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Radionuclides as natural tracers of the interaction between groundwater and surface water in the River Andarax, Spain

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ABSTRACT

The identification of specific aquifers that supply water to river systems is fundamental to understanding the dynamics of the rivers' hydrochemistry, particularly in arid and semiarid environments where river flow may be discontinuous. There are multiple methods to identify the source of river water. In this study of the River Andarax, in the Southeast of Spain, an analysis of natural tracers (physico-chemical parameters, uranium, radium and radon) in surface water and groundwater indicates that chemical parameters and uranium clearly identify the areas where there is groundwater-surface water interaction. The concentration of uranium found in the river defines two areas: the headwaters with U concentrations of 2 $\mu g\ L^{-1}$ and the lower reaches, with U of 6 $\mu g\ L^{-1}$. Furthermore, variation in the $^{234}U/^{238}U$ isotopic ratio allowed us to detect the influence that groundwater from the carbonate aquifer has on surface water in the headwaters of the river, where the saline content is lower and the water has a calcium bicarbonate facies. The concentration of ^{226}Ra and ^{222}Rn are low in the surface waters: $<1.6 \times 10^{-6}\ \mu g\ L^{-1}$ and $<5.1 \times 10^{-12}\ \mu g\ L^{-1}$, respectively. There is a slight increase in the lower reaches where the water has a permanent flow, greater salinity and a calcium-magnesium-sulphate facies. All this is favoured by the influence of groundwater from the detritic aquifer on the surface waters. The results of this study indicate the utility in the use of physico-chemical and radiological data conjointly as tracers of groundwater-surface water interaction in semiarid areas where the lithology of aquifers is diverse (carbonate and detritic) and where evaporitic rocks are present.

1. Introduction

Water resources in semi-arid areas are very important because of the scarcity of fresh water and the wide variability in inter-annual rainfall, which is commonly linked to extreme flood and drought events. As a result, sustainable water use becomes a priority (Molina-Navarro et al., 2016). The availability of water resources directly impacts on the area, whether the water is used for human consumption, agriculture, and to sustain ecosystems (Murgulet et al., 2016). The groundwater and surface water are considered a single resource within the hydrological system (Winter et al., 1998). It is therefore necessary to understand groundwater-surface water (GW-SW) interaction in all environments and at all scales to effectively manage water resources for human use and groundwater-dependent ecosystems (European Commission, 2000).

GW-SW interactions can be complex and so it becomes essential to better understand the conceptual framework of the processes occurring so that these water resources can be appropriately managed (Van der Kamp and Hayashi, 2009), and so that the requirements of the ecosystems that depend on groundwater can be identified (Tomlinson and Boulton, 2010). Moreover, the aquifers are often supplied from infiltration of surface water and so the river discharge becomes an important source of recharge to the aquifer (Benito et al., 2010; Constantz and Stonestorm, 2003).

There are numerous methods for establishing the GW-SW interaction (Kalbus et al., 2006). Comparison of methods for describing the GW-SW interaction on different scales has been done from other perspectives (Levy and Xu, 2012) and indirect methods have been used to detect movement of subsurface water using heat as a tracer (Anderson, 2005; Constanz and Stonestrom,

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2003; amongst others). Application of these methods on a regional scale has been infrequent, since experimental field studies tend to focus on small areas (Barthel and Banzhaf, 2016) and on the exchange of water between surface waters (lakes, wetlands and watercourses) and groundwater, especially in temperate climes (Hayashi and Rosenberry, 2002). In semiarid areas, the GW-SW interaction is highly complex and poorly understood. Several studies have also focussed on hydroecological and biogeochemical aspects of hydrology (Webb and Leake, 2006).

There are few studies of the GW-SW interaction in semiarid regions on a medium scale; this is because an extensive hydrological monitoring infrastructure is required to yield enough data to be representative of the extreme hydrological variability. In these areas, hydrochemical methods can contribute to the study of the GW-SW interaction and facilitate identification of areas where the GW-SW interaction is more intense. These methods offer advantages over methods based on physical parameters as they can provide accurate information on the spatial distribution of the GW-SW interaction, especially in medium-scale river basins, and require less investment in resources and control infrastructures (Cook, 2013).

A multi-parametric view of the GW-SW interaction can be gained by increasing or crossing comparison information from hydrochemical tracers with radionuclide data. A number of investigations have focussed on detecting the presence and behaviour of natural radionuclides in surface water and groundwater. The analysis of natural radionuclide concentrations and the radioactive disequilibrium between them have been used to analyse and quantify processes involved in water-rock interaction, mixing of groundwater from different sources, and other related physical and chemical processes (Eröss et al., 2012; Rodrigo et al., 2014).

The U-series profile of stream waters has been used to calculate the flow contribution from different water sources, such as deep and shallow groundwater (Camacho et al., 2010; Durand et al., 2005; Schaffhauser et al., 2014), since high $^{234}U/^{238}U$ ratios (representing enrichment of ^{234}U) in water during the alpha recoil process depend on the abundance of U under various geochemical conditions. Accordingly, numerous studies have focused on the U-series isotope composition of large river systems to understand basin-scale erosion rates (Robinson et al., 2004), whilst only a few studies have investigated the use of U-series isotopes as tracers of the different water sources to stream flow in small headwater catchments (Schaffhauser et al., 2014), of particular interest in semi-arid regions where stream flow generation is greatly affected by water sources with different residence times and various flow paths (Huckle et al., 2016; Liu et al., 2008).

Radium generally forms bivalent cations (Ra^{2+}) in natural environments under low salinity conditions (Dickson, 1990). Several studies have revealed a positive correlation between radium and salinity or chloride content (Gascoyne, 1989; Lauria et al., 2004), and between high radium content and low pH (Almeida et al., 2004). However, the dominant control of radium's mobility is the redox potential of the groundwater (Dickson, 1990). Retardation is high in oxidizing groundwater due to the adsorption of radium onto manganese and iron oxide surfaces (Ames et al., 1983). Therefore, radium has a significantly higher mobility under reducing and acidic conditions (Langmuir and Riese, 1985).

^{222}Rn is a radiogenic isotope produced from the decay of ^{226}Ra in the uranium decay series. The large contrast between activity in groundwater and surface water makes ^{222}Rn a useful tracer for examining GW–SW interaction from both qualitative and quantitative perspectives (Cartwright et al., 2011; Cook et al., 2003; Ellins et al., 1990), especially when studying transport processes in karst systems (Eisenlohr and Surbeck, 1995). However, it usually does not allow for the differentiation of deep and shallow groundwater. An additional challenge is the quantification of degassing rates within the stream, as these can vary spatially due to variability in turbulence and stream surface area (Blume and van Meerveld, 2015).

Therefore, the contrasting geochemical behaviour of uranium, radium, and radon can be applied to characterize mixing between different waters masses (Swarzenski, 2007). These radioisotopes can act as valuable natural tracers to study fluids on a regional scale, where different flow systems convey waters of different temperature, composition, and redox-state to a discharge zone (Eröss et al., 2012).

The River Andarax basin of Spain is characterised by wide hydrological variability, with outcrops of both carbonate and detritic aquifers. These factors, together with the semiarid climate, determine the hydrological dynamics of the river and lead to different types of current on both temporal and spatial scales. The River Andarax is therefore a good case for the study, characterisation, and evaluation of the GW-SW interaction in semiarid climates.

In this study, we used a suite of natural tracers to establish relationships between the surface water of the River Andarax and the groundwater of its associated aquifers. By conjointly analysing physico-chemical parameters and various radioisotopes, our aim was to obtain a more complete view of the dynamics and sources of the waters that make up this river system. This aspect is of particular interest in areas where surface waters are markedly dependent on groundwater a factor that must be considered as part of the sustainable conjoint use of groundwater and surface water resources.

2. Material and methods

2.1. Study area

The River Andarax is a typically Mediterranean watercourse, with a wide interannual variability of flow. It accommodates continuous, temporal, and ephemeral flows, both along its course and at various time scales (Sánchez-Martos, 2001). Along the river basin (Fig. 1), there are outcrops of metamorphic rocks (mica schists and phyllites) in the Sierra Nevada, and carbonate rocks (limestones and dolomites) in the Sierra de Gádor. In the middle part of the valley are conglomerates, sandy marls, and alluvial deposits. Hydrogeologically, two types of aquifer are distinguished: carbonate and detritic. The carbonate aquifer comprises limestone-dolomite outcrops along the northern edge of the Sierra de Gádor, while the detritic aquifer comprises alluvial as well as fluvio-deltaic sandy-silty conglomerates, all of which are in hydraulic connection with the River Andarax. Two areas are identified in the lower reach, denominated Rágol-Terque (DRT) and Santa Fe (DSF), which are close to each other and in hydraulic connection. In the headwaters, an area defined as DLT extends into the Laujar-Fondón depression. This is a small detritic aquifer, separated from the aforementioned two zones, which has a direct connection with the river Andarax, which flows longitudinally over it (Navarro-Martínez et al., 2016a).

Three sampling campaigns were carried out: in November 2015, and in February and March 2016. The sampling network comprises five surface-water points and five groundwater points. The five surface water points along the River Andarax allow an appreciation of the hydrochemical and radiological variability of the surface water, whilst the five groundwater points are representative of the main aquifers outcropping in the catchment area (Fig. 1).

2.2. Analytical procedures

Physicochemical parameters (pH, redox potential, dissolved oxygen, temperature, and electrical conductivity) were determined