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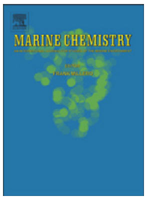

The influence of sediment sources on radium-derived estimates of Submarine Groundwater Discharge

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ABSTRACT

The influence of sediments on the determination of SGD by using Ra isotopes was investigated in the Port of Maó (Balearic Islands, NW Mediterranean). This natural harbor was selected because SGD occurs all along its southern boundary and it is covered by fine-grained sediments that are frequently resuspended due to vessel maneuvering. Comprehensive seasonal Ra mass balances were constructed for the waters of the Port of Maó using both short-lived (^{224}Ra) and long-lived (^{228}Ra) Ra isotopes. SGD flows to the Port of Maó obtained by using ^{228}Ra revealed a seasonal pattern, likely dominated by the recharge cycle, with maximum SGD rates during the wet seasons ($(180 \pm 100) \cdot 10^3\ \mathrm{m^3 \cdot day^{-1}}$ in fall) and minimum flows during summer ($(56 \pm 35) \cdot 10^3\ \mathrm{m^3 \cdot day^{-1}}$). The results also showed that the Ra flux from bottom sediments, through diffusion and due to releases associated to resuspension events, represented a significant source of Ra to the harbor waters. This sedimentary source accounted for a major fraction of the ^{224}Ra supplied to the system (30–90%, depending on the season), whereas the sediment influence on the ^{228}Ra mass balance was significantly lower (10–40%) due to its slower production rate. These findings suggested that attributing Ra inputs to the water column solely to SGD in systems covered by fine-grained sediments and/or affected by processes that favor Ra exchange across the sediment–water interface might not be accurate, requiring a detailed evaluation of the sediment sources. The inputs from sediments are often difficult to quantify, but using long-lived Ra isotopes to estimate the SGD flow may minimize the effect of a poor characterization of the sediment source.

1. Introduction

Submarine Groundwater Discharge (SGD) is the flow of water through continental margins from the seabed to the coastal ocean, with scale lengths of meters to kilometers, which is composed of fresh meteoric groundwater and former seawater recirculating through permeable sediments (Burnett et al., 2003; Moore, 2010). Some studies have shown that SGD is a relevant source of terrestrial compounds to the coastal ocean, including nutrients (Slomp and Van Cappellen, 2004), trace metals (Windom et al., 2006), dissolved inorganic carbon (Cai et al., 2003) and natural radionuclides (Garcia-Orellana et al., 2013). The magnitude of SGD into coastal waters is commonly determined by using natural tracers, such as the naturally occurring Ra isotopes (^{224}Ra ($T_{1/2} = 3.66$ days), ^{223}Ra ($T_{1/2} = 11.4$ days), ^{228}Ra ($T_{1/2} = 5.75$ years) and ^{226}Ra ($T_{1/2} = 1600$ years)). Ra isotopes have been successfully used as tracers of SGD in a wide variety of systems, mainly because they behave conservatively in seawater, they are highly enriched in SGD relative to coastal seawater and their half-lives vary in a wide range, allowing tracing processes at different time-scales and quantifying multiple sources of SGD (e.g., Charette et al., 2001; Moore et al., 2008; Rama and Moore, 1996). All the approaches used to estimate SGD by using Ra isotopes depend on the evaluation of the Ra flux supplied by SGD, which requires accurately constraining all the Ra sources other than SGD (e.g., releases from sediments, riverine discharge).

Seafloor sediments may be a continuous source of Ra isotopes to the water column not only through diffusion, erosion or resuspension, but also through short-scale recirculation processes (mm to cm), such as topography-induced advection, wave pumping, ripple migration, shear and bioirrigation (Breier et al., 2009; Garcia-Orellana et al., 2014; Rama and Moore, 1996; Santos et al., 2012). Most studies involving Ra isotopes as tracers of SGD have shown that inputs of Ra from seafloor sediments are often small in relation to the SGD source term (Beck et al., 2007; Charette et al., 2003; Garcia-Solsona et al., 2008b; Rama and Moore, 1996; Rodellas et al., 2012). Conversely, recent studies in shallow embayments with fine-grained sediments and/or affected by

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processes that favor Ra exchange across the sediment–water interface (e.g., bioirrigation, resuspension, hypoxia) have demonstrated that the sedimentary source can supply a relevant flux of Ra isotopes, which may be comparable to SGD-derived Ra inputs (Breier et al., 2009, 2010; Colbert and Hammond, 2008; Garcia-Orellana et al., 2014; Gleeson et al., 2013). The relevance of the sedimentary source may be particularly important for short-lived Ra isotopes (^{223}Ra and ^{224}Ra), since their fast regeneration time within the surficial sediments allows its almost-continuous release to the water column. Therefore, attributing Ra inputs to the water column solely to SGD may not always be well justified, requiring a detailed evaluation of the sedimentary source.

The natural harbor of Maó (Minorca, Balearic Islands, NW Mediterranean) is an ideal setting to assess the potential contribution of sediments on a Ra mass balance to estimate SGD, since: i) there are evidences of fresh groundwater inflowing along its southern shore; and ii) it is covered by fine-grained sediments that are subjected to frequent resuspension events provoked by maritime traffic of deep draft vessels (Garcia-Orellana et al., 2011), potentially representing a relevant mechanism to introduce Ra isotopes to the water column. We constructed seasonal comprehensive Ra mass balances for the waters of the Port of Maó, using both short- and long-lived Ra isotopes (^{224}Ra and ^{228}Ra, respectively), considering the differences among Ra isotopes and the potential seasonal variability of the Ra sources.

2. Methods

2.1. Field site

The Port of Maó (Fig. 1) is a semi-enclosed embayment with restricted exchange with the open sea, as a consequence of its elongated shape (5 km length and a maximum width of 0.8 km) and its shallow mouth (13 m). Indeed, the whole harbor is a shallow water body with depths lower than 10 m in the inner part and a maximum water column depth of 29 m in the central part of the harbor.

The Port of Maó is located in the middle of a fault that divides the island in two geomorphological settings: an impermeable northern sector of Mesozoic rocks and a broad permeable Miocene limestone platform that constitutes the main aquifer to the south (Fornós et al., 2004). This aquifer, named Migjorn, supplies most of the total extracted water from the island ($\sim 11 \cdot 10^6\ \text{m}^3 \cdot \text{yr}^{-1}$), mainly for tourism and agriculture purposes (Garcia-Solsona et al., 2010a). The aquifer permeability increases towards the coastline as a consequence of a major karstic development that results in direct or diffuse groundwater discharge to the sea (Fayas, 1972). Due to this hydrogeological division, most of the groundwater inputs into the harbor are located on the southern shoreline. Indeed, several natural wells and springs exist along the southern area of the harbor, and groundwater springs inflowing directly to the harbor can be visually identified. Aside from groundwater discharge, freshwater inputs are restricted to the discharge of a small stream in the inner harbor, named Torrent des Gorg, and runoff from eventual precipitation events from the northern shore and the towns of Maó and Es Castell. The average annual rainfall is about 600 mm, with dry summers and maxima in spring and autumn.

The Port of Maó has been subjected to continuous urban and industrial dumps from the city of Maó and the industries settled around the harbor. This has led, for instance, to a progressive contamination of seafloor sediments with metals (Ag, Cd, Cu, Ni, Pb, among others; Garcia-Orellana et al., 2011). It is also an important touristic destination, and cruises and large vessels frequently circulate along the harbor, especially during the summer season. Since most of these vessels have drafts between 6 and 9 m and given the shallowness of the harbor (the transit channel is 10–14 m deep), propellers of large vessels frequently resuspend significant amounts of sediments, particularly when maneuvering to dock, favoring the release of contaminants from the sediments to the water column (Garcia-Orellana et al., 2011).

2.2. Sample collection

Four seasonal surveys (July 2010, October 2010, March 2011 and June 2011) were conducted at the Port of Maó. 15 stations distributed along the harbor were sampled during each survey (Fig. 1). Depth profiles of temperature and salinity were measured at each station with a CTD (SBE-25, Seabird Electronics). Water samples for Ra isotopes were collected from 1 m depth (surface) at each station, and also at 10 and 20 m at station 19 in October 2010, March 2011 and June 2011. Samples for Ra analysis were stored in 60 L containers.

Groundwater was sampled for Ra isotopes, salinity and temperature measurements from 8 coastal wells distributed along the southern shoreline and two small islands within the harbor and from the small stream inflowing to the inner harbor (Fig. 1). Whereas on July 2010 and October 2010 the stream was sampled in the freshwater area, on March 2011 and June 2011 the samples were collected from the estuarine zone. Finally, one sediment core was also collected at the inner harbor to determine the diffusive fluxes of Ra isotopes from seafloor sediments to the harbor waters (Fig. 1).

In addition to the seasonal samplings, a 3-day intensive monitoring was conducted between 8 and 10 May 2012 to evaluate the relevance of sediment resuspension provoked by vessels maneuvering to dock as a source of Ra isotopes to the water column. Two resuspension events occurred during the studied period, driven by the same deep-draft

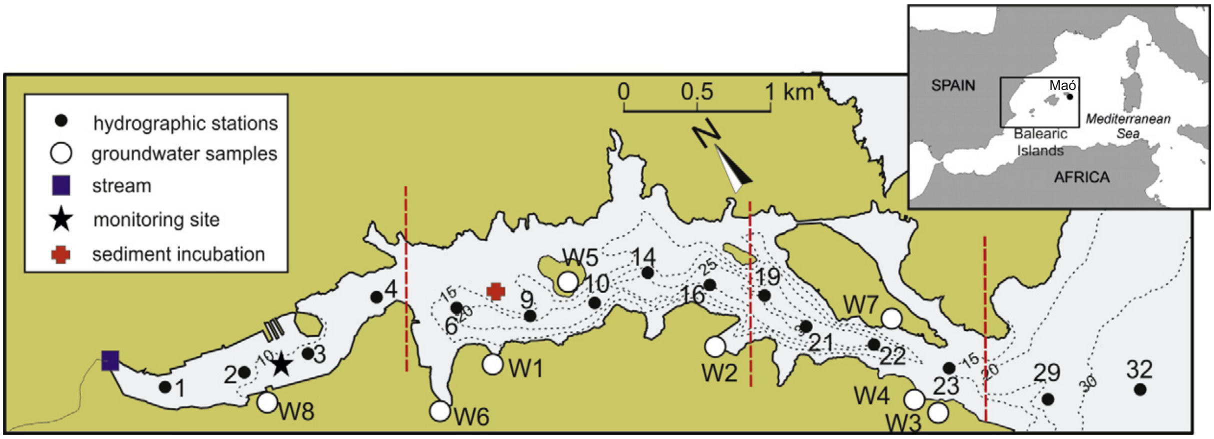

Fig. 1. Map of the Port of Maó including the location of all the hydrographic stations and the site where the three-day monitoring was conducted. The location of the groundwater samples, the inflowing stream and the sediment core collected are also shown. Dashed-lines differentiate (from the left to the right) the inner, middle and outer areas of the harbor, and the boundary of the study site.