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# Quantifying groundwater discharge from different sources into a Mediterranean wetland by using <sup>222</sup>Rn and Ra isotopes

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#### SUMMARY

Groundwater discharge constitutes the main water inflow of many coastal wetlands. Despite the potential of Ra isotopes and <sup>222</sup>Rn as tracers of groundwater discharge, the use of these radionuclides to quantifv the groundwater inflow in coastal wetlands has been only scarcely addressed in the literature. The main goal of this study is to evaluate the use of <sup>222</sup>Rn and Ra isotopes to estimate the contribution of distinct groundwater sources into a Mediterranean coastal wetland (the Peníscola marsh, Castelló, Spain). The Peníscola marsh is a small shallow wetland nourished by groundwater coming from four different flowpaths: (i) a deep flow from the regional carbonate aquifer of El Maestrat, (ii) a shallow flow and (iii) an intermediate flow, both from the Irta Range and the detritic Vinaròs-Peníscola aquifer, and (iv) seawater intrusion. Data on <sup>226</sup>Ra, <sup>222</sup>Rn and salinity obtained in summer 2007 revealed that the deep groundwater contribution was 15% of the total water inflow, whereas the shallow and intermediate flow paths represented 32% and 48%, respectively. Seawater accounted only for the remaining 5% inputs to the wetland. Ra isotopes also allowed estimating the marsh water age in 1.2 days. Both the groundwater contributions derived from <sup>222</sup>Rn measurements and the Ra-derived marsh water age agreed well with the direct measurements obtained using propeller flow meters, evidencing the effectiveness of the used methods. An interannual comparison between the estimated groundwater inflow and the precipitation revealed that shallow groundwater flows respond to local precipitation, whereas the deep groundwater flow from the carbonate aquifer is dominated by a constant baseflow.

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1. Introduction

The Mediterranean coast is characterized by numerous wetlands, which are among the most productive environments of the world and support high biodiversity of flora and fauna (Pearce and Crivelli, 1994). Unfortunately, the increase of anthropogenic pressure in coastal areas has led to the decline or even disappearance of large areas of coastal wetlands in recent decades, exceeding 50% in many countries (De Stefano, 2004). This decline together with an increasing appreciation of the essential functions provided by wetlands prompted the development of policies and laws addressed to its preservation and restoration. Since groundwater inflow is a major component of the water budget in many coastal wetlands, the development of policies for the sustainable management of wetlands requires a precise understanding of its interaction with surrounding groundwater systems. However, the groundwater inputs into a wetland are difficult to quantify because of the spatiotemporal heterogeneities that are characteristic of the aquifers (Krabbenhoft et al., 1990) and the potentially diverse groundwater sources that a wetland may receive (Schot and Wassen, 1993). In that sense, Darcian estimations, hydrologic models and direct seepage measurements are hampered by errors and uncertainties (e.g. determining the hydraulic conductivity of aquifers, the other water balance components, the spatial seepage variations) (Cook et al., 2008).

Several geochemical tracers have been used to define the groundwater inputs to a wetland, mainly because the waters integrate the tracers coming into the system via groundwater





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pathways (Burnett et al., 2006). An ideal tracer of groundwater discharge should (i) be enriched in groundwater relative to wetlands water, (ii) behave conservatively once released in the environment, and, in case of a radioactive tracer, (iii) have a half-life comparable to the water residence time (Corbett et al., 1997). The combined use of the naturally occurring Ra isotopes (<sup>223</sup>Ra, <sup>224</sup>Ra, <sup>226</sup>Ra, <sup>228</sup>Ra) and <sup>222</sup>Rn allows fulfilling all these requirements and thus are instrumental to quantify the groundwater discharge (Rama and Moore, 1996) and evaluate the residence time of waters (Moore, 2000; Moore et al., 2006).

Ra isotopes and <sup>222</sup>Rn have been widely used as tracers of groundwater discharge in several environments, including lakes (e.g. Corbett et al., 1997; Kluge et al., 2007), streams (e.g. Burnett et al., 2010), coastal lagoons (Garcia-Solsona et al., 2008a; Santos et al., 2008) or wetlands (e.g. Charette et al., 2003; Cook et al., 2008; de Weys et al., 2011). However, most of these works calculated overall groundwater discharge rates and only a few studies assessed the contribution of different groundwater sources to coastal wetlands (e.g. Charette, 2007; Young et al., 2008).

The main objective of this study is to estimate the relative contribution of groundwater from four distinct sources into a Mediterranean wetland by using Ra isotopes (<sup>223</sup>Ra, <sup>224</sup>Ra, <sup>226</sup>Ra and <sup>228</sup>Ra) and <sup>222</sup>Rn, coupled with salinity and temperature measurements. In addition, we also aim to test the effectiveness of these radionuclides by comparing the results obtained with direct measurements of marsh water flows, and to evaluate the temporal variability of groundwater discharges in an interannual basis.

#### 2. Methods

#### 2.1. Study site: Peníscola marsh

The Peníscola marsh is a relatively small (105 ha), shallow (<1 m), brackish-water wetland, located in the Spanish Mediterranean coast (Fig. 1). Although this wetland is separated from the sea by a coastal sandy barrier, the Peníscola wetland was artificially channelized to the sea by three main channels that converge into a single one before flowing into the Mediterranean Sea through a narrow outlet (Fig. 1).

Since there is no surface water inflow, the only water sources to the Peníscola marsh are rainfall (average annual precipitation of 450 L m<sup>-2</sup>; AEMET) and groundwater. Several groundwater sources converge into the wetland from four different pathways (Fig. 1): (i) a shallow and horizontal flow path of fresh groundwater from the detrital aquifer of the Vinaròs-Peníscola coastal plain and the Irta Range, (ii) an intermediate (mid-depth) flow of groundwater from the Vinaròs-Peníscola aquifer and the Irta Range that inflows to the wetland seeping through marsh sediments, (iii) a deep groundwater flow from the regional carbonate Jurassic aquifer of El Maestrat, also inflowing through marsh sediments, and (iv) intruded seawater that mixes with inflowing groundwaters either in the sediments or in the coastal aquifer. Although the Irta Range belongs to the hydrogeological unit of El Maestrat, here we differentiate this system because it refers to local shallow karstic flows of groundwater with its own hydrochemical signal. The regional carbonate Jurassic aquifer of El Maestrat is the most important groundwater reservoir in the area (recharge rates from  $3.7 \times 10^8$ to  $4.2 \times 10^8 \text{ m}^3 \text{ y}^{-1}$ ; Ballesteros et al., 2007) and is strongly karstified, mostly draining to the sea through coastal springs in Peníscola, Alcossebre and Badum (Garcia-Solsona et al., 2010; Mejías et al., 2008, 2012). A portion of this groundwater is advected to the Peníscola marsh ultimately passing through marsh sediments, where it converges with saline intrusion and groundwater from the mid-depth shallow systems and seeps into the Peníscola marsh as brackish groundwater. The upward-seeping of brackish groundwater through marsh sediments is mainly located in the central part of the wetland, developing several spring pools (locally named ullals) in topographical depressed areas.

Water outflows from the Peníscola marsh essentially occur through the surficial outlet to the Mediterranean Sea (evaporation can be neglected due to the short residence time of marsh waters). The micro-tidal conditions of the Mediterranean Sea (10–20 cm) preclude observing any tidal modulation in the Peníscola marsh.

#### 2.2. Sampling

Water sampling was conducted in the Peníscola marsh in August 2007, in February 2011 and between April 2007 and February 2008



**Fig. 1.** (a) Location of the Peníscola marsh in the Mediterranean Sea Basin. (b) Schematic map of the Peníscola marsh area displaying the wetland channels and the spring pools. The flow direction of channelized waters is also indicated. The different systems (El Maestrat, Vinaròs-Peníscola and Irta Range) are represented together with the groundwater flow paths inflowing into the wetland. The solid arrows represent shallow horizontal flows, whereas the dashed ones illustrate upflowing groundwater discharging through marsh sediments.

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