



U-isotopes and ^{226}Ra as tracers of hydrogeochemical processes in carbonated karst aquifers from arid areas



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ABSTRACT

Sierra de Gádor is a karst macrosystem with a highly complex geometry, located in southeastern Spain. In this arid environment, the main economic activities, agriculture and tourism, are supported by water resources from the Sierra de Gádor aquifer system.

The aim of this work was to study the levels and behaviour of some of the most significant natural radionuclides in order to improve the knowledge of the hydrogeochemical processes involved in this groundwater system. For this study, 28 groundwater and 7 surface water samples were collected, and the activity concentrations of the natural U-isotopes (^{238}U , ^{235}U and ^{234}U) and ^{226}Ra by alpha spectrometry were determined.

The activity concentration of ^{238}U presented a large variation from around 1.1 to 65 mBq L⁻¹. Elevated groundwater U concentrations were the result of oxidising conditions that likely promoted U dissolution. The PHREEQC modelling code showed that dissolved U mainly existed as uranyl carbonate complexes. The $^{234}\text{U}/^{238}\text{U}$ activity ratios were higher than unity for all samples (1.1–3.8). Additionally, these ratios were in greater disequilibrium in groundwater than surface water samples, the likely result of greater water-rock contact time.

^{226}Ra presented a wide range of activity concentrations, (0.8 up to about 4×10^2 mBq L⁻¹); greatest concentrations were detected in the thermal area of Alhama. Most of the samples showed $^{226}\text{Ra}/^{234}\text{U}$ activity ratios lower than unity (median = 0.3), likely the result of the greater mobility of U than Ra in the aquifer system.

The natural U-isotopes concentrations were strongly correlated with dissolution of sulphate evaporites (mainly gypsum). ^{226}Ra had a more complex behaviour, showing a strong correlation with water salinity, which was particularly evident in locations where thermal anomalies were detected. The most saline samples showed the lowest $^{234}\text{U}/^{238}\text{U}$ activity ratios, probably due to fast uniform bulk mineral dissolution, which would minimize the impact of solubility-controlled fractionation processes. Furthermore, the high bulk dissolution rates promoted greater groundwater $^{226}\text{Ra}/^{234}\text{U}$ ratios because the Ra has a comparatively much greater mobility than U in saline conditions.

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1. Introduction

Sierra de Gádor is a complex karstic aquifer system located in southeastern Spain, in the province of Almería, which supports the two main economic activities in this arid area, agriculture and tourism (Vallejos et al., 2015a).

Natural radionuclides have not been studied previously in this area. Such knowledge can be used to improve the understanding of

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water-rock interaction processes, and mechanisms that regulate this complex system.

Uranium presents three long-lived natural radionuclides: ^{238}U (half-life = $4.49 \cdot 10^9$ y), ^{235}U (half-life = $7.0 \cdot 10^8$ y) and ^{234}U (half-life = $2.48 \cdot 10^5$ y), with relative atoms abundances in % of 99.274, 0.7200 and 0.0055, respectively. ^{238}U and ^{235}U are the heads of two natural decay chains, while ^{234}U is the third daughter isotope in the ^{238}U decay series. The ^{226}Ra (half-life = 1600 y), is the fourth isotope in the ^{238}U decay series, being the isotope of radium with the longest half-life, and therefore, it can be used to mark many kinds of environmental processes.

In closed systems, such as the aquifer host rock, after a period of about 1 million years the decay nuclides of a chain achieve secular equilibrium when the activity of the parent is equal to all successive members, but due to water-rock interactions, in both surface and groundwater, significant disequilibria are found (Von Gunten, 1995; Hoehn, 1998).

The ^{234}U activity concentration is generally higher than those of ^{238}U in the dissolved phase, resulting in a $^{234}\text{U}/^{238}\text{U}$ activity ratio >1 (Cherdynstev, 1971; Osmond and Cowart, 1976). The preferential dissolution of ^{234}U is mainly caused by two related mechanisms: the preferential leaching due to the instability in crystalline lattices after alpha emission from ^{238}U , and the recoil ejection of the ^{234}Th nucleus into the aquatic system due to the alpha recoil phenomenon (Kigoshi, 1971; Fleischer and Raabe, 1978; Fleischer, 1980; Porcelli and Swarzenski, 2003).

On the other hand, intense chemical weathering should not cause significant disequilibrium of the $^{234}\text{U}/^{238}\text{U}$ activity ratio, because this type of weathering generates fast uniform bulk mineral dissolution, which should not significantly fractionate ^{234}U from ^{238}U (Hussain and Krishnaswami, 1980; Andersen et al., 2009). Thus, the $^{234}\text{U}/^{238}\text{U}$ activity ratios vary widely in natural waters, ranging from values close to unity to values higher than 20 found in groundwater from closed systems (Bourdon et al., 2003).

In natural environments, uranium is usually found in the oxidation states IV and VI. Under reducing conditions, uranium is predominantly in the tetravalent state, and tends to precipitate forming insoluble minerals; consequently, its concentration in natural water is extremely low. In oxidising conditions, uranium appears mainly as U(VI) in the form of the highly soluble uranyl ion UO_2^{2+} . The uranyl ions form complexes primarily with carbonate and phosphate under near-neutral conditions and with sulphate and fluorides at lower pHs (Porcelli and Swarzenski, 2003).

Radium forms bivalent cations of Ra(II) in natural environments under low salinity conditions, but it may form weak complexes with chloride, sulphate and carbonate in saline waters (Porcelli and Swarzenski, 2003; Vaaramaa, 2003). In contrast to U, Ra is rather immobile under oxidising conditions and can occur at higher concentrations in groundwater under reducing conditions (Szabo and Zapezca, 1991; U.S. EPA, 1998; Martin et al., 2003).

The presence and behaviour of natural radionuclides in surface water and groundwater have been studied widely throughout the world. The analysis of natural radionuclide concentrations and the radioactive disequilibrium between them have been used to analyse and quantify the processes involved in water-rock interaction, age of the waters, mixing of groundwater from different sources and other related physical and chemical processes (Tricca et al., 2001; Bonotto and Jiménez-Rueda, 2007; Eröss et al., 2012; Paces and Wurster, 2014; Rodrigo et al., 2014).

Taking into account the previous facts, the main aim of this work has been to study the behaviour of both U-isotopes and ^{226}Ra in the aquifer system of Sierra de Gádor (Spain), in order to improve the understanding of the factors and processes that regulate the

composition of the waters. A second objective is to provide a baseline of the natural concentration of radionuclides in this aquifer system.

2. Study area

Sierra de Gádor is a dome-shaped mountain range located in southeastern Spain, with an area of more than 900 km² and reaching 2242 m a.s.l. This mountain range is bound by the Andarax River Valley to the north and east, the Adra River to the west and the Campo de Dalías to the south (Fig. 1).

Geologically, Sierra de Gádor belongs to the Alpujarride Complex of the Internal Zones of the Betic Cordillera. It is a Triassic age complex aquifer system formed by highly permeable, fractured and karstified limestones and dolomites with interbedded gypsum (Martín-Rojas et al., 2007), on low-permeable Permian to Triassic metapelites (Martín-Rojas et al., 2009). A neogene-quaternary series surrounds the Sierra de Gádor, composed of calcarenites, conglomerates, sandstones, silts and marls, which support some of the most important adjacent aquifers.

This aquifer system is geometrically complex as a consequence of the intense alpine compressional tectonics of the region. The study area is affected by an intense fracturing that originates deep flows, which are probably related to the existence of thermal anomalies (Morell et al., 2008; Vallejos et al., 2015a).

In the highly permeable carbonates, most of the rainwater is infiltrated and constitutes its main recharge (Vallejos et al., 1997; Pulido-Bosch et al., 2000). This water circulates underground giving rise to accumulation zones, springs, feeding rivers, as well as discharging to other aquifers, or directly to the sea.

The Sierra de Gádor is hydraulically connected to the Campo de Dalías supporting the aquifers of this coastal plain (Pulido Bosch et al., 2000; Molina et al., 2002), which is the most important agricultural area of the province of Almería. In the Campo de Dalías, carbonate rocks forming the Sierra de Gádor are buried under Miocene and Pliocene sediments that can reach a thickness of up to 500 m. The Andarax and Adra Rivers are also fed by these groundwaters in some sections (Vallejos et al., 2015b), but while the riverbed of the Andarax River in the middle and lowest stretch remains dry nearly the whole year, the Adra River remains flowing all year.

Southeastern Spain is one of the most arid regions in Europe. The climate of the study area is semiarid with hot, dry summers and mild winters. The main characteristics of rainfall in southeastern Spain are the scarcity, spatial-temporal irregularity and high intensity (Capel Molina, 1982, 1990). The average annual precipitation is around 400 mm for the whole of the Sierra de Gádor (Martín-Rosales, 1997). The mean annual temperature for the southern slopes of the Sierra de Gádor is 17.2 °C, slightly lower than the Campo de Dalías, estimated at 18.5 °C (Martín-Rosales, 1997). The climate characteristics of the study area give rise to high evapotranspiration losses, around 70% of the annual precipitation (Pulido-Bosch, 1998; Contreras, 2006).

The intense exploitation to which the Sierra de Gádor has been subject, exceeding the annual average resource, has produced falls in the piezometric level, deterioration in water quality and seawater intrusion in some sectors of the southern edges (Pulido-Bosch et al., 1997; Molina et al., 2003).

3. Materials and methods

During June 2012, 35 representative sampling points were selected; 28 groundwater points from boreholes, springs and a gallery, and 7 surface water points (5 from the Andarax River and 2 from the Adra River) (Fig. 1).

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