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Constraining the temporal variations of Ra isotopes and Rn in the groundwater end-member: Implications for derived SGD estimates

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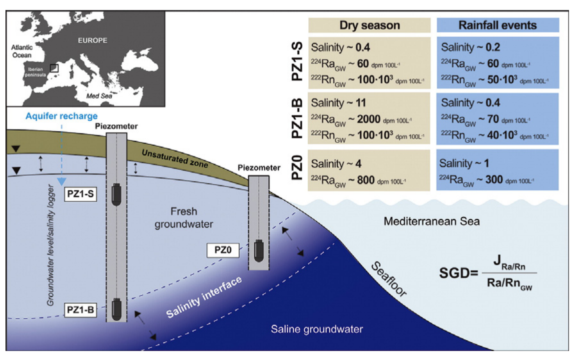
HIGHLIGHTS

- Ra isotopes and ^{222}Rn were measured for nearly two years in a coastal piezometer.
- High Ra variability was registered, especially during intense rainfall events.
- ^{222}Rn displayed minor variations due to the no influence of groundwater salinity on radon emanation.
- The hydrodynamics of coastal aquifers must be considered as essential to understand SGD fluxes.

GRAPHICAL ABSTRACT



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ABSTRACT

Submarine groundwater discharge (SGD) has been recognized as an important supplier of chemical compounds to the ocean that may influence coastal geochemical cycles. Radium isotopes (^{223}Ra, ^{224}Ra, ^{226}Ra, ^{228}Ra) and radon (^{222}Rn) have been widely applied as tracers of SGD. Their application requires the appropriate characterization of both the concentrations of tracers in the discharging groundwater and their distribution in the coastal water column. This study evaluates the temporal evolution of Ra isotopes and ^{222}Rn concentrations in a dynamic subterranean estuary of a microtidal Mediterranean coastal aquifer that experiences large displacements of the fresh-saltwater interface as a necessary initial step in evaluating the influence of SGD in coastal waters. We show that changes in groundwater salinities due to the seaward displacement of the fresh-saltwater interface produced large variations in Ra activities in groundwater (by a factor of ~19, ~14, ~6, and ~11 for ^{223}Ra, ^{224}Ra, ^{226}Ra and ^{228}Ra, respectively), most importantly during rainfall events. In contrast, the ^{222}Rn activities in groundwater oscillated only by a factor of 3 during these rainy periods. The large temporal variability in Ra activities hampers the characterization of the SGD end-member when using Ra isotopes as tracers, and thus presents a challenge for obtaining accurate SGD estimates. This study emphasizes the need to understand the hydrodynamics of coastal aquifers to appropriately constrain the Ra isotopes and ^{222}Rn concentrations in groundwater and when applying both tracers in dynamic microtidal coastal systems.

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1. Introduction

Submarine Groundwater Discharge (SGD) includes both meteoric fresh groundwater flowing into the sea and seawater recirculation through coastal aquifers (Burnett et al., 2003). Both flows mix in coastal aquifers, so-called subterranean estuaries (STEs), where biogeochemical reactions occur as a consequence of interactions between terrestrially derived groundwater, recirculated seawater and the geological matrix (Moore, 1999). This dynamic mixing zone influences the transfer of several chemical constituents to the coastal ocean (Tovar-Sánchez et al., 2014; Sadat-Noori et al., 2016). SGD is now recognized as a relevant source of nutrients, trace metals and other compounds and contaminants to the coastal sea (Kim et al., 2003; Johnson et al., 2008; Gonneea et al., 2014; Pavlidou et al., 2014; Rodellas et al., 2015b; Trezzi et al., 2016).

Radium (Ra) isotopes (^{223}Ra, ^{224}Ra, ^{226}Ra, ^{228}Ra) and radon (^{222}Rn) have been widely used as tracers to quantify SGD (e.g., Charette et al., 2001; Moore, 2003; Burnett et al., 2006; Burnett et al., 2008; Lee et al., 2012). Ra isotopes and ^{222}Rn, which are continuously produced in geological materials by the decay of their uranium and thorium parents, are appropriate SGD tracers, mainly because they behave conservatively once released to the sea and because they are significantly enriched in SGD fluids relative to seawater (Burnett et al., 2006). The approach used to estimate SGD flows using Ra isotopes or ^{222}Rn is based on characterizing the flux of Ra/Rn supplied by SGD (J_{Ra} or J_{Rn}) using the Ra/Rn distribution in coastal waters and the Ra/Rn concentration in groundwater inflowing to the sea, the so-called SGD end-member (Ra_{GW} or Rn_{GW}) (Burnett and Dulaiova, 2003; Moore, 1996a).

Most SGD studies have been devoted primarily to estimating the fluxes of Ra and Rn (J_{Ra} or J_{Rn}) (e.g., Kim et al., 2005; Beck et al., 2008; Smoak et al., 2012), whereas the Ra and Rn concentrations in the groundwater end-member have been largely overlooked, even though they are a critical component of the tracer-derived estimates (Cho and Kim, 2016; Burnett et al., 2007; Gonneea et al., 2008, 2013). Ra activities in subterranean estuaries can vary significantly (one or two orders of magnitude) over space and time at a given study site (Ollivier et al., 2007; Beck et al., 2008). Thus, the lack of constraint on this term remains a significant source of uncertainty in Ra-derived SGD estimates (Charette, 2007; Gonneea et al., 2013).

Several factors influence Ra activities in SGD, including the presence of Mn-Fe oxides (Gonneea et al., 2008), the pH of the subterranean estuary (Beck and Cochran, 2013), the ionic strength (Elsinger and Moore, 1980; Webster et al., 1995), the properties of the geological matrix (Swarzenski, 2007) and the residence time within the STE (Rodellas et al., 2017). Among them, the ionic strength of the solution (i.e., its salinity) has long been recognized as the main factor influencing the Ra activities in the SGD end-member, and Ra desorption increases significantly with salinity (Cho and Kim, 2016; Elsinger and Moore, 1980; Webster et al., 1995). As a consequence, Ra activities in SGD may vary substantially depending on the position of the freshwater-saltwater interface within the subterranean estuary. The position of this interface may oscillate, due to variations in the hydraulic gradient of the fresh groundwater (caused by, e.g., recharge and abstraction) and marine driving forces (e.g., tides, wave and storms) (Gonneea et al., 2013; Heiss and Michael, 2014). These temporal oscillations of Ra activity in STEs, along with the spatial heterogeneity of coastal aquifers, make it difficult to characterize the Ra_{GW} end-member, which is needed to provide accurate estimates of SGD (Michael et al., 2011).

Unlike Ra, Rn is an inert gas. Thus, its chemical behavior is not influenced by the physicochemical characteristics of the coastal aquifer (e.g., groundwater salinity, temperature or redox conditions). Radon activities in coastal aquifers are thus primarily controlled by the content of ^{226}Ra in the aquifer solids and dissolved in groundwater (Dulaiova et al., 2008). However, the physical and geochemical processes occurring in coastal aquifers (e.g., manganese cycling or ionic exchange) can affect the ^{226}Ra distribution, thus driving changes in the ^{222}Rn concentration of groundwater (Dulaiova et al., 2008).

In contrast to many coastal areas of the world, the Mediterranean Sea is characterized by a microtidal regime, with tidal amplitudes commonly lower than 0.2 m. Therefore, these coastal aquifers are not significantly influenced by tidal pumping. As a consequence, the location and movement of the salinity interface in subterranean estuaries in the Mediterranean region, as well as in other microtidal sea regions (e.g., the Caribbean Sea or the Baltic Sea), are mainly regulated by hydrogeological factors, such as aquifer properties and the aquifer water budget. Thus, understanding the hydrogeological characteristics (i.e. recharge, discharge, etc.) of coastal aquifers in microtidal regions and their impacts on the Ra and Rn concentrations in groundwater is particularly important for improving tracer-derived estimates of SGD.

This study evaluates the temporal evolution of Ra isotopes and ^{222}Rn concentrations in a Mediterranean microtidal coastal aquifer (Argentona, Catalonia, Eastern Iberian Peninsula) over almost 2 years. During this period, two piezometers (PZ) were continuously monitored to measure variations in groundwater levels, salinity and the Ra and ^{222}Rn concentrations in the groundwater. The aim of this study is to assess hydrogeological dynamics affecting the variability in the concentrations of Ra isotopes and ^{222}Rn in groundwater from this coastal microtidal aquifer. This variability may have critical implications for the quantification of Ra/Rn-derived SGD fluxes and therefore their implications for coastal biogeochemical cycles.

2. Study area and methods

2.1. Study area: the Argentona alluvial aquifer and the oceanographic setting

The Argentona alluvial aquifer is located between the Catalan Littoral Mountain Range and the Mediterranean Sea (Barcelona, NW Mediterranean) and extends in the SW-NE direction (Fig. 1). It has an area of approximately 35 km^2 that is mainly devoted to agricultural uses. The climatology of this region is characterized by Western Mediterranean conditions, and the region experiences high temperatures in summer (mean ~23 °C) and mild temperatures in winter (mean ~10 °C). The annual precipitation of the area ranges from 500 to 800 mm, and

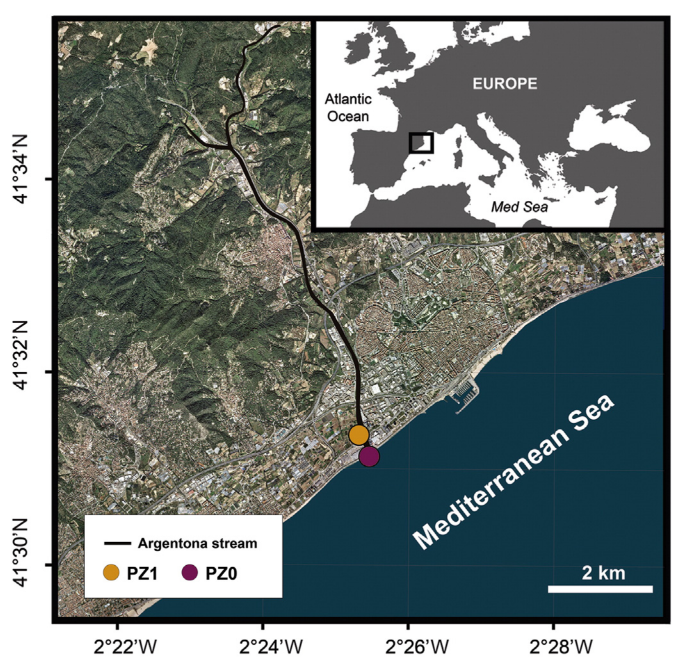

Fig. 1. Location of the Argentona stream in the NW Mediterranean Sea, including the location of the two monitored piezometers (PZ).