although there was a variation depending on soil type and land management. Average weighted nitrate leaching rates increased by 24% if management practices were kept constant, whereas a status quo is expected when management options are changed too (table 2, see annexe p49). However, Daisy is sensitive to inputs in the soil organic N pool and a better understanding of how this pool develops in a climate change situation is required if reliable predictions should be obtained together with an assessment of the effect of land management changes.

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Nitrate concentrations in drinking water for animals – Data of the « Centre AntiPoison Animal et Environnemental de l'Ouest ».

Martine KAMMERER[24], Sabrina LECLERC[24], Alexandra PONCET[24]

The "Centre AntiPoison Animal and Environmental de l'Ouest" (CAPAE-Ouest) is a telephone information and research service in animal and environmental toxicology, attached to the Pharmacology and Toxicology department of the National Veterinary School of Nantes. It often receives questions about drinking water quality for animals, because a lot of farms are supplied with water from private wells or bore-holes which do not comply with quality norms for human drinking water. Now, in Europe there are no specific norms for animal drinking water. In this poster, calls about nitrate concentrations are presented and discussed in relation with animal health and characteristics of the source (60 calls). The concentrations are spread out between 0 and 195 mg/l. These data enable progress to be made in the knowledge of toxic doses of nitrate for animals and of quality of groundwater in French agricultural areas.

Keywords : nitrate, groundwater, drinking water, animal, poison center

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Comparison of a low-nitrogen – high flux alpine catchment with a high-nitrogen – low flux lowland catchment by isotopes of nitrogen and oxygen in nitrate

M. Kralik[25], F. Humer[25], & J. Grath[25]

The nitrogen budget of two sub-basins of the river Danube have been calculated by the empiric emission model MONERIS (Behrendt et al. 1999) by SCHILLING et al. (2006).

The mainly alpine Ybbstal catchment is dominated by forested karst mountains (up to 1800m) at the northern front of the Eastern Alps. Just the area close to the Danube is used for intensive agriculture. High yearly precipitation rates (up to 1750 mm/a) and low mean temperatures results in high recharge rates with relatively low nitrate concentrations.

The second low-land catchment Wulkatal is close to the Hungarian border in the Pannonic climate with low precipitation rates between 500 – 600 mm/a. Intensive agriculture causing high nitrate concentrations in the groundwater and in the out-flowing river Wulka.

The Umweltbundesamt started a project aiming to evaluate the estimated and calculated nitrogen emissions transported by groundwater using isotopes of nitrogen and oxygen in nitrate. The combination of theses isotope should also help to identify sources of nitrogen coming from atmospheric deposition, mineralisation of organic soil, nitrate fertilizer and nitrate coming from manure or septic waste tanks.

The selection of sampling sites depends on background information and data previously measured by SCHILLING et al. (2006) as well as nitrogen source locations mentioned above.

The so far evaluated measuring results are in good agreement with the designated fields for the nitrate sources by MAYER et al. (2002) based on KENDALL & MCDONNELL (1998). A second sampling campaign supported the first measuring results.

The results of this investigation has to be compared with the calculations of the empiric emission model MONERIS (BEHRENDT et al. 1999) verifying primarily the assessment regarding the pathway groundwater by the use of stable isotopes.

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Identification of the nitrate contamination sources of the Brusselian sands groundwater body (Belgium) using a dual-isotope approach

Samuel Mattern, Marnik Vanclooster

Knowledge of the groundwater pollution source is of primary importance to define appropriate remediation strategies. Yet, the identification of the contamination sources remains a complicated task. A dual isotope approach (combination of $\delta^{15}N$ and $\delta^{18}O$ of nitrate) has been used to provide information for tracing sources of nitrate in water.

In this study, we used the naturally occurring stable isotopic composition of groundwater nitrate (1) to evaluate the origin of nitrate in the Brussels sands aquifer (Belgium") and (2) to study the temporal dynamics of the isotope signature of groundwater nitrate in this region.

Potential N sources sampled in the region, including e.g. ammonium and nitrate mineral fertilizers, sewage and rain, had isotopic signatures that fell within the corresponding typical ranges found in literature. Some of them however deviated from the isotopic ranges corresponding to typical N sources, illustrating the impact of processes affecting the isotopic signature of the nitrate sources.

During a pluri-annual sampling campaign, groundwater samples were collected at 10 moments between June 2007 and February of 2009 over 9 monitoring stations located in the western part of the study area. The isotopic data time series suggest that, most of the time, N applied on the soil has been cycled in the soil by micro-organisms before leaching to the groundwater, while the isotopic data and the high nitrate concentrations strongly suggests that nitrate of the groundwater sampled in January 2008 principally originates from mineral fertilizers.

The isotopic data measured at some of the 114 monitoring stations across the study area strongly suggests that the sources of nitrate are mineral fertilizers used in agriculture and golf courses, manure leaching from unprotected stockpiles in farms, domestic gardening practices, cesspools and probably cemeteries.

Isotopic data are particularly helpful when associated with other information like historical data about monitoring stations, land use, chemical parameters of water or statistical and deterministic models and must therefore be considered as one of the many elements of pollution sources identification.

Nitrate Contamination of Groundwater in Quaternary Sand Aquifer: A Case Study in Dar es Salaam, Tanzania

MTONI, Yohana[26 27], MJEMAH, Ibrahimu Chikira[28] & WALRAEVENS, Kristine[26]

The quaternary sandy aquifer in Dar es Salaam region is an important aquifer which provides a significant contribution to domestic water supply. However since recent decades, the demographic expansion of Dar es Salaam population and lack of proper sanitation have resulted in a strong deterioration of groundwater quality. High nitrate concentrations have been encountered in various parts of the aquifer especially in the high-density housing settlements. Water samples for water quality analysis were collected from 40 boreholes located on both shallow aquifer and lower aquifer. Over 50 percent of water samples show raised

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concentrations of nitrates in shallow aquifer and out of these nearly 50 percent have higher than permissible value of 50mg/L according to World Health Organization standard.

Elevated nitrate levels (40–100 mg/l) within the City Centre can be related to the leaking from unrehabilitated aging sewerage system. Nitrate values (> 100mg/l) in dense informal settlement areas are due to a higher density of pit latrines. 75 percent of the city's residents live in unplanned and unserviced settlements. About 80 percent of residents living in these settlements use pit latrines, which are usually poorly constructed causing health and major environmental problems. Tanzania Health Policy (1990) recognizes water borne diseases are among the critical challenges in Tanzania, as they are in other developing countries. Apart from domestic sources of pollution, groundwater is also at risk from industrial effluents and coastal salinization.

Both Tanzania National Environmental Policy (1997) and Water Policy (2002) support the overall national objective of providing clean and safe drinking water for its inhabitants. The former promotes efforts to protect water sources and prevent environmental pollution whereas the latter promotes water management system which ensures protection of the environment and protection of the ecological system and biodiversity. In spite of the existence of these policies, the situation is continuously deteriorating. Most residents in informal settlements do not have access to adequate housing and lack access to safe water and sanitation, while untreated waste surrounds them affecting their health. In order to improve and expand the water and sanitation services, devoted efforts are needed to enhance intersectoral coordination and cooperation, and frameworks facilitating stakeholder participation.

Keywords: Dar es Salaam, Quaternary sand aquifer, Nitrate contamination, Water and sanitation, services, Informal settlement

Application of the multi isotope approach to tackle nitrate pollution in water resources from Lombardy (Northern Italy)

E. Sacchi[29,30], C. Delconte[30], E. Allais[31]

The Po plain supports most of the agricultural and industrial activities of Northern Italy, and hosts several large urban settlements, all associated with groundwater exploitation and pollution. In Lombardy, the implementation of the EC directives has lead to the designation of large areas vulnerable to nitrate pollution, covering about half of the plain area, where the use of fertilisers, especially manure, is restricted. Nevertheless remedies undertaken seem not to be effective. When multiple potential nitrate sources exist, stable isotopes of dissolved nitrates (^{15}N and ^{18}O) represent a powerful investigation tool, enabling the identification of nitrate sources, the assessment of their relative contribution to nitrate pollution and the quantification of nitrate transport and removal processes. Additional information can be provided by B and Sr isotopes, allowing a better discrimination between manure and sewage derived nitrates.

This research project is co-funded by CNR-IGG and Regione Lombardia, Department of Agriculture. The project investigates nitrate origin and attenuation processes using isotope techniques within the unsaturated zone, in surface water (main rivers and irrigation channels) and in groundwater from the phreatic aquifer.

The project is currently in its second year.First results indicate that synthetic fertilisers and leakage from the sewage

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network represent the main nitrate sources in the investigated area. Very little non-point source contamination seems to originate from manure spreading. By attributing each sample to one of the sources or processes identified, a regional map highlighting the more vulnerable areas has been obtained. Results of the project are currently being used by regulators to implement more effective, source-oriented remediation measures and improve their social acceptance.

Characterization of a preparation protocol of water samples for δ_{15}N and δ_{18}O analysis of dissolved nitrates at CIRCE lab in Caserta (Italy)

Luisa Stellato[32], Fabio Marzaioli[32], Antonio d'Onofrio[32], Carmine Lubritto[32], Mario Palumbo[32], Carmina Sirignano[32]

The development of effective management practices to preserve water quality from nitrate pollution and action plans for already polluted areas requires the identification of sources and the comprehension of the processes that influence the local presence of nitrates. In many cases the study of isotopes provides a direct means of identifying sources, as different sources of nitrates often have distinctive isotopic composition of nitrogen (N) and oxygen (O) (Kendall, 1998). The measurement of nitrogen isotope ratios of nitrate (NO_3^-) usually occurs in three phases: (a) extraction of NO_3^- from the sample; (b) conversion of extracted NO_3^- in gaseous N_2; (c) N_2 isotopic ratio determination by isotope ratio mass spectrometry (IRMS). The oxygen isotope ratios of nitrate are generally measured by quantitatively converting nitrate oxygen to CO or CO_2 gases, which are analyzed by means of IRMS. We decided to adopt the method of Silva et al. (2000) to perform isotopic analysis of N and O of dissolved nitrates since it allows, for the analysis of isotopic ratios of both nitrogen and oxygen, a unique preparation by means of a chemical conversion of dissolved nitrates to solid silver nitrate ($AgNO_3$).

The protocol was validated using samples of standard aqueous solutions of potassium nitrate (KNO_3), previously characterized versus isotopically certified IAEA reference materials (N_1, N_2, NO_3, USGS-32) through direct combustion of salts by an elemental analyzer (EA or TC/EA) coupled with a CF-IRMS system (continuous flow isotope ratio mass spectrometry). After the production of solid $AgNO_3$, tests were carried out to determine the background, precision and accuracy of different treatments for the conversion of silver nitrate to CO_2 (or CO) and gaseous N_2: a) analyses of $AgNO_3$ samples by means of EA-CF-IRMS (elemental analyzer coupled with a continuous flow isotope ratio mass spectrometer) to measure δ^{15}N; b) analyses of $AgNO_3$ samples by means of TC / EA-CF-IRMS system (high temperature conversion elemental analyzer in absence of oxygen coupled with a continuous flow isotope ratio mass spectrometer) to measure δ^{18}O.

The precision of the preparation protocol of aqueous samples, reported as standard deviation (1 δ) of $AgNO_3$ measurements, is 0.8 ‰ and 0.2 ‰ for δ^{15}N and δ^{18}O, respectively.

The accuracy of the protocol, expressed as deviation from the 1:1 slope obtained from a comparison of the method of direct combustion (reference) and the preparation protocol was found to be 14.3 ± 1.7% for δ^{15}N and 4.9 ± 0.3% for δ^{18}O.

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Results of monitoring for Nitrates Directive in EU-27 in period 2004-2007

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The Nitrates Directive requires that Member States submit a report to the Commission every four years. This report should contain information pertaining to codes of good agricultural practice, designated nitrate vulnerable zones (NVZ), the results of water monitoring and information about the action programmes in NVZ.

The poster presents information about nitrate concentration in groundwater and surface water, submitted by EU 27 Member States referring to the period 2004-2007. Moreover, results of trend in nitrate concentration since the previous reporting period are presented. The total number of sampling sites in the EU 27 is 31,000 and 27,000 for groundwater and surface waters, respectively

Monitorisation of a Nitrate Vulnerable Zone using experimental plots and the development of risk maps based on coupling a GIS with a nitrate leaching model

Kelly-Jane Wallis[35]

For the present study, the Sa Pobla sub-basin (Majorca, Spain) which was defined as a Nitrate Vulnerable Zone in the year 2000 was selected to assess the fate of nitrogen in the soil. Data was gathered from 4 experimental plots from 2003-2007 and a total of 9 crop cycles were observed (8 potato and 1 onion), each following specific agricultural management practices. Field work was set out to obtain information regarding the hydrodynamics of water infiltration and chemical aspects of the vadose zone in order to control the transport of nitrogen to the aquifer. For this, various instruments were installed and monitored including piezometers- to monitor the water table elevation and chemical composition; suction cup lysimeters- for soil water collection; tensiometers- to monitor soil matric potential, as well as Time Domain Reflectometry probe access tubes (TRIME-FM, Imko®)- to obtain volumetric soil moisture data. Soil and plant samples were also taken and meteorological conditions were controlled.

Gathered data from field and laboratory work were used to adapt the GLEAMS model v.3.0 (***Groundwater*** Loading Effects of Agricultural Management Systems) to local conditions and to evaluate model performance. The parameters controlling runoff and crop nitrogen uptake were identified as sensitive parameters through a sensitivity analysis. These parameters were used to calibrate to hydrology and nutrient modules of the GLEAMS model respectively. Observed soil water content and soil nitrogen content data for the period 2004-2007 from the experimental plot E5 were used for model calibration. Validation was carried out with data from the experimental plot E4 for the same time period. Statistical evaluation of model validation gave model efficiency values of 0.45 and 0.33 for soil water content and soil nitrogen content respectively, indicating that the numerical model was able to predict these parameters satisfactorily under experimental conditions. Results indicate that on a yearly basis the water balance was distributed between 480 mm being percolated below the root zone whilst 390 mm resulted in evapotranspiration. In regards to nitrogen leaching, percolating water carried an average load of 182 kg N/ha which represented 98% of nitrogen

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applied as inorganic fertiliser, whilst 109 and 80 kg N/ha were attributed to crop extraction and denitrification respectively.

Risk maps can be elaborated by combining a simulation code with a GIS to simulate the temporal (numerical model component) and spatial (GIS component) assessment of contamination loads transported to groundwaters. Spatial data required by the simulation model was managed through base maps projected as layers in a vector type GIS (ESRI ArcMap 9.1). Four base maps were elaborated containing climate, nitrate in irrigation water, land use and soil data covering an area of 165 km^2 corresponding to the Sa Pobla sub-basin. Currently this GIS-GLEAMS system is being used to simulate the spatial distribution of nitrogen leaching for the elaboration of risk maps. Furthermore, different scenarios of agricultural practices will be simulated for analysis.

Identification and quantification of nitrate inputs into surface water in Flanders, Belgium

Dongmei Xue[36,37], Bernard De Baets[37], Jorin Botte[36], Oswald van Cleemput[36], Kor van Hoof[38], Pascal Boeckx[36]

Nitrate (NO_3^-) contamination in surface water in Flanders (Belgium) is a pressing environmental problem. These NO_3^- loads are attributed to intensive agriculture, use of fertilizers and manure and discharge of human sewage. The Flemish Environmental Agency (VMM) has an operational network for monitoring surface water quality. An apriori NO_3^- source classification has been provided based on NO_3^- concentration variation and land use. The 5 potential NO_3^- source classes are as follows: greenhouses, agriculture, agriculture with groundwater dilution, households and a combination of horticulture and agriculture. However, NO_3^- concentration data alone can not fully assess the extent of the input of various NO_3^- sources, which is a key aspect in monitoring water quality. Hence, this study will apply a dual isotope approach ($\delta^{15}N$- and $\delta^{18}O$-NO_3^-) and a Bayesian isotope mixing model (SIAR) (http://cran.r-project.org/web/packages/siar/siar.pdf) to identify and quantify NO_3^- sources in surface water.

Thirty sample points (6 sample points per apriori NO_3^- source class), distributed over the whole of Flanders, were selected for NO_3^- source identification and quantification based on monthly measured $\delta^{15}N$- and $\delta^{18}O$-NO_3^- data. So far (from October 2007 to March 2009) we observed isotopic values ranging from -9.5 to 28.6‰ for $\delta^{15}N$ and -9.1 to 51.1‰ for $\delta^{18}O$. The output of proportional NO_3^- source contributions via SIAR revealed that all of the water samples are a mixture of multiple nitrate sources, with manure or sewage as the dominant source. Furthermore, the outputs of source contributions analyzed by SIAR are used to redefine the source classes of the 30 isotope monitoring sample points, as some points might be classified into the wrong class only based on expert-knowledge.

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Sources and fate of nitrate and sulfate in a sandy aquifer: a multi-isotope study

Yan-Chun Zhang[39], Caroline P. Slomp[39], Hans Peter Broers[40], Hilde F. Passier[40], Michael E. Böttcher[41],[42] & Philippe Van Cappellen[39,43]

Nitrate and sulfate are common pollutants in groundwater in areas with intensive agriculture. In this study, we combine multi-isotope analyses ($\delta^{34}S$-SO_4, $\delta^{18}O$-SO_4, $\delta^{15}N$-NO_3, $\delta^{18}O$-NO_3) with geochemical analyses and groundwater age dating ($^3H/^3He$) to identify the sources, sinks and the relevant transformation processes of nitrate and sulfate in a sandy aquifer at Oostrum, the Netherlands. We specifically focus on the role of denitrification coupled to pyrite oxidation and compare results for sites in cultivated land to a site in an adjacent forested area.

The groundwater in our study area is characterized by extremely high nitrate and sulfate concentrations, with maximum concentrations of 8 mM (500 mg/L) and 4 mM (400 mg/L), respectively. The isotope composition of groundwater from shallow depths (<10 m) at cultivated and forested sites is, in general and regardless of age, rather similar, suggesting mostly common sources of nitrate and sulfate. Only at the forest site, a slightly higher atmospheric deposition is inferred from both $\delta^{18}O$-SO_4 and $\delta^{18}O$-NO_3 values. Sulfate concentrations increase and nitrate concentrations decrease in groundwater in a “reaction zone” between 10 and 20 m depth in groundwater in cultivated areas. The changes in isotopic composition of the groundwater in this reaction zone confirm geochemical analyses suggesting that denitrification is coupled to pyrite oxidation in this aquifer [1]. Isotope analyses of groundwater from the deeper part of the aquifer (> ~25m) indicate sulfate removal through microbial sulfate reduction.

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Posters session on Friday 11 December

Management of Nitrate Pollution in Nubian Sandstone Aquifer

Mohamed Mustafa Abbas[44], Marwa Faisal Salman[45]

Nitrate is a problem as a contaminant in drinking water (primarily from groundwater and wells) due to its harmful biological effects. Nubian Sandstone Aquifer is located in the North Africa and shared between four different countries (Sudan, Egypt, Libya and Chad).

In Nubian Sandstone Aquifer basin in Sudan most of the boreholes are contaminated with nitrate, which indicated that there are pollution sources should be isolated.

Provision of a safe and adequate supply of water is an essential component in the primary health care, to achieve these goals, different surveillance and control program are applied to ensure safe water for domestic uses in the Nubian Sandstone Aquifer.

The paper discusses two options for achieving safe nitrate levels in the Nubian Sandstone Aquifer, particularly in Sudan, which are non-treatment techniques and treatment processes.

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The Infuence of Climate Variations on Natural Background of Nitrate in Percolated Water

Branka BRAČIČ ŽELEZNIK[46], Barbara ČENČUR CURK[47]

Climate Change affects fresh water resources and may have significant influence on public drinking water supply. One of the most important impacts of Climate Change is on fresh water resources, causing diminishing water quantity and alterations in quality and water demand. Climate Change may affect the ability of suppliers to provide enough water of sufficient quality to consumers and their planning for the future. Land use activities exert pressure on water resources and will change according to Climate Change. It is crucial for safeguarding future water supply to anticipate these changes in climate and land use activities and to assess its impacts on water resources. The main problems are directly and indirectly related to the significant decrease of groundwater level and deterioration of groundwater quality observed in the last decades as an effect of landuse practices and very likely to Climate Change.

Public Water Utility of Ljubljana City is responsible for public water supply availability and safety. Groundwater is a drinking water source for more than 270000 inhabitants of Ljubljana City and vicinity. It is stored in an unconfined porous aquifer with dynamic capacity of groundwater flow ~ 3-4 m^3/s. Measurements from the last fifty years show us the changes in precipitation intensity, quantity and type. When the source for drinking water is the unconfined porous aquifer all extreme events and changes in the weather and the climate influence on groundwater recharge.

Well field Kleče is, with total capacity of 1270 l/s, the most important water well field for Ljubljana's drinking water supply system. About 35% of the recharge area of the well field Kleče is used for agriculture, predominantly for intensive vegetable production. In the nineties, nitrate (NO_3^-) concentration levels of the groundwater in Ljubljana aquifer were increasing. Disconcerting trends prompted Public Water Supply Company to set up several monitoring systems of nitrate concentration levels to gain overview of the situation, determine trends and main polluters as well as to take preventive measures to decrease existing pollution. For this reason a lysimeter in the well field Kleče area was installed. Since the year 2002 concentration of NO_3-N in percolated water is monitored. On the premises of the Kleče water field no fertilizers are used, therefore the results represent the nitrate natural background levels, which come from air to soil. Nitrate quantity in the percolating water changes during the season and during years and depends on the precipitation amount, season, plant uptake and soil processes.

Keywords: percolation water, natural background, NO_3-N concentration, drinking water resources management

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GESRO – A GIS tools for surface water quality diagnose at a river basin scale

Maria Ilinca Cheveresan[48], Laurentiu Ichim[49], Bogdan Cheveresan[49], Radu Drobot[48], Maria Marinescu[50], Aurora Vasiu[51], Elena Tuchiu[51], Collin Schenk[52], Marc Soutter[52]

According to the Water Framework Directive 2000/60/EC the water bodies have to achieve the good status till 2015. In order to fulfill this objective the qualitative management must be improved. An integrated GIS application, called GESRO, was created in the frame of INWAQ (Integrated Water Quality Management System) project. After the finalization of the project this application continued to be developed. GESRO is now an extension to ArcGIS that uses its functionality to automatically diagnose the surface water quality on the base of measured values. This classification is done for chemical and biological indicators, dangerous substances, drinking water, vulnerability to nitrates and fish fauna.

GESRO has a toolbar in ArcMap with functional buttons regarding: data import from MS Excel, data input, computation, reports, layout and help (Fig. 1)

Figure 1. GESRO toolbar

The data are entered in an Access database on river water bodies. The division of rivers into water bodies is done by the specialists from the monitoring department in Water Directorates on several criteria like: the measurements sections, the existence of economical agents, the river confluences. The input of data has several options like adding more measurements for the same monitoring section for the same day, modifying the existing values and also the possibility to not enter any values if there weren't measured.

For chemical and biological indicators the computation is based on formulas. For the other functionalities the computation is based on a comparison between the measured values and their limits from the normatives. After the computations reports can be automatically generated. The application has also the functionality of identifying the potential pollution sources.

At present GESRO has been implemented at National Administration Romanian Waters and its subordinated Water Directorates at national level for River module. Also the application is being extended for Lakes, Groundwater, Coastal and transboundary rivers and Used waters.

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Investigating uncertainties and complexities in the designation of Nitrate Vulnerable Zones in England

Cunning, R.[53], Willows, R.[54], Page, T.[53], Watson, N.[53], Pope, L.[54], Crane, N.[54] and Haygarth, P.[53]

The control of nitrate loading to surface waters has received considerable attention from the scientific and policy communities over the past two decades due to environmental concerns and the implementation of the Nitrates Directives amongst EU member states. Despite this attention, however, nitrate continues to be a difficult issue for many European countries. Furthermore, high nitrate concentrations are threatening to prevent many countries from reaching 'good water status' standards by 2015 as required by the Water Framework Directive. In England the implementation of the Nitrates Directive is conducted via the designation of Nitrate Vulnerable Zones (NVZs), which cover approximately 70% of the country. The designation of NVZs is a complex challenge, and one that is particularly contentious due to the costs and restrictions imposed upon farmers within zones. The Environment Agency (EA) is responsible for developing and implementing a methodology for designating NVZs on behalf of Government, and for ensuring that farmers comply with Action Programme measures. In doing so, the EA target measures in a way that most fully protects the environment whilst avoiding the imposition of unnecessary controls. The aim of this EPSRC/EA funded project is to investigate the impact that uncertainties and complexities associated with data, monitoring, and policy decisions have on the overall designation of protection zones, such as NVZs, in England. Uncertainties and complexities arise at all stages of the designation process, from collection and generation of data, statistical analysis to identify polluted catchments, and policy decisions on whether to designate or not. The EA adopt a risk based approach to the assessment of nitrate polluted waters and consequent designation, guided by the appropriate legislation. While this approach identifies and quantifies some uncertainties this project highlights areas where risk assessors and policy makers could incorporate more relevant and more comprehensive information regarding uncertainty into their future decision making. This poster introduces a methodology that has been developed in Matlab, using water quality data, which allows different policy scenarios to be generated, and demonstrates potential changes in the extent of designated areas using the different policy choices. Using this methodology a number of key questions regarding different aspects of uncertainty may potentially be addressed:

- How may changes to the monitoring network in England, associated with the implementation of the WFD, impact the designation process?
- How may policy maker's risk attitude, and the level of environmental precaution shown, impact decisions made during the designation process and ultimately the area designated?
- What is the impact of using different statistical approaches during the designation process?

Preliminary results, based upon a realistic, theoretical data set are presented, demonstrating the potential impact that data confidence could have on protection

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zone designation. Further work is currently being completed to address the other questions regarding uncertainties within the designation process, and ultimately it is hoped to include an economic analysis that will demonstrate the costs associated with different scenarios, allowing policy makers to identify the most cost efficient and environmentally effective decisions.

Impact of land use changes on drinking water quality in the Mancha Oriental System (MOS). Period: 1970-2004

Moratalla, A[55]., Gómez-Alday, J.J.[56] & De las Heras,J.[55]

The study determines the impact of land use changes on drinking water quality during the period 1970- 2004. In the MOS, the surface of irrigated crops has growth from 170 km^2 in 1975 to 1000 km^2 in 2002 and population has increased from 204247 in 1970 to 238730 inhabitants in 2004. During the study period some pollutants, such us NO_3^-, in groundwater have increased in tandem with the augmented irrigated crop area and urban development. GIS techniques and multivariate statistical analyses were applied to describe the impact of antropogenic pressures on water quality. GIS based maps of NO_3^-, Cl^- and Na^+ isocontents show that spatial distribution patters were similar which suggests common pollutant sources. A similar spatial distribution of SO_4^{2-}, Mg^{2+} and Ca^{2+} concentrations in groundwater can also be observed in the resulting maps. Two factors were extracted to explain the contributions influencing chemical composition of groundwater. Factor 1 indicates the influence of land use on groundwater chemistry and can be interpreted as agricultural and urban-derived contamination. NO_3^-, Cl^- and Na^+ contents are largely influenced by irrigation, cereal, fallow and population factors. Factor 2 corresponds to groundwater salinization. The high correlation among electrical conductivity, SO_4^{2-}, Mg^{2+} and Ca^{2+} indicate that these ions play an important role on groundwater mineralization processes.

Under this scenery, the use of groundwater resources for human purposes could represent a public health risk if water management measures do not change in the future. The main goal of the Water Framework Directive is that water bodies attain good status by 2015 (extended until 2021), through protection of resources and by preventing their deterioration.

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A long term experience (almost 10 years) with nitrogen removal in a wooded experimental site

Bruna Gumiero[57], Bruno Boz[58], Giustino Mezzalira[59], Paolo Cornelio[60], Sergio Casella[58] and Marina Basaglia[58]

Riparian zones, located at the interface between terrestrial human activities and aquatic ecosystems, play a key role as a buffer system. Low order streams can be considered the most suitable for controlling nitrogen fluxes because of their

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great interaction potential with both riparian and agricultural areas. However, in our study, we explored the possibility of reducing the in-stream nitrate concentration of high-order water courses by creating natural or semi-natural floodplains, where water flow must be strongly managed as in a drained wetland.

The contamination of surface and ground waters by nitrates is still a considerable problem in the northern part of Italy. For this reason the Veneto Region funded the "Plan for pollution prevention in the watershed flowing directly into Venice Lagoon". The plan comprised many activities, and we will present a selection of them:

The Dese Sile Drainage Authority built (1999), along the Zero River (low plain), 30 ha of forested buffer area within which the efficiency of the buffering capacity of wooded areas respect to non point pollution sources of nitrogen was monitored in an experimental scale (0,7 ha). In this newly established riparian woodland in semi-permeable soil (loamy-clay), the hydrology is totally regulated through a series of pumps with water irrigated into the woodland through a series of parallel ditches.

The experimental site, located 15 km from Venice, was designed to evaluate the efficiency of the buffering capacity of a wooded area on non-point pollution sources of nitrogen. One of the main goals of the experimental design, carried out on this pilot site, was to demonstrate the efficiency of the wooded riparian soil to remove nitrogen excess from the river flow, supporting in the meantime the growth of specific, newly introduced tree vegetation. A detailed monitoring program has been carried out since October 1999, so a huge data base of meteor, hydrology, water quality, soil chemical parameters and denitrfication rates, is now available.

The results allow some interesting suggestions for improving the management of buffer zones. Moreover, from 2009 to 2011, we are also analysing the composition and the dynamic of microbial communities, the efficiency of the system after adding higher amounts of nitrogen and then after partially wood cutting.

Future research by Veneto Agricoltura (Veneto Region Agency) is going to explore the effectiveness of these wooded areas in removing nitrogen from the slurry which has been loaded by the biogas plants.

Nitrate migration and drainage losses in clay laom irrigated soils: case study of Kalaat Landalous (Tunisia)

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Soils in arid and semi arid regions are poor in Nitrogen. This deficit concerns especially ammonium and nitrate forms, the main constituents of the soil mineral Nitrogen. Nevertheless, its high level in the irrigated soils due to the fertilizers supply could induce environmental problems. This study aims at the evaluation of the rest of mineral nitrogen in the soil profile during two seasons (2006/2007 and 2007/2008) and to assess nitrogen transfer to the aquifer and drained water. Trials were carried out in 2007/2008 on 5 ha sized plot of the irrigated district of Kalaat Landalous (Tunisia). The used clay loam textured soil confers higher mineralization capacity due to its wide water holding capacity, but also to both its low nitrification rate and high exchange capacity effects on the soil absorbent complex.

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In terms of nitrogen balance, the difference between outputs and inputs for the tomato crop is positive (53 Kg / ha) and this translates into a stock of mineral nitrogen remaining fairly important in soil and we should consider for fertilization for the next crop. However in the case of wheat, the result of nitrogen balance is negative (-66 Kg / ha). For reasonable fertilization and in order to reduce leaching of nitrates and their transfer to the water, a good fertilizer management could better manage the stock of residual nitrogen in the soil through the process of crop rotation. The stock of residual mineral nitrogen measured during our monitoring study during the years 2007-2008 didn't currently cause bad effects on water quality of the surface water. However, the high load in mineral nitrogen in drainage water shows signs of eutrophication at the outlet of the water with the Mediterranean Sea.

Key words: Irrigated soil, fertilizers, residual mineral nitrogen, nitrates, drainage water, nitrogen balance

Nitrate pollution of the groundwater in Oran (Algeria)

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There are very few freshwater resources in Oran, and residents are increasingly calling upon private wells. Water is either drawn straight from the well, or sold to the population by hawkers. These wells are used for drinking water, but are not submitted to any controls and the water is rarely analysed.

A study was conducted to estimate the nitrate pollution of 50 wells in the Bouamama area, in the west part of Oran. Sampling was carried out during the winter, to measure nitrate concentration, pH and temperature. Results showed that in 19 wells (38%), nitrate concentration is up to 50 mg/l and can reach 131 mg/l.

Investigations were made in parallel, about the characteristics of the wells and activities in the vicinity. But it is very difficult to know the part played by agriculture and that of domestic sewage in the responsibility for this pollution.

Keywords : nitrate, groundwater, drinking water, Algeria

Nitrates in Water in Mendoza's Northern and Central Oases (Argentina): Areas irrigated by the Mendoza and Upper Tunuyán Rivers

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Located in Argentina's semiarid central-western region (at 32º 30' – 33º 50' south latitude and 67º 50' – 69º 30' west longitude), Mendoza has the largest area under irrigation in the country. Aridity is offset by its five snow-fed rivers flowing west to east, which form the so-called "cultivated oases" (4% of the total area of the province), where most of the population has settled and major agribusiness activities take place. The most important oases are the "Northern Oasis" (formed by the Mendoza and Lower Tunuyán rivers), which includes the Greater Mendoza metropolitan area with over 1 million inhabitants, and the "Central Oasis" (Upper Tunuyán River), which comprises the Valle de Uco region. The locus of interest of researchers and water administrators (*Departamento General de Irrigación*-DGI and users' organizations) has shifted through time. Nowadays, reality calls for stressing the preservation of water quality through adequate

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monitoring of physico-chemical and microbiological parameters.

The objectives of this paper are: to assess contamination levels, identify spatial and temporal variations of man-made pollution by nitrates in both rivers –Mendoza and Upper Tunuyán–, and to provide recommendations on water management and policy guidelines to ensure availability of water and water quality.

Selection of georeferenced sampling sites on both rivers was based on the various types of pollutants and discharge points in the area. Sixteen (16) sampling sites were selected along the Mendoza River and its irrigation and drainage system and samples were drawn during the period 2003-2009. For the Upper Tunuyán River basin, six (6) sampling sites were selected and two measurement periods –1999-2000 and 2007-2009– were compared.

Results confirm the hypothesis of nitrate pollution of the Mendoza River water and of the irrigation canal system, with significant differences (α=0.05) the further it gets from the head of the system. The maximum average value observed is 6.2 $mg.L^{-1}$.

Significant differences (α = 0.05) between sampling periods were found in the Upper Tunuyán River. Spatial analysis of each period showed that for 1999-2000 there were significant differences only between Aº Aguanda (A) and Costa Anzorena (CA). On the other hand, no differences between sampling sites were detected during 2007-2009. The maximum observed average value was 2.33 $mg.L^{-1}$. Increasing contamination confirms the need for adequate monitoring to improve irrigation system management to preserve water quality. To this end, all stakeholders should be involved in the implementation of impact mitigation policies.

Key words: water contamination, pollution, impact, water quality

Assessment of potential nitrate pollution sources in the Marano Lagoon (Italy) and set-up of an environmental monitoring programme (FONIMAR)

Saccon, P. and A. Leis[70]

The aim of the project FONIMAR is to identify and differentiate the main anthropogenic nitrogen sources present and their impact on the Marano Lagoon and its catchment area by applying a combined approach of hydrochemical, isotopic and remote sensing techniques.

The present investigation developed by the Institute of Water Resources Management of Joanneum Research (Graz, Austria) represents a new study, which, beside the traditional hydrochemical analyses (main ions and nutrients), introduces the whole suite of stable isotopes of the nitrate molecule ($\delta^{15}N$, $\delta^{17}O$, $\delta^{18}O$), the stable isotope signature of boron ($\delta^{11}B$) and the stable isotopes of water ($\delta^{2}H$ and $\delta^{18}O$). The analysis of stable isotopes in the nitrate molecule will be used to differentiate between nitrate coming from agriculture (synthetic and natural fertilizer), airborne nitrate and nitrate from nitrification processes in soils. Boron isotopes will be used to identify the impact of domestic wastewater on the aquatic system. The stable isotopes of the water molecule are useful tracers to calculate mixing ratios between sea and fresh water and the mean altitude of the recharge area of surface water. Moreover, this study represents a very new innovative approach for the investigation of the complex hydrogeochemical processes at the mixing interface between sea and fresh water. In addition to the analytical part, the monitoring programme will also include remote sensing techniques. Remotely sensed data from the satellites Landsat 1 MSS, Landsat 5 TM and Landsat 7 ETM+ will be analysed and processed. This analysis is to assess the

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multi-temporal and spatial evolution of most superficial algae flora activity and the water temperature of the Lagoon as main indicators of eutrophication and, additionally, to identify the main environmental and morphological changes of the Lagoon since the beginning of the seventies.

The project has been funded by the Government of Friuli-Venezia Giulia/Regional Agency for Rural Development.

Potential groundwater and surface water contamination from nitrate in the Po River Delta (Northern Italy): results from an applied research within the Water Framework Directive

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Nitrogen losses from agricultural sources have been recognised as one of the most serious threats in industrialised and emerging countries, determining ecosystem eutrophication and groundwater nitrate contamination. This issue has recently become a priority within the European Community Framework Directive for water protection (WFD), which has established a list of measures and limitations to be applied in areas declared "vulnerable to nitrate from agricultural sources". An example is the Ferrara Province (Northern Italy), an intensively cultivated area, located in the Po Delta and affected by serious nitrate pollution since decades.

In defining a strategy for reducing nitrate losses in agriculture and relative effects on groundwater and surface water it is essential to characterize the most important processes regulating N transformation and transport. For this purpose a range of field and laboratory experiments have been performed to quantify N-species fate in the four most representative soil types of the Po River Delta.

Experimental plots (1 ha total surface, 0.5-0.05% slope), cultivated with maize, were fertilized with 240 kg N/ha as urea. Core logs down to 2 m b.g.l. were collected at each field site to characterize soil water content, soil texture, organic matter content and bulk density. Each field site was equipped with tensiometers and soil moisture probes, a meteorological stations, drains and suction cups to monitor soil water and nitrogen transport in the unsaturated zone. Nested piezometers, screened from 1.5 to 5 m b.g.l., were installed and monitored to quantify the presence of N-species in the shallow unconfined aquifer. Monitoring started in February 2008 and is still on. Undisturbed soil cores were used in laboratory evaporation experiments to determine soil hydraulic properties.

From collected data, both in field and laboratory studies, input parameters were derived to implement the finite element model HYDRUS-1D. Results showed a good model fit of water content and head pressure at various depth, thus a robust estimation of cumulative infiltration and evapotranspiration has been derived and the water balance obtained was considered reliable. SOILN software was used to obtain the N mass balance immediately after harvest and after 1 year from fertilization. Results showed a large control of N leaching by organic matter and acetate availability, soil texture and head gradient of the unconfined aquifer. On the base of achieved results a GIS mapping of the intrinsic vulnerability to nitrate of the unconfined aquifers has been derived while for further research advancement stable isotopes seem to be the most promising approach to be carried out both at the field and laboratory scale.

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Joining forces for improved water quality: the INPAR network (Isotopes for improved management of nitrate pollution in aqueous resources)

Angelika Nestler[75], Michael Berglund[75], Lutgart van Nevel[75], Philip Taylor[75]

Despite the efforts in the European community legislation nitrate (NO_3^-) is still a major pollutant. Nitrate is degrading drinking water and water resources quality. It is one of the nutrients causing eutrophication of surface and marine waters in the European Union (EU). Isotope data provide support to identify nitrate pollution sources, to investigate the fate of nitrate in the environment and to stipulate appropriate measures to reduce nitrate pollution. Thus, the use of isotope data enables improved management of nitrate contamination in ground, surface and marine waters. With the intention to make this methodology more accessible for stakeholders and to share best practices, the network 'Isotopes for improved management of Nitrate Pollution in Aqueous Resources (INPAR)' has been initiated by the European Commission, Joint Research Centre - Institute for Reference Materials and Measurements, in 2006. The network aims in particular to promote the use and development of isotopic techniques as a tool for better water management in relation to nitrate pollution across Europe by means of multi-disciplinary knowledge exchange (stable isotope analysis, hydrogeology, environmental chemistry, geochemistry and statistical data analysis), joint research projects and training activities.

[75] European Commission, Joint Research Center, Institute for Reference Materials and Measurements, Isotope measurements

A new method for decreasing of the nitrate concentration in portable waters

Parviz I. Normatov[76], Asliya S. Rajabova[76], Umeda Tolibova[76]

The modern requirements to quality of potable water and also various behavior of chemical compounds in water in depending on presence of a wide spectrum of impurity and ingredients are stimulated search and workings out of progressive methods of selective definition and reduction of the maintenance of chemical components. In the present work results of researches on working out of a method of electrosedimentation for sharp reduction of the maintenance of nitrates in underground waters as water supply sources are presented. The main principle of the offered method consists in application of electric field for destruction nitride complexes and reduction of nitrates-ions in the form of their fast definition with high accuracy. It is promoted by ample opportunities of a variation of electric field and created good circulation of investigated water. The developed method was tested at research of underground waters of the Kulob areas of Tajikistan. The method of electro-sedimentation provides high effect of removal from water of pollution in the form of suspensions (a mineral organic and biological origin), colloids (connections of iron, the substances causing chromaticity of water, etc.), and also the separate substances which are being a molecular and ionic condition. The physical and chemical analyses have shown that after application of a method of electrosedimentation the concentration of the nitrates have decreased three times,

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the intestinal stick is not found. A microbiological parameter (E-coli) investigated test of water it was characterized by presence more 1100 intestinal sticks in one liter of water.

Superficial waters of Vosse region were following object of research. Test - B (the centralized water supply) is taken from a kishlak "Pushyon" which is in 20 km from the region centre. Test - C is taken from the open channel of the same kishlak. It is necessary to notice, that for the kishlak population the given sources are used as potable water.

In the test B after electrosedimentation concentration of nitrates decreases up to 45% and coli- index and the intestinal stick is not found which specifies in suitability of water to the use (fig.2, annexe p50).

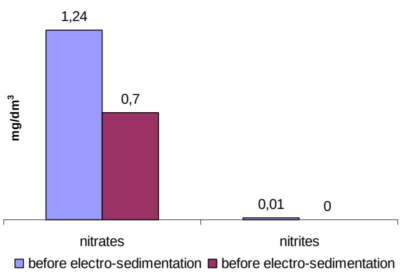

Fig. 2. Results of physical and chemical analyses of test C (the open channel)

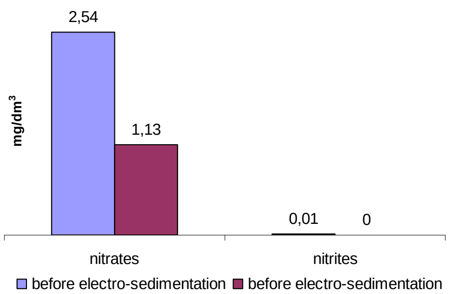

Fig. 3. Results of physical and chemical analyses of test B (the centralized water supply)

Appeareanse of the risk contamination of drinking water at infleunce of arinfall on the underground water resoucres

Parviz Normatov[77], Muslima Kholmirzoeva[78], Inom Normatov[78]

Tajikistan is a mountainous country which one is posed in an interval of altitudes from 300 up to 7000 m above the sea level, cities, settlements and kishlak (villages) are located basically in valleys of the rivers, which anthropogenesis loading on superficial reaches maximum. According to results of the water control analyses during storm rains there is a bacterial pollution of the rivers prick an index can reach numerous amounts of intestine sticks in 1 liter of water (Varzob River – 3800 intestine sticks in 1 liter of water). The basic importance of a waterway of infection transfer is especially evident at study of dynamic of disease by a typhoid, which is always characterized as very high level. Thus between maximum (1984-69,0 on 100 thousand population) and minimum (1992-16,9) its parameters exists distinguished distinctions (4 and more time), reflective rare fluctuations of epidemic activity of waterway transfer including separate territories. In particular, because of lack of means for maintaining achieved quality of water-service and sanitarian clearing of territory expect further rising of epidemic activity of the water factor and case rate by a typhoid on high levels of last years, is equal as other widely spread intestinal taints. In connection with named above conditions cased by typhoid of village population in 2 and more times is higher, than urban. Its greatest levels are recorded in valleys from 2.5 up to 150

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times above than in foothill and mountainous zones of republic accordingly. In many districts of valley zone, first of all in cotton planting the case rate by a typhoid was extremely high in 1994-2000 years. As a rule, it exceeds republican parameters caused by high activity of a waterway transfer and extremely potent fecal pollution of sources used in the agricultural-potable purposes. The significant number of diseases by typhoid (41-82 %) is recorded at acute water epidemic flashes. The underground waters take appreciable place in supplement of the population of Tajikistan by potable water. Water is one of dynamical components of the ecosystems possesses ability promptly to transfer various pollution and infectious diseases on greater territories. Though it concerns basically to superficial waters but not exception is also underground waters. First of all is caused by that superficial and underground waters constantly are in dynamic interaction and takes thus a place penetration and diffusion of pollution to the reservoirs of underground waters. Earlier it was observed that significant seasonal change of concentration of nitrates in underground waters: during the droughty periods concentration of nitrates did not exceed unit and during rains reached 18 mg/dm^3. Tajikistan is the agrarian country and basic agricultural production is cotton. For get of the good harvest many farmers breaking the established norms apply enough lots mineral fertilizers and pesticides. It is necessary to note that the majority of sources of mass water delivery of rural population are near to the irrigated grounds and is not excluded that at rains the mineral fertilizers and pesticides is not hit to the underground water reservoirs. The present work is devoted to researches of change of a chemical compound of underground waters of Tajikistan in dependences of the period of year and quantity of precipitation. For this purpose two sources of underground waters have been chosen: 1-Kafarniganski and 2- East unit. Results of researches are presented on fig.1, fig.2 and fig.3. (annexe p). The presented figures are demonstrated that in the summer at insignificant quantities of atmospheric precipitation the difference of the maintenance of chlorides in sources 1 and 2 strongly differs. In the autumn at increase in quantity of deposits the maintenance of chlorides in these sources are almost equated. Such picture is found out under the maintenance of nitrates, sulfates and other chemical components.

Assessing the well water pollution problem by nitrates in the small scale farming systems of the Niayes region, Senegal

M. Sall[79], M. Vanclooster

Human activities exert many pressures on the quality of groundwater, and advanced assessment programmes are needed to design sustainable water management strategies. To contribute to this challenge, the nitrate pollution problem of groundwater wells in the small scale farming systems of the Niayes region in Senegal is assessed and explained in terms of well characteristics and land use properties. A field campaign was performed in 2007 to collect basic background data of the small scale farming systems and well water was analysed in 131 wells for nitrate content, pH and electrical conductivity. For a subset of wells, soil analyses were made of the well environment for assessing the attenuation properties of the protecting soil. Cluster analysis was used to define a well typology, while principal component and multiple correspondence analyses

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were used to relate the nitrate pollution to well characteristics and land use properties.

The study confirms that the wells are seriously affected by the nitrate pollution problem. Wells can be classified in three well classes which exhibit highest nitrate content in the southern part, while the salinity affects particularly the wells in the northern area of the region. The nitrate levels exceeding 50 mg/L are more common in residential areas than in the horticultural fields. The results further show that, even if direct pollution problem of wells cannot be excluded, pollution from leaching out of the root zone of vegetable crops to the groundwater is likely. This is confirmed by the assessment of the farming activities in this area and this is consistent with the low attenuation properties of the soils characterizing this region.

Considering the nitrate pollution threshold, very few non-polluting crops can be distinguished in this region, which calls for an urgent adoption of agriculture management to protect water resources from further deterioration.

Keywords: Horticulture; Nitrate pollution; Shallow groundwater

The influence of Nitrate Vulnerable Zones in the catchment of Lower Jiu

Adina Sanda Serban[80]

The awareness of ecological problems caused by agriculture was considerably increased in the last two decade. Consequently, legislative activities at the European Union and the national level have been launched as a reaction to public pressure which demands the protection of environment. The interrelation between agricultural production and the environment and the relating problems have been discussed intensively.

Therefore, the Nitrates Directive (91/676/CEE) was born.

The goal of the Nitrates Directive is to reduce and prevent water pollution caused by nitrates from agricultural sources. The directive obliges the member states to monitor the nitrate concentration and trophic status of water bodies.

The first step in achieving this goal is to assess the areas polluted with nitrates from agriculture and then to establish and implement programs of measures to reduce it.

In Romania, the first designation of Nitrate Vulnerable Zones was made in 2005. According to this assessment only 7% of the Romanian territory was vulnerable at nitrates from agriculture. The second evaluation (2008) has showed that about 58% of the Romanian territory is vulnerable.

The case study made on the Lower Jiu river basin, situated in the south-west of Romania, in plain area, proved that 80% of its catchment is vulnerable at nitrates from agriculture.

Due to the intense agriculture between1960-1989, the water quality decreased very much comparative with the reference state from 50's.

Although now the agriculture is not developed too much, the negative effects are present in the groundwater (the threshold value of 50 mg/l is overcome), and the ecological status established for Lower Jiu (water body Jiu Bratovoiesti locality - Danube confluence) is moderated due to the nitrogen elements.

Because it is very hard to clean the groundwater, it's important to take measures in order to prevent new

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pollutions and to reduce the one that already exists.

These measures must contain: intensive monitoring of nitrate ion in surface water and groundwater, the use of fertilizers and manure must respect a certain calendar, creating “buffer zones” from grass and trees along water courses.

So, the question that is arisen is if the measures launched under this directive will be effective enough to restrict nutrient surpluses to a level which might be tolerated by society in the long run. This question involves the interaction between the agricultural policy in general and specific environmental issues.

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Nitrate Directive 91/676/CEE

Lithostratigraphy of Nigeria: an overview

Shitta Kazeem Akorede[81]

Nigeria lies very close to the equator (hot country) West coast Africa between latitude 4° N and 14° N degree and longitude 2° E and 15° E degree. The country is located at the Northern end of Eastern branch of west coast of Africa rift system. Nigeria geological set up comprises broadly sedimentary formation and crystalline basement complex, which occur more or less in equal proportion all over the country. The sediment is mainly Upper Cretaceous to recent in age while the basement complex rocks are thought to be Precambrian. The studied area lies between latitude 12.4° and 11.11°W and longitude 13.81° and 14.13° S. The studied area is underlain by Precambrian basement complex of southern western Nigeria .The major rock in the area is charnokite and granite rock. The granite rock which is member of the older granite suite occupies about 65% of the total area .The principal granite is petrographic variety are recognized .The fine grained biotite-granite medium-coarse, non porphyritic biotite -hornblende granite and coarse-porphyritic biotite -hornblende granite. Also three main textural type of Charnokitic rock are also distinguished are coarse grained, massive fine grained and gneissic fine grained .The mode of occurrence of rock is three (1) core of the granite rock as exemplified by study area and few smaller bodies (2) Margin of the granite bodies as seen in Ijare and Uro edemo-idemo Charnokitic bodies and (3) Discrete bodies of the gneissic fine grained Charnokitic rock within the country gneisses as seen in Ilaro and Iju and Emirin village. All the charnokite in the region are dark-greenish to greenish-gray rocks with bluish quartz and greenish feldspar.

Hydrological modelling of the EU Nitrates Directive Actions Programme: new developments in the Walloon Region (Belgium)

Ir. C. Sohier[82]**, Prof. Mme S. Dautrebande**[82]**, Dr. A. Degré**[82]

Wallonia (Southern Region of Belgium) implemented the Nitrates Directive through a first actions plan in 2002 followed by a second action plan in 2007. It designated vulnerable zones and introduced various mandatory practices in order to reduce the nitrate contamination risk. At the same time, the government decided to fund non mandatory practices focused on agro-environment. Some of these (like buffer

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strips) should also be useful in nutrient mitigation.

In Wallonia, nitrate-related problems are obvious in several groundwater bodies and their trends over the past 30 years are worrying. The main part of the contamination level is due to agricultural diffuse pollution. Nevertheless, some pollution peaks are observed mainly coming from domestic sewage.

In order to assess the global effectiveness of all the mitigation practices, we have been developing a hydrological model spatially distributed using a 1km² grid cell on the whole Region (16 900 km²). The EPICgrid model represents the root zone and the vadose zone. In Wallonia, groundwater tables are more than 30 m deep in 8% of the territory. It is therefore of major importance to fill the gap between the root zone and the groundwater bodies. It allows us to assess the nitrate transfer time and forecast the mitigation measures' effect in time, space and amplitude. On the ground, runoff and sediment yield are modelled at the small watershed scale in order to assess buffer strips' effect on sediment deposition and its consequences on N and P mitigation.

The model produces results like

- The mean transfer delay from the root zone to the groundwater table. In a few zones, the delay exceeds 15 years. This means that 15 years are needed for a new cropping practice to influence the groundwater recharge quality,
- Nitrate concentration in the water leaving the root zone. It is a fast indicator of the effect of cropping and grazing systems on nitrate concentration,
- Nitrate concentration in recharge water. It shows the direct pressure on the groundwater body, as a consequence of the cropping history and the characteristics of the upper vadose zone,
- Contamination level of surface water bodies, as a consequence of runoff and rapid interflows transfer,

The poster will explain the more recent results that consist in forecasting action plans' effect until 2015 (on both surface water bodies and groundwater bodies) and modelling of the current buffer strips' effect.

Climate Change and Eutrophication of Shallow Lakes

Edvinas Stonevicius[83]

Climate change will be a major factor influencing hydrological, thermal and ice regimes of water bodies. All these changes will affect the eutrophication of shallow lakes.

The hydrological regime of a lake is best reflected by its water balance. The climate change would affect the ratio between the water balance components. Climate warming should raise water temperature of lakes. Water temperature affects the speed of chemical reactions and productivity of plants.

Shallow lakes are most vulnerable to the changes of environment. The exchange of material between the near-bottom and surface water layers is more intensive in unstratified lakes. The photosynthesis zone in shallow lakes includes a relatively larger part of water mass than in deep lakes. In transparent lakes, where the zone of photosynthesis may reach the bottom, large water plants – macrophytes – are prevalent. Turbulent water inhibits

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macrophyte growth and their place is taken by phytoplankton which is even a greater obstacle to penetration of light into deeper water layers. There is a permanent competition for nutrients and light between the both chains of primary production. The equilibrium between macrophytes and phytoplankton may change under the influence of changing climate, water balance and biogenic loads.

Thornthwaite–Mather water balance model coupled with dynamic ecosystem model PCLake was used to evaluate the dynamics of water balance, thermal, ice regime and eutrophication rates of shallow Lithuanian lakes in 21st century.

Climate change in the 21st century will speed up eutrophication processes in the shallow Lithuanian lakes. The main decisive factors of eutrophication changes will be: higher water temperature, shorter time spans with ice cover and lower water level of lakes.

Annexes

Modelling the influence of climate change on N-Leaching and the water balance: a regional study of farmland in Denmark, Jensen, N.H. & Veihe, A.[84]

Table 1 Temperature (T) and precipitation (mm) used for the present and future model scenarios, here shown as half-year average. Changes in precipitation and temperature are based on Andersen *et al.* (2006).

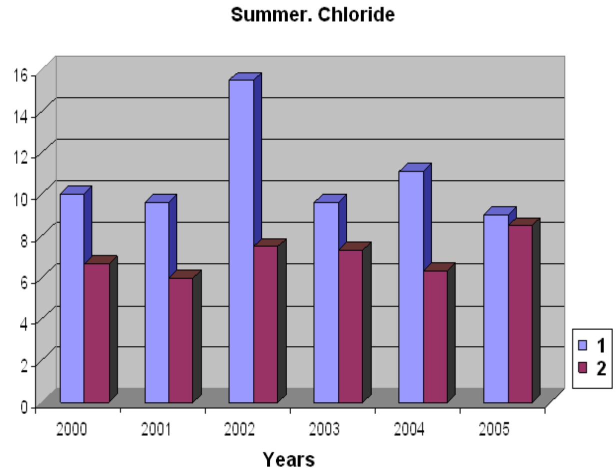
	Temperature (°C)			Precipitation		
Half-year	Present	Future	Δ T	Present (mm)	Future mm)	% change
Winter	3.4	6.7	3.2	295	362	22.7
Summer	13.4	16.6	3.2	333	276	-17.1

Table 2. Average weighted nitrogen balances for the three scenarios. There was no N fixating crops in the crop rotation. In the balance is included a seed N input of 3 kg/ha. Atm. deposition = atmospheric deposition, NH_3 vol. = NH_3 volatilization.

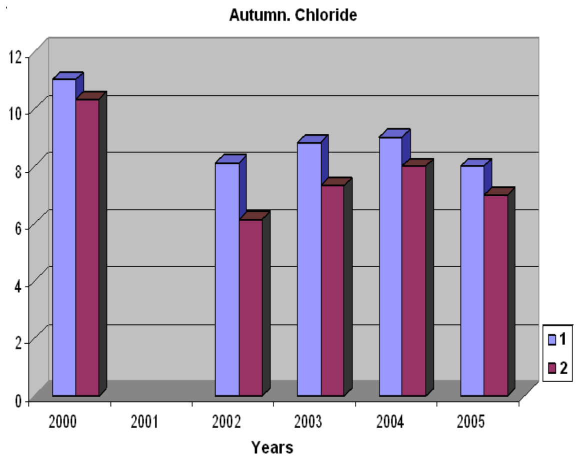
Scenarios	N fertilizer	N manure	Atm. deposition	Harvest	N leached	NH_3 vol.	Denitrification	Balance
1 (Present)	128	45	15	143	57	4	15	-28
2 (Future climate)	128	45	15	136	75	4	18	-42
3 (Future climate and changed management)	125	45	15	151	57	4	19	-43

[84] Department of Environmental, Social and Spatial Change, Roskilde University, House 02, P.O. Box 260, 4000 Roskilde, Denmark. E-mail: nhj@ruc.dk

Appearance of the risk contamination of drinking water at influence of rainfall on the underground water resources, **Parviz Normatov, Muslima Kholmirzoeva, Inom Normatov**



a



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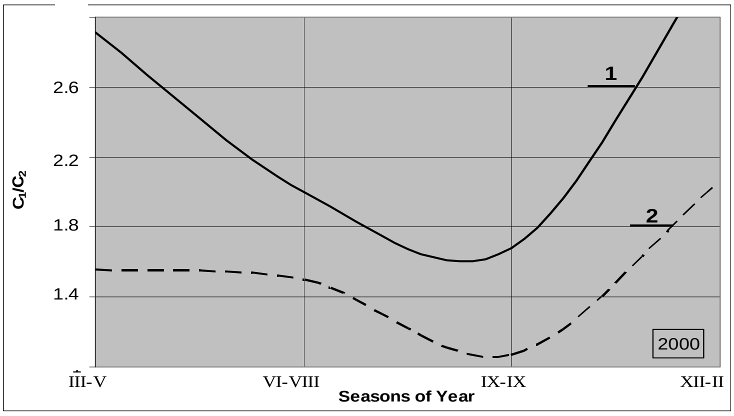
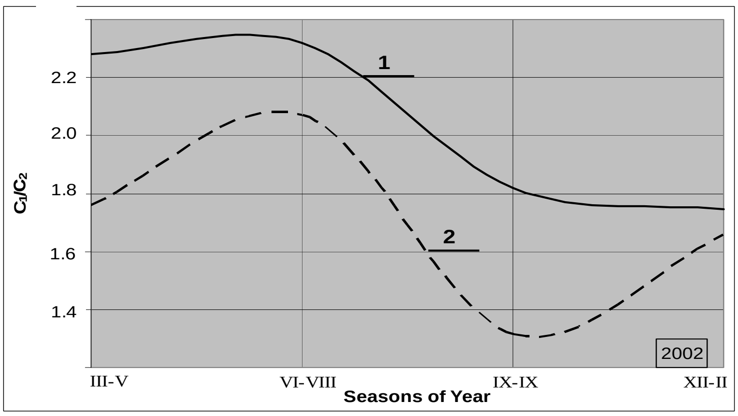


a

Fig .1. Average annual of the chloride concentration (mg/l) in underground water sources in summer (a) and autumn (b). 1- Kofarniganski. 2-East unit



b

Fig.2. Relative change of the chloride (a) and nitrate (b) concentration in underground water sources Kofarniganski (C_1) and East unit (C_2) depending on seasons of year

Practical information

Contact

- **For more information on the project**

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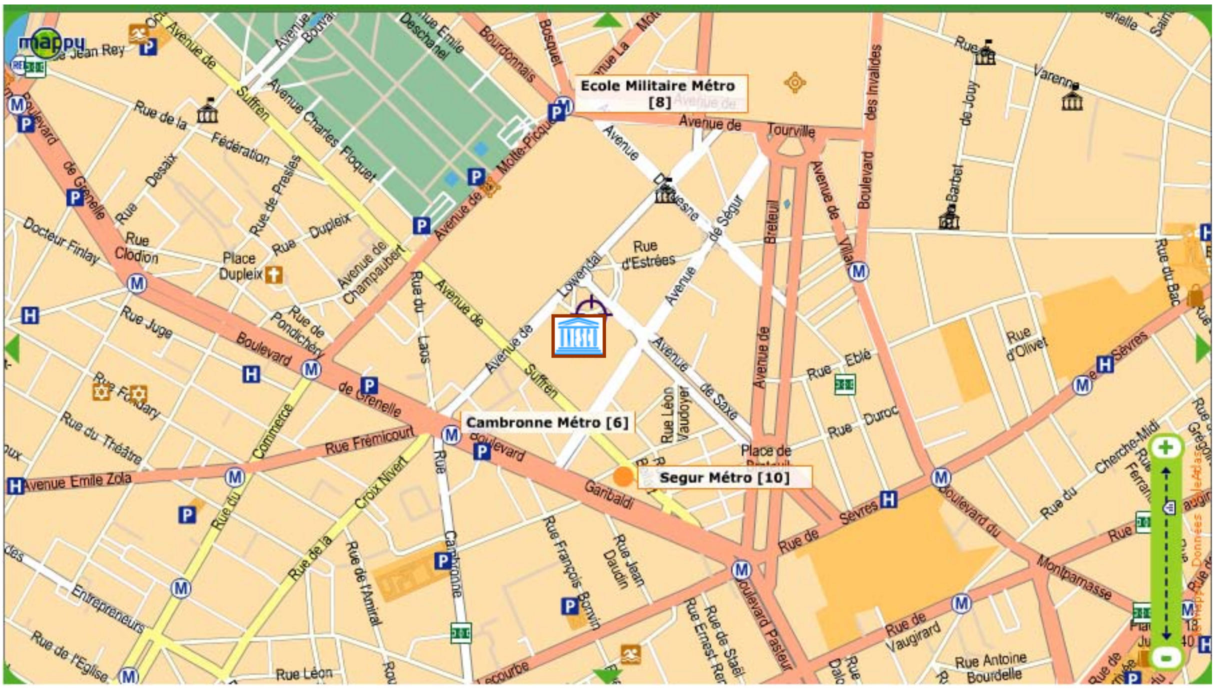
  On http://isonitrate.brgm.fr , you can download documents and have access to hotel recommendations

Venue

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



CONTENT

Friday 11 December 2009