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The use of nitrate isotopes to identify contamination sources in the Bou-Areg aquifer (Morocco)

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Abstract

The Bou-Areg coastal aquifer (Morocco) is affected by high nitrate levels in groundwater, with possible consequences for the natural environment and human health. The use of environmental tracers, including $\delta^{15}N_{NO3}$ and $\delta^{18}O_{NO3}$, allowed identifying the main sources of nitrate contamination in groundwater samples collected in 2010. These are manure and septic effluents, especially in urban areas, and synthetic fertilizers in agricultural areas. This work represents a preliminary step for a more detailed nitrate vulnerability assessment to support groundwater management and protection in the studied region.

"Keywords: Bou-Areg; Urban; Rural; Nitrate; Isotopes; Vulnerability"

1. Introduction

Nitrate contamination is a concern affecting several regions worldwide [e.g. 1, 2, 3]. In particular, in areas interested by increasing population and intense human activities, diffuse nitrate pollution can have severe impacts on ecosystems and human health. These concerns are even more crucial if water resources are scarce and precipitation rates are low, like in coastal zones in arid and semi-arid regions. Here, in fact, shallow aquifers often represent the main water source upon which human development rely on. For this reason, in order to develop effective policies for reducing contaminant loads and protect water resources,

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it is of paramount importance to clearly identify the main anthropogenic sources of human induced nitrate contamination and to adequately understand the governing factors of groundwater vulnerability [3].

Under these premises a hydrogeochemical investigation has been conducted in the Bou-Areg coastal aquifer (Morocco). General chemistry and environmental isotopes ($\delta^{15}N_{NO3}$ and $\delta^{18}O_{NO3}$) have been used to identify the main pollution sources and the processes occurring in the aquifer. This work represents a preliminary study for the development of a complete nitrate vulnerability assessment and mapping of the Bou-Areg aquifer, to be used as a support for decision making processes in the region.

The alluvial plain of Bou-Areg, located in the Northern shore of Morocco, covers a surface of about 190 km^2 and is separated from the Mediterranean Sea by the coastal Lagoon of Nador. Although being characterized by intense agricultural activities, covering more than 62% of its surface area [4, 5], the region is currently concerned by an increase in urban population (in the cities and suburbs of Nador, Beni Ensar and Kariat Arekmane) and by a development of tourism related activities. Moreover, besides agricultural purposes, groundwater is also used to sustain domestic and industrial activities in the region. It is therefore vital to reduce contaminant loads and to prevent groundwater from further contamination.

2. Methods

A total of 39 groundwater samples have been collected in the Bou-Areg coastal plain during two campaigns performed in June and November 2010 [6]. Samples were taken in both equipped and hand dug well in the rural (32 samples) and urban/sub-urban part (7 samples) of the aquifer. Physicochemical parameters (pH, Eh, Electrical Conductivity, groundwater temperature and alkalinity) have been measured directly *in situ*. About 2L of water have been collected in each sampled sites and stored for analysis. Chemical analyses of water samples have been performed at the Department of Earth and Environmental Sciences of the University of Pavia (Italy), using ion chromatography. Samples for stable isotope analysis have been collected and prepared according to standard procedures [7]. All gases were analyzed on a Finningan™ MAT 250 Mass Spectrometer at ISO4 s.n.c., Turin, Italy.

3. Results and Discussion

Hydrogeochemical results allowed classifying groundwater samples of the Bou-Areg aquifer as sodium-chloride type. Groundwater is characterized by a general high natural salinity, mainly due to water-rock interaction processes, such as dissolution of evaporative rocks and carbonates [8], and by high levels of dissolved nitrates. Most samples (29 out of 39) have, in fact, nitrate concentrations (as NO_3^-) exceeding the drinking water standard of 50mg/L (0.8 meq/L) [9]. The highest values are found in the urban and peri-urban areas, with average of 3.4 meq/L (ranging from 0.5 to 4.7 meq/L), and only one well meets the drinking standards. On the other hand in the rural area 23 out of 32 samples are above the standards, with mean concentration of 1.1 meq//L (ranging from 0.15 to 2.7 meq/L).

By comparing Cl^- and NO_3^- concentrations, two main trends can be observed (Fig. 1a). On the one hand some wells, mainly located in the urban and sub-urban parts of the aquifer show high NO_3^- concentrations with relatively low Cl^- values (dashed grey line in Fig. 1a), on the other hand some wells, are characterized by the opposite trend (black line in Fig. 1a). These two trends suggest possible distinct origins of dissolved nitrates, related to different land uses or anthropogenic activities. Being the second trend associated to wells located in the rural zone, NO_3^- origin might be related to widespread use of (N)-fertilizers for agricultural practices. An adequate nitrogen supply is essential for crop production, but if exceeding crops uptake capacity, released nitrates can be leached and transported in depth by irrigation water, resulting in diffuse groundwater contamination. Moreover, in agricultural areas, the high Cl^- concentrations, although being due to natural processes, might be increased by the use of groundwater for irrigation and by the consequent leaching of salts deposited in the vadose zone (i.e. agricultural return flow [8]). Finally, some wells (black oval in Fig. 1a) characterized by relatively low nitrate concentrations (< 1.1 meq/l) do not appear to belong to neither trend, suggesting the presence of mixed nitrate sources or processes affecting nitrate contents (e.g. denitrification).

In order to better discriminate among NO_3^- origins, $\delta^{15}N_{NO3}$ was studied (Fig. 1b). The obtained isotopic data for Bou-Areg groundwater are coherent with the isotopic composition of $\delta^{15}N_{NO3}$ of animal and human waste origin (10-15‰, mainly in urban wells), and with soil organic matter (~ 5‰) and fertilizers (~ 0‰) in rural areas [7].

The isotopic composition of $\delta^{18}O_{NO3}$ has been then studied to further constrain the identification of nitrate sources in the system and to highlight the possible occurrence of denitrification (Fig. 2). Most wells collected in the urban and suburban areas appear to be clearly affected by pollution from manure and septic effluents systems (~ +12‰ in Fig. 2). Among urban groundwater, two samples (collected in November 2010) are clearly enriched in both $\delta^{15}N_{NO3}$ and $\delta^{18}O_{NO3}$, providing evidence of the occurrence of denitrification processes, and suggesting that seasonal variations, together with land use and environmental settings, could have an impact on groundwater composition.

As concerns wells located in the rural part, many of them have an isotopic signature coherent with mineralized fertilizers or natural soil organic matter ($\delta^{15}N$ ~ +4 to +10 ‰). Nevertheless, an isotopic enrichment in $\delta^{15}N$ could also be obtained in cases of a combined impact of fertilizers and animal/human wastes, a more likely interpretation since nitrate concentrations are higher than 0.8 meq/L [7].

4. Conclusions

Hydrogeochemical results on groundwater samples collected in 2010 show that the Bou-Areg aquifer is vulnerable to nitrate contamination. The isotopic composition of dissolved nitrates indicates two main drivers for human induced pollution: (i) manure and septic effluents, especially in urban areas and (ii) synthetic fertilizers in agricultural areas. In the latter, $\delta^{15}N$ enriched values point to a mixture of those sources, possibly related to unbalanced fertilization and use of polluted groundwater for irrigation. The identification of both non-point and point sources of nitrate pollution represent the first step of a more complete vulnerability assessment of the Bou-Areg aquifer. Furthermore, ongoing investigation focuses on seasonal effects and distinction between animal and human effluents with the use of boron isotopes.

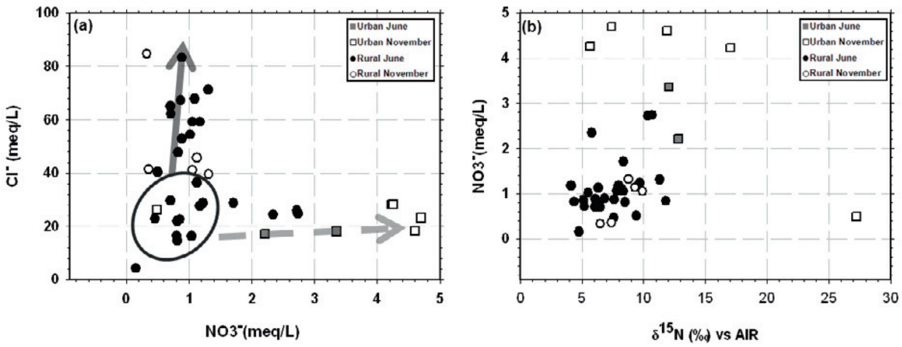

Fig. 1. (a) Plot of NO_3^- vs Cl^- (meq/L). Arrows represent the main processes described in the text and have no mathematical meaning; (b) plot of NO_3^- vs. $\delta^{15}N_{NO3}$. $\delta^{15}N_{NO3}$. Ranges for different sources are from [10].

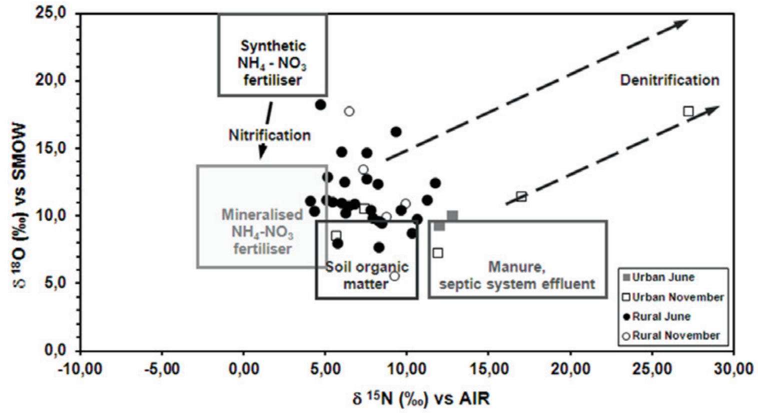

Fig. 2. Isotopic composition of dissolved nitrates (‰) for groundwater in the Bou-Areg aquifer. Ranges are for groundwater with $\delta^{18}O_{H2O} \sim -4‰$. (modified after [10]).

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