Environmental isotopes (^{15}N and ^{18}O) in the assessment of groundwater degradation: Aveiro Quaternary aquifer (NW Portugal)

P. G. Fernandes · P. M. Carreira · D. Nunes

Abstract The Aveiro region, situated on the Northwest coast of Portugal is one of the most industrialized areas of Portugal. The shallow Quaternary aquifer system, mainly of detrital sediments of Pleistocene and Holocene ages, is still today an important water resource for this region despite growing evidence of diffuse pollution problems. Isotope techniques have been used to evaluate the aquifer vulnerability to nitrate contamination (δ^{18}O and δ^{15}N from NO$_3$ and δ^2H and δ^{18}O from H$_2$O). Nitrogen isotopes were used to identify nitrogen sources and assess agriculture, cattle-breeding, urban and industrial contributions to the nitrogen cycle in the Aveiro ecosystem.

Keywords Groundwater contamination · Nitrogen isotopes · Environmental isotopes

Introduction

Large-scale diffuse pollution is of great concern in most European countries where nitrate concentrations in public water supplies have risen above acceptable levels largely as a result of overuse of fertilizers in agriculture practices, as well as contamination by factories, human and animal wastes. Related to these possible anthropogenic inputs that leads to the degradation of water resources, this study focused on origin/sources of nitrate in water resources (surface and groundwater bodies) using nitrogen isotopes. The studied area, Aveiro region, is located in the NW of Portugal, presenting important industrial and agriculture activities, with an impact on the water quality of the shallow Quaternary aquifer and the Vouga River.

The water supply in the Aveiro region is guaranteed using both surface and groundwater resources. Drinking water supply is guaranteed by integrated management of surface water resources from the Vouga River and groundwater from the Cretaceous aquifer. In some parts of the region, surface water resources are used also to irrigate the crops in the river, stream and lagoon banks.

From the hydrogeological point of view, the shallow Quaternary aquifer system consists mainly of detrital sediments of Pleistocene and Holocene age (dunes, fluvial terraces and ancient beaches) related to different marine regression events. These units are very permeable, presenting high rate of recharge from direct infiltration of the rainfall or by water from irrigation [1]. Owing to easy exploitation and high productivity, these water bearing units represented, until the late sixties, the main groundwater resource in the region. The second groundwater system consists of a confined multilayer sequence of Cretaceous age, mainly made up of sandstones and clays, where the carbonate layers make up only between 1 and 8% of total thickness. This multilayer is made up of stratified layers of quartz sandstones and clay sediments overlying the schist-greywacke complex [2, 3].

Experimental

In this study 16 samples of groundwater from the shallow Quaternary aquifer were collected for ^{2}H and δ^{18}O determinations in the water molecule and for determination of δ^{18}O and δ^{15}N values from NO$_3$, all the water samples have nitrates concentrations higher than 25 mgL^{-1}. In all

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the samples pH, temperature and electrical conductivity were analysed in situ.

The Nuclear and Technological Institute (Instituto Tecnológico e Nuclear—ITN) in Portugal carried out the determinations of $\delta^{18}O$ and δ^2H values from H_2O by mass spectrometry, applying, respectively, the Epstein and Mayeda [4] and Friedman [5] methods. The water samples were measured by the mass spectrometer Sira 10 VG ISOGAS with an analytical precision of $\pm 0.1‰$ for $\delta^{18}O$ and $\pm 1‰$ for δ^2H. The isotopic content of ^2H and ^{18}O in the water samples are reported as a deviation from Vienna-Standard Mean Ocean Water (V-SMOW) [6]. Delta notation (δ^2H and $\delta^{18}O$) is used throughout the paper to report the measured isotopic variation defined by the following equation:

$$\delta(‰) = \left(\frac{R_{sample}}{R_{standard}} - 1 \right) \times 1000 \quad (1)$$

where R represents the isotopic ratio ($^2H/^1H$ and $^{18}O/^{16}O$) of the sample and the standard [6].

The determination of $\delta^{18}O$ and $\delta^{15}N$ from NO_3 samples requires the collection of nitrate from waters sample. This collection had followed the method described in Silva [7] according to which nitrate is collected passing the water sample through cation and anion exchange columns, subsequently this nitrate is extracted from the anion column, converted to $AgNO_3$ and analysed for its isotopic composition. Nitrate is eluted from the anion exchange column with HCl; this nitrate-bearing acid is neutralized with Ag_2O, and then freeze-dried to obtain solid $AgNO_3$ for $\delta^{15}N$. For $\delta^{18}O$ analysis, aliquots of the neutralized eluant are processed further to remove non-nitrate oxygen-bearing anions. Barium chloride is added to precipitate sulphate and phosphate; the solution is then filtered, passed through a cation exchange column to remove excess Ba^{2+}, re-neutralized with Ag_2NO_3, and freeze-dried. The resulting $AgNO_3$ is then analysed by spectrometry coupled to a EUROVECTOR elemental analyser, using as standard IAEA-N1 and IAEA-N2 reference materials.

Results and discussion

From previous studies it is known that the Quaternary aquifer represents a superficial aquifer unit, collecting groundwater samples from wells and springs (with mean depths of 20 m), it is possible to admit that these water group represents the isotopic composition of Baixo Vouga actual precipitation [8]. The isotopic composition oscillates between −29 to −25‰ and −5.0 to −4.4‰ for δ^2H and $\delta^{18}O$, respectively—Fig. 1 [8].

The samples analysed in this study present values of δ^2H and $\delta^{18}O$ slightly enriched relatively with the values mentioned above [8] (Table 1), however, it is important to mention that the samples from this study were mainly collected in dug-wells, with possible isotopic fractionation due to water evaporation.

The major sources of nitrate, responsible for the water resources degradation present isotopically distinct $\delta^{15}N$ values. Using these features, stable nitrogen isotopes can offer a direct way of source identification. The relative contribution of the different sources to groundwater or surface water can be estimated by mass balance. However, in some situations, such as soil-derived nitrate and fertilizer, nitrate shows overlapping $\delta^{15}N$ values, preventing their separation using $\delta^{15}N$ alone. So the analysis of $\delta^{18}O$ of nitrate in conjunction with δN is fundamental to improve the ability to trace nitrate origins [9].

Figure 2a shows the normal range of δN and $\delta^{18}O$ values for dominant sources of nitrate. Nitrate deriving from ammonium fertilizer, soil organic matter, and animal manure has overlapping $\delta^{18}O$ values; for discriminating among these sources ^{15}N has to be considered [9]. In contrast, nitrate derived from nitrate fertilizer or atmospheric sources is readily separable from microbial nitrate using $\delta^{18}O$, even though the $\delta^{15}N$ values are overlapping. The conducted dual isotope study of groundwater nitrate in Aveiro groundwaters proved to be useful in source identification (Fig. 2b) allowing establishing the manure and

Fig. 1 δ^2H versus $\delta^{18}O$ represented by samples from the Cretaceous multiaquifer system and from the Quaternary aquifer. Correlation coefficients between δ^2H and $\delta^{18}O$ were based on the δ values. Regression line: $\delta^2H = (8.29 \pm 1.07)$ $\delta^{18}O + 12.06$ ($r = 0.83$; $n = 19$). Mean isotopic composition is from the station "Serra do Pilar". The ellipse delimits the Quaternary aquifer mean isotopic composition [8]
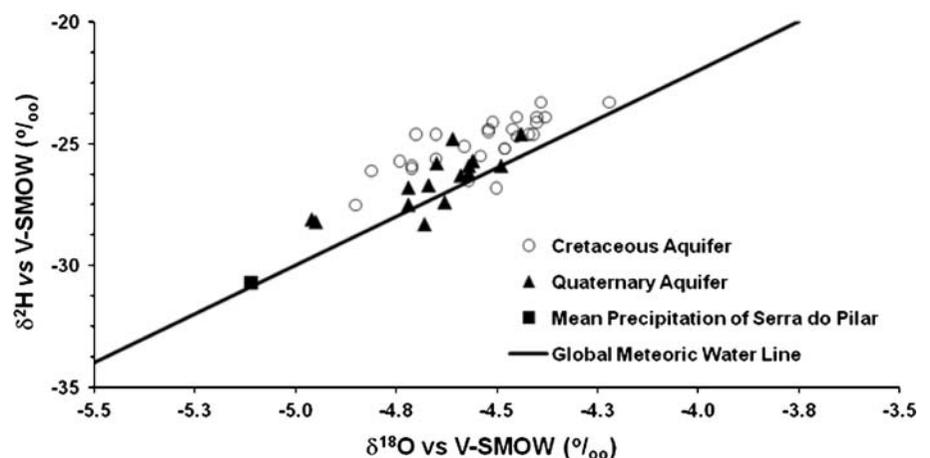
Table 1 Isotopic composition and field parameters of the water samples collected in the Aveiro Quaternary aquifer

Sample	pH	EC μS/cm	T °C	δ^{18}O‰	δ^{2}H‰
1	6.13	837	13	−3.76	−21.2
2	6.11	668	16	−4.02	−18.8
3	6.40	923	12	−4.17	−27.8
4	6.21	844	16	−3.89	−24.6
7	6.15	429	12	−3.85	−24.3
9	6.94	913	10	−4.08	−25.9
10	6.66	482	16	−3.94	−24.5
11	7.48	588	7	−3.85	−25.6
12	6.04	350	15	−4.16	−27.5
13	7.03	460	18	−3.89	−24.7
14	6.97	535	9	−4.18	−26.0
15	6.89	570	12	−3.93	−24.7
16	6.77	360	10	−3.90	−24.1
18	6.59	620	12	−2.57	−18.7
25	6.84	785	12	−4.00	−25.9
26				−4.07	−21.9

septic waste as the main nitrate source in the analysed waters. It was also identified three samples with nitrate deriving from NH$_4$ of fertilizer and rain, which correspond to agricultural locations or industrial surroundings.

It is likely that the O$_2$ (and perhaps H$_2$O) available to nitrify in the small soil pores has been significantly affected by microbial processes, being commonly enriched in ^{18}O relative to "bulk" compositions. When ^{18}O-enriched sources of oxygen are utilized by microorganism, the resulting nitrate is also enriched in ^{18}O. If microbial nitrate is "labeled" by the δ^{18}O value of ambient water, the seasonal change in the δ^{18}O of water might cause a seasonal change in soil nitrate δ^{18}O. Alternatively, if fields are irrigated with evaporated water at the same time that ammonium fertilizer is applied, the nitrate formed might reflect the evaporated signature of the water δ^{18}O [9].

In order to evaluate if δ^{18}O value of nitrate was affected by changes in the ^{18}O values of water and O$_2$ the obtained results were plotted in Fig. 3. It is possible to notice that the obtained values do seem to present neither NO$_3$ δ^{18}O values for microbial nitrification with ambient H$_2$O δ^{18}O nor O$_2$-δ^{18}O values from atmosphere.

Conclusions

The Quaternary aquifer represents a shallow aquifer unit representing the isotopic composition of Baixo Vouga actual precipitation [8]. The isotopic composition oscillates between −29 to −25‰ and −5.0 to −4.4‰ for δ^{2}H and δ^{18}O, respectively. The conducted dual isotope (δ^{15}N and

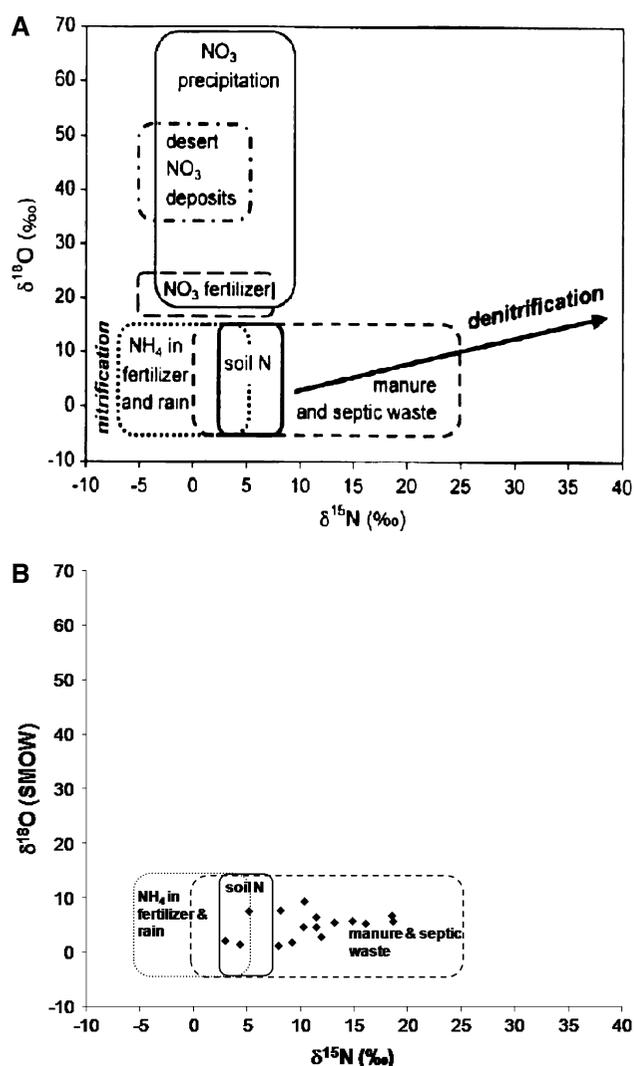**Fig. 2 a** Typical ranges of δ^{15}N and δ^{18}O values of nitrate from various sources [9]; **b** δ^{15}N versus δ^{18}O values of nitrate of Aveiro Quaternary aquifer samples

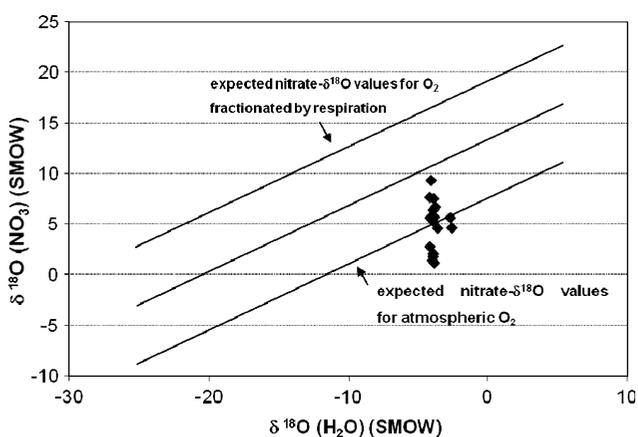**Fig. 3** δ^{18}O (H$_2$O) versus δ^{18}O (NO$_3$), adapted from Kendall [9]

$\delta^{18}O$) study of groundwater nitrate proved to be useful in source identification allowing to establish manure and septic waste as the main nitrate source in the analysed waters. It was also identified with nitrate deriving from NH_4 of fertilizers and rain, corresponding to agricultural locations or industrial surroundings.

References

1. Condesso De Melo, M.T., Silva, M.M.: In: Edmunds, W.M., Shand, P. (eds.) The natural baseline quality of groundwater, p. 488. Blackwell Publishers, Oxford (2007)
2. Silva, M.A.M.: Hidrogeología del sistema multiacuífero Cretácico del Bajo Vouga—Aveiro (Portugal). Ph.D. Thesis, Universidad de Barcelona, Spain, p. 436 (1990)
3. Rocha, F.: Argilas Aplicadas a Estudos Litoestratigráficos e Paleoambientais na Bacia Sedimentar de Aveiro. Ph.D. Thesis, University of Aveiro, Aveiro, p. 399 (1993)
4. Epstein, S., Mayeda, T.: Geochim. Cosmochim. Acta **4**, 213 (1953)
5. Friedman, I.: Geochim. Cosmochim. Acta **4**, 89 (1953)
6. Gonfiantini, R.: The δ-notation for expressing stable isotope ratio variations. In: Gat, J.F., Gonfiantini, R. (eds.) Stable isotope hydrology. Deuterium and Oxygen-18 in the water cycle. Technical Reports Series No 210, p. 35. International Atomic Energy Agency, Vienna (1981)
7. Silva, S.R.: J. Hydrol. **228**, 22 (2000)
8. Carreira, P.M.M.: Paleoáguas de Aveiro. Ph.D. Thesis, University of Aveiro, Aveiro, p. 377 (1998)
9. Kendall, C.: In: Kendall, C., McDonnell, J.J. (eds.) Tracing nitrogen sources and cycling in catchments, isotope tracers in catchment hydrology. Elsevier Science B.V., Amsterdam (1998)