Assessing agriculture pollution in the Beja aquifer using nitrogen isotopes (South Portugal)

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Abstract. This paper intent to give scientific support for political decisions, considering the sustainable development of rural regions under semiarid conditions exploiting shallow aquifers, and promote appropriate use of nitrogen fertilizers, based on EC Water Framework Directive and EC Groundwater Framework Directive in the context of vulnerable aquifers.Stable nitrogen isotopes ($^{15}N/^{14}N$ ratios) can offer a direct way to identify the pollutant sources in groundwater systems. In the research area two major sources of nitrate were identified, fertilizer and manure, which present different isotopic $\delta^{15}N$ signatures. The relative contributions of these two sources to groundwater or surface water can be estimated by mass balance. The analysis of nitrate $\delta^{18}O$ together with $\delta^{15}N$ improves the ability to trace nitrate sources and cycling.According field practice in the rural area of Beja, major cause of pollution comes from fertilizers.Isotope results are not conclusive about the possibility that major source of nitrate-N in groundwater comes from agriculture as expected. Further work is required regarding seasonality sampling and laboratory techniques with sufficient precision accuracy.

1. Introduction

Large-scale diffuse pollution is of great concern in most European countries. Soils and groundwater bodies show increasing nitrates and pesticides concentrations due to intensive agriculture.
This paper will focus on *Assessing the Impacts of Agriculture on Groundwater Quality Using Nitrogen Isotopes* namely in the "Gabbros of Beja Aquifer System" ($350 \ km^2$) in the vicinities of Beja (south Portugal). This Aquifer System represents the most productive hard aquifer in the region and the best agriculture land use with direct consequences regarding nitrate diffuse pollution.

Nitrate diffuse pollution greatly concerns the scientific Portuguese community and the National Water Authorities (INAG). This situation must be changed according to the EU Nitrate Framework Directive (91/676/EEC) and EC Water Framework Directive (2000/60/EC). In particular, authorities should revaluate aquifer vulnerability and mobilize funds to promote Nitrogen-use Efficiency and Nitrogen Management, regarding Environmental Farming Proposals (91/2078/EEC) and Drinking Water Regulations (80/778/EEC).

Isotopes of nitrogen were used to distinguish pollutant sources. Nitrate-nitrogen and oxygen isotopes can facilitate the distinction between fertilizer and waste as pollutant sources.

2. Study area overview

The study area is located in South Portugal, between Ferreira do Alentejo and Serpa, covering an area of about 350 km^2 in Ossa-Morena geotectonic unit. A case study has been established nearby the city of Beja (Fig. 1).
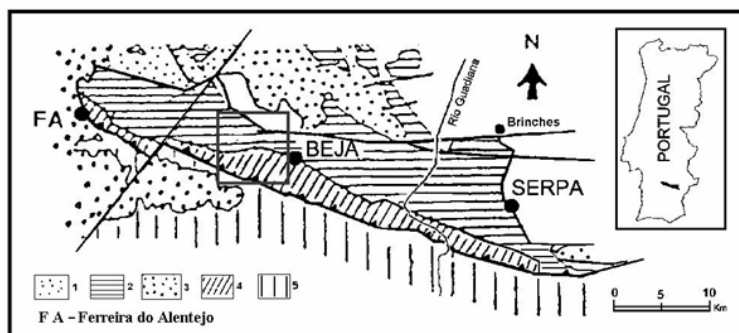

FIG. 1. Geographical location of "Gabbros of Beja" Aquifer (350 km^2) and study area (50 km^2). General geology adapted from Ref. [1]. 1-Odivelas Volcano-sedimentary Complex. 2-Maphic and intermediate plutonic rocks (Beja`s Gabbro Complex). 3-Plutonic acid and sub-volcanic rocks (Baleizão Porphirs). 4-Beja-Acebuches Ofiolitic Complex (meta-gabbros and basic meta-volcanites). 5-Pulo do Lobo Accretion Terrain (South Portuguese Geotectonic Unit – schists).

The gabbro-dioritic shallow aquifer is one of the most productive formations of the Alentejo region (south Portugal). Recharge is calculated between 10 % and 20 % (some places more) of average annual rainfall (500 mm/yr) according to recent recharge models, and occurs mainly between January and March/April [2][3].

In the study area well productivity's range from 1 to 15 L/s with most frequent average values around 5 L/s and unproductive drills less than 20 %. A hydrochemical monitoring was carried out between July 1997 and July 2000 to assess spatial and temporal variability of nitrate contents in the aquifer due to seasonal fertilization and rainfall episodes. A large range of values was recorded but more frequently classes were 50-60 and 70-80 mgNO$_3$/L. The intra-annual analysis has a large range variation reaching 100 mg/L and median range from 53 mg/L to 86 mgNO$_3$/L.

Increasing concentrations of nitrate in groundwater supplies for Beja municipality was recognized early in the 1940s due to excessive fertilization directed to increase national grain production. Land use is mainly cereal (wheat) and sunflower or corn as alternative crops. Under intensive cereal crops fertilizer application in the range of 100-150 kgN/ha/yr is common. The nitrate ion content in groundwater is thought to be due mainly to processes of natural nitrification, decomposition of organic material and human pollution, namely agriculture related to the use of nitrogenous fertilizers in farming.

3. Isotopic approach

This paper documents the development of appropriate and innovative techniques to enable isotope measurements in order to discriminate nitrogen source in groundwater of unconfined shallow aquifer near Beja (South Portugal) recently declared as vulnerable area to nitrate diffuse pollution.

The isotopic analyses of the water samples were performed in Instituto Tecnológico e Nuclear (Sacavém-Portugal). All the isotopic determinations ($\delta\,^2$H, $\delta\,^{15}$N, δ^{18}O$_{NO3}$ and $\delta\,^{18}$O) were carried out using a mass spectrometer for light isotopes.

Pollution associated to agriculture has had a direct and indirect effect on groundwater recharge and on aquifer biogeochemistry rates and composition. Direct effects include dissolution and transport of

excess quantities of fertilizers [4]. Using the mass spectrometry methodology, isotopic differences are found in most terrestrial materials has $\delta^{15}N$ compositions between -20 and +30 $^o/_{oo}$ [5].

The dominant source of nitrogen is the atmosphere ($\delta^{15}N=0$ $^o/_{oo}$). Many plants fix nitrogen and organisms cycle this nitrogen into the soil. Other sources of nitrogen to watersheds include fertilizers produced from atmospheric nitrogen with compositions of 0 to 3 $^o/_{oo}$ and animal manure with nitrate $\delta^{15}N$ values generally in the range of +10 to +25 $^o/_{oo}$. Two factors control the $\delta^{15}N$ values of any N-bearing compound in the subsurface: (1) variations in the $\delta^{15}N$ values of inputs (sources) and outputs (sinks) of the compound in the subsurface, and (2) chemical, physical and biological transformations of materials within the soil or groundwater that produce or remove the compound.

The analysis of both $\delta^{18}O$ and $\delta^{15}N$ of nitrates provides excellent separation of nitrate sources. The nitrates formed in waters with $\delta^{18}O$ values in the range of -25 to -5 $^o/_{oo}$ should have $\delta^{18}O$ values in the range of -9 to +4 $^o/_{oo}$. The $\delta^{15}N$ of atmospheric nitrate has a moderate range of composition around 0 $^o/_{oo}$ [6].

Under ideal circumstances, stable nitrogen isotopes offer a direct mean of source identification, because the two major sources of nitrate in many agricultural areas, fertilizer and manure, have isotopically distinct $\delta^{15}N$ values. The relative contributions of these two sources to groundwater or surface water can be estimated by mass balance. However, soil-derived nitrate and fertilizer nitrate commonly have overlapping $\delta^{15}N$ values, preventing their separation using $\delta^{15}N$ alone, but the analysis of nitrate $\delta^{18}O$ together with $\delta^{15}N$ improve the ability to trace nitrate sources and cycling.

In hydrology studies $\delta^{15}N$ are used also as a tracer in the identification of aquifer mixtures. According to Ref. [7] the relationships between various aquifers that are linked in succession along a general flow gradient, the nitrate concentrations and the different isotopic $\delta^{15}N$ content on groundwater allow the identification and quantification of the interconnection between different groundwater systems.

The methodologies and techniques proposed in this study may be obtained through the bibliography. The critical analysis of the methods, with the necessary rigor, would occupy space that isn't available in the format of this paper.

3.1. Results

Field sampling was carried out during December 2004 and May 2006.Waters are medium mineralized, with electrical conductivity (EC) between 300 and 1300 µS/cm and calcium-magnesium facies. Nitrates in groundwater are in the range of 2 to 150 $mgNO_3/L$ with most common records overlap 40 $mgNO_3/L$.Water sample from wastewater treatment facilities (sample nº1) shows the highest mineralization (EC= 2370 µS/cm) and low NO_3 and $N-NO_3$ content (less than 2 mg/L).

The isotopic composition of the groundwater samples collected in December 2004 was plotted in a δ^2H vs $\delta^{18}O$ diagram (Fig. 2). Also in this figure the Local Meteoric Water Line (LMWL) have been represented, estimated from the isotopic composition of precipitation in Beja meteorological station (ITN database; monthly samples from 1988-2001). The equation of the LMWL is $\delta^2H = 7.67\ \delta^{18}O + 8.93$.

From the diagram it is possible to observe that the spring is plotted relatively closer from the LMWL, as well as the majority of the borehole water samples. The shallow groundwater samples and sewage present a deviation from this line, most probably related with isotopic fractionation due to evaporation processes. Also from the diagram a good relation between the isotopic composition of the sewage and the isotopic composition of the shallow groundwater samples (wells) can be observed.

Previous work indicates that samples nº 2, 4 and 9 could have domestic/sewage contribution to nitrate content [8]. Fertilizers should influence other samples, since wells are located in the open field (samples nº 3, 5, 6, 7, 8, 10, 11, 12, 13, 14, 15 and 16). Isotopic data was used to confirm conceptual model and the magnitude of source contribution. Results of isotopic analyses are showing in Table 1.
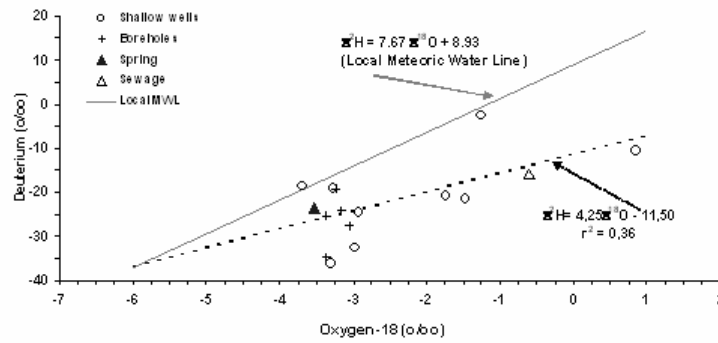
FIG. 2. δ^2H vs $\delta^{18}O$ for groundwater samples from the study area (December 2004).

Nitrogen isotope ratios on groundwater show a range in $\delta^{15}N$ from +1 $^o/_{oo}$ to +26 $^o/_{oo}$. For sewage sample, $\delta^{15}N$ is +16.14 $^o/_{oo}$. These results overlap between the $\delta^{15}N$ values of both animal and septic tank wastes (Fig. 3).

Table 1. Isotope data analyses (December 2004 and May 2006)

Code	December 2004				May 2006		
	NO$_3$ (mg/L)	$\delta^{15}N$ ($^o/_{oo}$)	$\delta^{18}O$ (H$_2$O) ($^o/_{oo}$)	δ^2H (H$_2$O) ($^o/_{oo}$)	NO$_3$ (mg/L)	$\delta^{15}N$ ($^o/_{oo}$)	$\delta^{18}O$ (NO$_3$) ($^o/_{oo}$)
1- Sewage	1.28	16.14	-0.60	-15.90	.....	.....	.....
2- Well	38.97	18.22	-1.46	-21.60	.....	.....	.....
3- Well	37.78	12.42	-1.26	-2.60	48.37	6.88	4.29
4- Well	61.73	.....	-2.93	-24.60	113.00	8.13	5.35
5- Well	18.91	26.17	0.86	-10.80	144.20	17.71	-4.71
6- Well	66.30	3.69	-3.27	-19.20	110.60	1.67	5.35
7- Well	52.88	3.07	-3.29	-36.30	34.50	16.41	2.63
8- Well	58.06	13.38	-3.69	-18.70	.....	.....	.....
9- Well	53.76	13.63	-2.96	-32.60	.....	.....	.....
10- Well	2.66	11.95	-1.73	-20.90	.....	.....	.....
11- Borehole	40.96	8.12	-3.37	-25.30	58.40	7.66	-8.16
12- Borehole	40.34	26.12	-3.37	-34.80	77.70	3.06	4.79
13- Borehole	45.92	.....	-3.17	-24.20	49.60	5.63	9.95
14- Borehole	56.11	3.50	-3.24	-19.30	.....	.....	.....
15- Borehole	41.67	.....	-3.05	-27.60	.....	.....	.....
16- Spring	41.50	.....	-3.53	-23.60	52.70	.....	7.83

Oxygen isotope $\delta^{18}O$ (H$_2$O) data are in the range of -3.5 $^o/_{oo}$ to $+ 0.9$ $^o/_{oo}$ for groundwater and is -0.6 $^o/_{oo}$ for sewage. Oxygen isotope $\delta^{18}O$ (NO$_3$) data are in the range of -8 $^o/_{oo}$ to $+ 10$ $^o/_{oo}$.

Fig. 4 shows the normal range of $\delta^{18}O$ and $\delta^{15}N$ values for dominant sources of nitrate [5]. Nitrate derived from ammonium fertilizer, soil, organic matter and animal manure have overlapping $\delta^{18}O$ values; for these sources $\delta^{15}N$ is a better discriminator. In contrast, nitrate derived from nitrate fertilizer or atmospheric sources are readily separable from microbial nitrate using $\delta^{18}O$, even though the $\delta^{15}N$ values are overlapping. The dual isotope method has proved quite useful for source identification in some surface-groundwater studies [6].
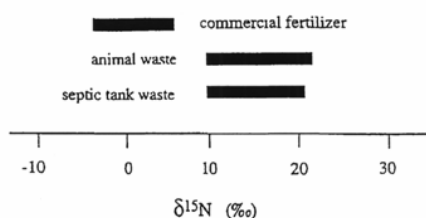
FIG. 3. Range of $\delta^{15}N$ values for the major sources of nitrates into groundwater [8].

Nitrification of ammonium and/or organic-N in fertilizer, precipitation, and organic waste can produce a large range of δ values. Soil waters tend to have higher NO_3-$\delta^{18}O$ values and a larger range of NO_3 - $\delta^{18}O$ values than groundwaters due to higher $\delta^{18}O$ values of O_2 and/or H_2O in soils.Oxygen isotope from the NO_3 determinations indicates that fertilizers do not provide major source of nitrate to groundwater. The combination of both $\delta^{15}N$ and $\delta^{18}O$ data indicate that signatures observed in groundwater are the result of ammonia nitrification originating from either animal wastes or septic tank wastes, with no significant influence from commercial fertilizers.
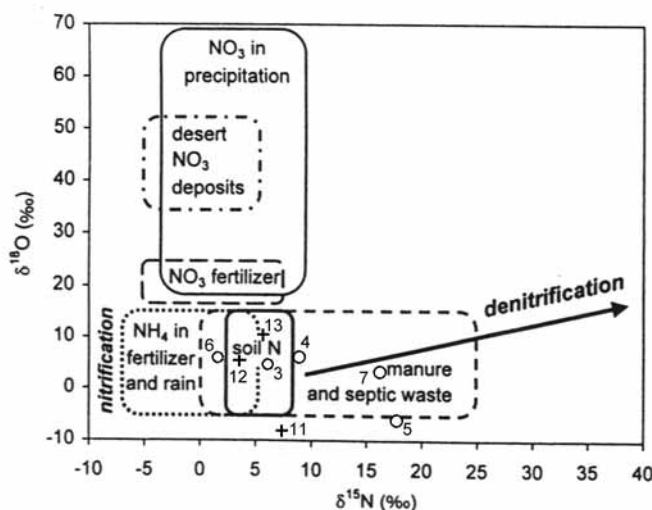

FIG. 4. Schematic of typical ranges of $\delta^{18}O$ and $\delta^{15}N$ values of nitrate from various sources (adapted from Ref.[5]) and sample plot (May 2006).

4. Conclusions

Progress has been made in Portuguese research centres to allow determination of $\delta^{18}O$ and $\delta^{15}N$ in nitrates. Further work is required to ensure robust techniques with sufficient precision accuracy.

Using the current techniques it is possible to discriminate different sources of anthropogenic contamination into ground and surface systems.

According field practice and previous monitoring, conceptual model indicates that major cause of pollution comes from fertilizers.

However, preliminary results are not conclusive about the possibility that major source of nitrate-N in groundwater comes from agriculture. There are several factors in the ecosystems than can significantly modify de $\delta^{15}N$ values. Mixing of point and non-point sources along shallow flowpaths makes determinations of sources, extent and denitrification processes very difficult to identify.

Further work is necessary to confirm or not the real origin of nitrate in "Gabbros of Beja" aquifer system and source contribution.

ACKNOWLEDGEMENTS

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