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Identification of contamination sources through the application of nitrogen, oxygen and deuterium isotopes in the Estarreja shallow aquifer, Aveiro (Portugal)

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Abstract. Agriculture, chemical industry and livestock activity are the most important activities in the Estarreja municipality and have put at risk the quality of surface water and groundwater, leading to a great vulnerability of the Estarreja shallow aquifer. In this respect, the main goal of the present study is the identification of contamination sources through the application of nitrogen and oxygen isotopes, beside the deuterium and oxygen isotopes in the Estarreja shallow aquifer. Results of $\delta^{15}N$ and $\delta^{18}O$ in the nitrate indicate isotopic signatures for ammoniacal fertilisers, wastewater and animal manure, clearly showing the influence of industrial and agricultural activities. The $\delta^{2}H$ and $\delta^{18}O$ in the water enrichment of some samples could suggest salinization phenomenon.

Keywords: Estarreja; Groundwater; Nitrate; N origin; Stable isotopes

1 Introduction

The Nitrate Directive (91/676/EEC) concerns about the protection of the water quality against pollution caused by nitrate from agricultural sources. It aims to reduce the quantities of nitrate in water and prevent its continued rise. Additionally, the Urban Wastewater Directive (91/271/EEC) aims to protect the environment from the harmful effects caused by wastewater discharges. The implementation of Nitrate Directive and Water Framework Directive (2000/60/EC) led to the designation of large areas vulnerable to nitrate pollution, designated as Nitrate Vulnerable Zones (NVZs). NVZs are areas at risk from agricultural nitrate pollution in which groundwater contain or could contain (if no action is taken to reverse trend) more than 50 mg/L of NO_3. The objectives are to ensure that the nitrate concentration in surface water and groundwater does not exceed the limit of 50 mg/L, as well as to control the incidence of the eutrophication phenomenon. The NVZ of Estarreja-Murtosa, Aveiro is the study case area to consider. In Estarreja region, the groundwater shows nitrate concentration of up to 140 mg/L. Agriculture, chemical industry and livestock activity are the most important activities in the Estarreja municipality with a perfect symbiosis between them since the 1930s. Around the 1950s, the installation of the Estarreja Chemical Complex (ECC) took place with a huge investment mainly in the production of ammonia for the manufacture of nitrogen fertilisers used in agriculture.

The literature has described some approaches in order to distinguish the different sources of nitrate in groundwater, generally with $\delta^{15}N$ and $\delta^{18}O$ in the NO_3. The $\delta^{2}H$ and $\delta^{18}O$ in the H_2O are useful to understand the hydrological cycle, especially the aquifer recharge, as well as salinization phenomenon. The present study aimed to discriminate the contamination sources through the application of these two isotopic couples in water samples from the Estarreja shallow aquifer.

2 Materials and Methods

The study area is characterized by Holocene and Pleistocene detrital sedimentary deposits [1]. This area has two important aquifer systems [2]: (a) the Aveiro Cretaceous Multi-Aquifer System (ACMAS) and (b) the Aveiro Quaternary Aquifer System (AQAS) which is essentially made up of three main aquifer units with different hydrogeological and hydraulic characteristics between them [3]. The upper aquifer is laid in modern deposits from Holocene that comprise dune formations or dune sands and alluvial deposits [4]. The second aquifer unit, a semi-confined aquifer, is laid in Pleistocene deposits, at Quaternary base aquifer [3]. The third aquifer unit is made up of Cretaceous Sandstones and Clays and Schists from Precambrian (before 540 Ma). One field campaign was carried out in Estarreja for water sampling at wet season (4th and 5th May 2018). A total of 35 wells or small diameter holes were sampled with a maximum depth of 7 meters at the Estarreja shallow aquifer (Figure 1). The $\delta^{2}H$ and $\delta^{18}O$ in the H_2O measurements (vs. V-SMOW – Vienna-Standard Mean Ocean Water) were performed by Mass Spectrometry at the Stable Isotopes and Instrumental Analysis Facility (SIIAF) in the Faculty of Sciences, University of Lisbon (Portugal). The nitrate extraction as well as $\delta^{15}N$ and $\delta^{18}O$ in the NO_3 determination were carried out in frozen samples shipped to the Environmental Isotope Laboratory (EIL) in the University of Waterloo (Canada), and analysed with a continuous flow isotope-ratio mass spectrometer, with precision of 0.5‰.

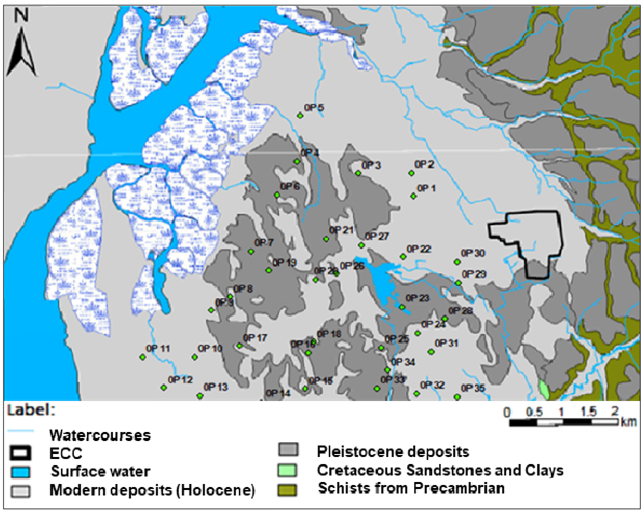

Fig. 1. Geologic Framework [3]

3 Results and Discussion

3.1 δ^2H and δ^{18}O in the H_2O

The sampled groundwater has meteoric origin considering the Global Meteoric Water Line (GMWL, [5]) represented by the equation $\delta^2H = 8\ \delta^{18}O + 10$ or the Regional Meteoric Water Line in Portugal (RMWL, [6]) with isotopes relation following the equation $\delta^2H = (6.78 \pm 0.10)\ \delta^{18}O + (4.45 \pm 4.65)$, R = 0.95, because all the samples are plotted around the lines [6] and all the deviations can be explained by physical processes as the slope of the evaporation line is 5.58, a value between 3 and 6. The samples show excess of deuterium (d) values are between 4.9 ‰ and 13.8 ‰. In Figure 2, it is possible to identify different groups of water: δ^2H isotopes enriched samples probably associated to a great humidity at the recharge area (black dots); samples enriched in heavy isotopes showing a shift to the right of the water lines that could be affected by evaporation or mixed with seawater (blue and green dots); samples depleted in heavy isotopes can be related with far way recharge area, representing condensation phenomena (orange dots).

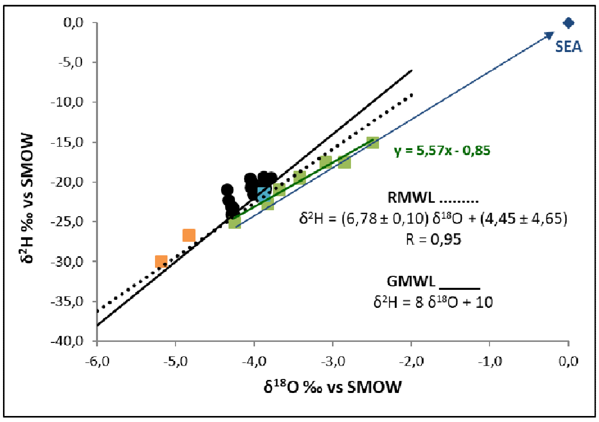

Fig. 2. Isotopic composition of δ^2H and δ^{18}O from the Estarreja shallow aquifer and its location in relation to the GMWL [5] and the RMWL [6].

3.2 δ^{15}N and δ^{18}O in the NO_3

The dissolved nitrate in groundwater have three different types of δ^{15}N isotopic signature: overlap between wastewater and animal manure (Figure 3, $10 \leq \delta^{15}N \leq 20$ [7] [8]), overlap between ammoniacal fertilisers and wastewater ($5 \leq \delta^{15}N \leq 8$, [8]) and a typical signature of wastewater ($8 \leq \delta^{15}N \leq 10$, [8] [9]).

4 Conclusions

In terms of δ^2H and δ^{18}O in the H_2O, the samples represented by blue and green dots samples can suggest a salinization phenomenon as they can be mixed with seawater, assuming δ^2H and δ^{18}O values for seawater are close to zero. In relation to δ^{15}N and δ^{18}O in the NO_3, it is possible to conclude that the samples with an isotopic signature of overlap between wastewater and animal manure could indicate clearly an agriculture component, in contrast to the samples with an isotopic signature of overlap between ammoniacal fertilisers and wastewater which can suggest an industrial and/or an agriculture component. The isotopic signature of ammoniacal fertilisers can have its origin as industrial products or as fertilisers applied in soils.

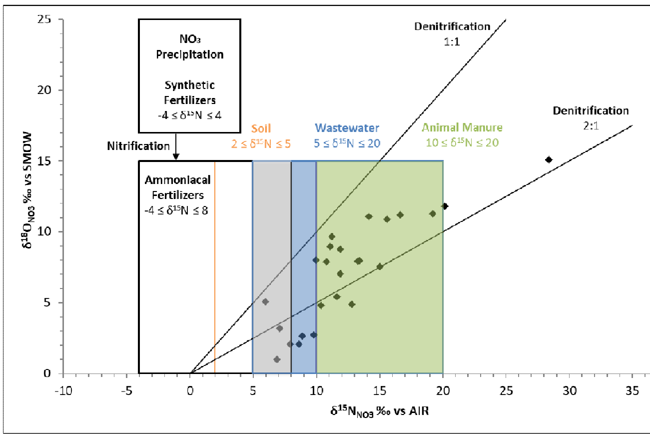

Fig. 3. Stable isotope composition of dissolved nitrate in groundwater: $\delta^{15}N$ and $\delta^{18}O$; fields are according to bibliography (see 3.2 Results and Discussion); the trends resulting from nitrate transformation processes, nitrification and denitrification [7].

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