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Application of stable isotopes ($\delta^{34}S-SO_4$, $\delta^{18}O-SO_4$, $\delta^{15}N-NO_3$, $\delta^{18}O-NO_3$) to determine natural background and contamination sources in the Guadalhorce River Basin (southern Spain)

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HIGHLIGHTS

- Nitrate and sulphate sources in groundwater identified by dual isotope analysis
- Nitrates were derived from fertilisers and organic sources (manure and sewage).
- SO_4^{2-} showed natural (gypsum) and human (fertiliser and sewage) isotopic signatures.
- SO_4^{2-} natural background levels determined with $\delta^{34}S$ and $\delta^{18}O$ binary mixing model

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ABSTRACT

The integrated use of isotopes ($\delta^{34}S-SO_4$, $\delta^{18}O-SO_4$, $\delta^{15}N-NO_3$, $\delta^{18}O-NO_3$), taking into account existing hydrogeological knowledge of the study area (mainly hydrochemical), was applied in the Guadalhorce River Basin (southern Spain) to characterise SO_4^{2-} and NO_3^- sources, and to quantify natural background levels (NBLs) in groundwater bodies. According to Water Framework Directive 2000/60/EC and, more recently, Groundwater Directive 2006/118/EC, it is important to determine NBLs, as their correct assessment is the first, essential step to characterising groundwater bodies, establishing threshold values, assessing chemical status and identifying trends in pollutant concentrations. In many cases, NBLs are high for some parameters and types of groundwater, making it difficult to distinguish clearly between factors of natural or human origin. The main advantages of using stable isotopes in a complex area like the Guadalhorce River Basin that exhibits widely varying hydrogeological and hydrochemical conditions and longstanding anthropogenic influences (mainly agriculture, but also many others) is accurate determination of pollution sources and precise quantification of NBLs. Since chemical analyses only provides the concentration of pollutants in water and not the source, three isotopic sampling campaigns for sulphates ($\delta^{34}S-SO_4$, $\delta^{18}O-SO_4$) were carried out, in 2006, 2007 and 2012, and another one was conducted for nitrates ($\delta^{15}N-NO_3$, $\delta^{18}O-NO_3$), in 2009, in groundwater bodies in order to trace the origins of each pollutant. The present study identified different pollution sources of dissolved NO_3^- in groundwater using an isotopic composition and quantified the percentage of natural (lithology, chemical and biological processes) and anthropogenic (fertilisers, manure and sewage) SO_4^{2-} and matched a concentration associated with the percentage in order to determine the NBLs in the basin.

1. Introduction

The European Union (EU) Water Framework Directive (WFD) (EU, 2000; article 17) stresses the obligation for Member States to distinguish any significant and sustained upward trends of contaminant concentrations and establish the starting points for trend reversal. Specifications and criteria about how to achieve this objective, and some others, were developed by Groundwater Directive (GWD) (EU, 2006) which is based on two clear objectives. These are: (1) assessing the status of groundwater bodies (GWB), which involves the prior determination of natural background levels (NBLs) and the establishment of threshold values (TVs) (Hinsby et al., 2008); and (2) the identification of significant and sustained trends of contaminant concentrations (Visser et al., 2007; Hansen et al., 2011).

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In this context, the correct assessment of NBLs for each GWB has a high importance in the proper implementation of the GWD, since they constitute the first and main step in the evaluation of the groundwater chemical status. This is also important for determination of threshold values (although these may also be derived directly from target values for groundwater dependent or associated ecosystems; Hinsby et al., 2008, 2012), the good or the poor chemical status of groundwater bodies, and identification of upward trends.

GWD defines NBLs in Article 5.2 as "the concentration of a substance or the value of an indicator in a body of groundwater corresponding to no, or only very minor, anthropogenic alterations to undisturbed conditions". Hence, NBLs are the result of numerous natural factors, such as geology of the area, water–rock interaction, the residence time of groundwater, recharge by rainfall, and relations with other aquifers. In addition, variation of concentrations with space and depth are often observed within a single groundwater body (Edmunds and Shand, 2008).

Despite the simple definition reflected by the GWD, the number of factors responsible for the final hydrochemical composition of groundwater in aquifers makes distinguishing between natural processes and the result of human activities a complicated task, subject to many errors and uncertainties. Application of radioactive and stable isotopes are useful tools for assessing human impacts on groundwater quality, e.g., through evaluation of groundwater residence times, pollution history and trends in groundwater bodies (Bohlke and Denver, 1995; Hinsby et al., 2001, 2007; Visser et al., 2007), and for identification of different pollution sources (Aravena et al., 1993 etc.).

NBLs have been commonly determined following the methodology described in the BRIDGE project (Background cRiteria for the iDentification of Groundwater thresholds) (Müller et al., 2006; Hinsby et al., 2008). This methodology consists of a first phase in which samples are pre-selected in order to eliminate those affected by anthropogenic factors (Wendland et al., 2005) in accordance with specific criteria (limit concentrations for certain parameters). After these samples have been eliminated, the NBLs are located at the 90th percentile of the remaining samples (Hinsby et al., 2008). This pre-selection methodology had the main advantage of simplicity and accessibility, but also the weakness of subjective values since the criteria for eliminating samples was based on the location of the cut-off point at the 90th percentile without taking in account the different possible distributions (Urresti-Estala et al., 2013). For this reason, other statistical techniques such as "iterative technique 2σ" or the "distribution function" have been specifically employed to determine NBLs (Nakić et al., 2010).

Other techniques, based on objective criteria, which have also been commonly used, were the mentioned statistical methods. These techniques are more powerful and realistic tools for this specific task (Apitz et al., 2009; Masetti et al., 2009; Peh et al., 2010). One of the first approaches in determining the NBLs based on statistical criteria was carried out with probability plots and the upper limits of the obtained ranges (Sinclair, 1974; Stanley and Sinclair, 1989; Tobias and Bech, 1997). Usually, the statistical methods previously employed were based upon the idea that the empirical frequency distribution, $f_{obs}(c)$, of the concentration, c, of a given environmental parameter can be modelled as a mixture of two contributions, $f_{nat}(c)$ and $f_{inf}(c)$ (Eq. (1)) respectively representing the natural and influenced component (Molinari et al., 2012).

$$f_{obs}(c) = f_{nat}(c) + f_{inf}(c). \qquad (1)$$

Normally, it is assumed that baseline geochemistry fluctuates around the central value of a data set with a normal distribution, which is represented by the mean value and the related standard variation, in order to identify the proportion of "unusually high" (outside the normal range) values in a database. Since natural data sets may not be normally distribution, other statistical methods more suited like the "iterative technique 2σ" as the "distribution function" may be applied (Nakić et al., 2010; Urresti-Estala et al., 2013), but still always have a level of uncertainty.

The difference between an accurate characterisation of NBLs and a conventional characterisation, realized by sample pre-selection methodologies (such as the one described by the BRIDGE project), supposes possible errors when defining the chemical status of groundwater bodies, which can lead to the result of poor status and therefore the implementation of action plans when they would not be strictly required. Thus it is necessary to make a more precise determination of NBLs, particularly in complex areas where natural and human sources converge. In this respect the use of isotopes techniques may suppose an improvement in the differentiation and quantification of both types of sources.

The Guadalhorce River Basin (Fig. 1) has a wide variety of hydrogeological and hydrochemical characteristics reflecting the lithology of the aquifers and thus, different NBLs (Urresti-Estala et al., 2013). Specifically, evaporite Triassic substratum provides a very high sulphate concentration to groundwater from upper basin (Figs. 1 B and C). In addition to natural factors, determining NBLs is hampered by a longstanding anthropogenic influence in a large part of the watershed. These include agriculture and livestock activity in the northwest sector of the basin that are diffuse sources of pollution in the catchment (Fig. 2) (Carrasco et al., 2008). Other sources of contamination including urbanised areas, grassland, or golf courses also exist over ground water bodies of the basin, but the largest surface area is affected by agriculture, which apply fertilisers that contain sulphate and nitrates (Sánchez, 2013). Therefore, it is difficult to differentiate what sulphate or nitrate is natural or due to the use of fertilisers, manures, or any other anthropogenic source.

The use of stable isotopes as a way to identify contamination sources has been widely applied (Otero et al., 2008a,b; Hosono et al., 2011; Folch et al., 2011; Saccon et al., 2013; Pastén-Zapata et al., 2014). Stable isotope ratios of NO_3^- ($\delta^{15}N$, $\delta^{18}O$), SO_4^{2-} ($\delta^{34}S$, $\delta^{18}O$) and C ($\delta^{13}C\text{-}HCO_3$) have been successfully employed to trace the main origin of pollution in a large variety of contexts (Aravena and Robertson, 1998; Vitòria et al., 2008; Houhou et al., 2010; Tichomirowa et al., 2010; Merchán et al., 2014), and to determine the physicochemical processes that may influence pollutant transport and fate (Kaown et al., 2009; Otero et al., 2009; Baily et al., 2011). In this context it is important not only to identify sources of pollution, but also try to quantify. Groundwater mixing models have commonly been used to describe the mixture between groundwater of different origins (Moncaster et al., 2000). In this regard, mixing between distinct groundwater can be quantified by simple linear algebra using the proportion of mixing for a given sample in relation to its position on a mixing line, according to the following equation:

$$\delta_{sample} = \chi \cdot \delta_A + (1-\chi)\delta_B. \qquad (2)$$

In order for such a model to be appropriate it must be possible to (1) identify the significant inputs into representative end-member values and (2) establish that the particular compound is not removed from the system.

Recently, isotope mixing models have also been used to quantify the contribution of each source of contamination (Xue et al., 2012; Delconte et al., 2014). Using this approach, this paper characterises the sources of NO_3^- and SO_4^{2-} using $\delta^{15}N\text{-}NO_3$, $\delta^{18}O\text{-}NO_3$, $\delta^{34}S\text{-}SO_4$, and $\delta^{18}O\text{-}SO_4$ in groundwater bodies not only to recognize pollution sources, but also to quantify each source and assign precise values of natural concentration ranges representing the NBLs.

2. Study area

2.1. Site description

The Guadalhorce River Basin is located in southern Spain, at the western edge of the Mediterranean Sea (Fig. 1). The basin has an area