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Using the radium quartet to quantify submarine groundwater discharge and porewater exchange

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Abstract

The specific ingrowth rates of different radium isotopes make them valuable tracers to distinguish processes occurring at different temporal scales. Here we demonstrate the use of the radium quartet (^{223}Ra, ^{224}Ra, ^{226}Ra and ^{228}Ra) to differentiate flows of submarine groundwater discharge and porewater exchange to a coastal embayment (Alfacs Bay, NW Mediterranean Sea), based on the assumption that these processes occur on different time scales. In order to evaluate the seasonal dynamics of groundwater and porewater inputs to the bay, we conducted three seasonal samplings at Alfacs Bay, during which samples for Ra isotopes were collected from bay waters, groundwater springs, porewaters and irrigation channels. Activities of short-lived Ra isotopes in the bay showed a strong seasonality, (e.g. average ^{224}Ra activities in summer ($\sim$32 dpm 100 L^{-1}) up to 4 times higher than in winter ($\sim$8 dpm 100 L^{-1})). In contrast, the activities of the long-lived Ra isotopes were fairly constant throughout the year (e.g. activities of ^{226}Ra were $\sim$16 and $\sim$14 dpm 100 L^{-1} in summer and winter, respectively). The relatively short exposure to sediments of recirculation fluxes resulted in porewaters significantly enriched in short-lived Ra isotopes relative to the long-lived ones (e.g. ^{224}Ra = 1100–1300 dpm 100 L^{-1}; ^{226}Ra = 17–99 dpm 100 L^{-1}), whereas coastal groundwaters were enriched in all the Ra isotopes (e.g. ^{224}Ra = 120–150 dpm 100 L^{-1}; ^{226}Ra = 200–400 dpm 100 L^{-1}). The distinct signatures of different sources allowed us to construct seasonal Ra mass balances to estimate both groundwater discharge, which ranges from $(40 \pm 60)\cdot10^3\ m^3\cdot d^{-1}$ in summer to $(310 \pm 200)\cdot10^3\ m^3\cdot d^{-1}$ in winter, and porewater exchange fluxes, ranging from $(1200 \pm 120)\cdot10^3\ m^3\cdot d^{-1}$ in summer to $(270 \pm 40)\cdot10^3\ m^3\cdot d^{-1}$ in winter. Whereas the seasonal variability of groundwater inputs is likely governed by the terrestrial hydraulic gradient, a qualitative evaluation of the drivers of porewater exchange suggested that the strong seasonality of the seawater recirculation inputs is likely mediated by seasonal cycles on the activity of benthic infauna. Ra isotopes are thus valuable tracers to differentiate fluxes of both submarine groundwater discharge and porewater exchange, allowing a more accurate evaluation of the fluxes of freshwater and solutes to coastal ecosystems, as well as their implications for coastal biogeochemical cycles.

Keywords: Radium isotopes; Submarine groundwater discharge; Porewater exchange; Bioirrigation; Mediterranean; Alfacs Bay

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1. INTRODUCTION

The term submarine groundwater discharge (SGD), as it is commonly defined, incorporates a broad spectrum of physical processes, fluid compositions and origins (Burnett et al., 2003; Moore, 2010). In addition to the flow of fresh groundwater driven by the hydraulic forcing of coastal aquifers, SGD also includes large-scale (meters to kilometers) seawater recirculation through permeable sediments driven by pressure gradients mainly forced by tides, waves or density-driven water convection (Taniguchi et al., 2002; Moore, 2010; Santos et al., 2012). Inputs of groundwater are a source of new dissolved compounds (e.g. nutrients, metals, pollutants) to coastal systems, because concentrations of solutes in groundwater are commonly higher than those measured in receiving water bodies (Weinstein et al., 2011; Beusen et al., 2013). These elevated concentrations are mainly derived from natural (e.g. vegetation, rocks, microorganisms) and anthropogenic (e.g. agriculture, sewage, mining waste) sources to coastal aquifers, as well as from the biogeochemical transformations occurring when fresh groundwater mixes with seawater in the coastal aquifer (Moore, 1999; Slomp and Van Cappellen, 2004; Knee and Paytan, 2011). On small spatial and short time scales, porewater exchange driven by bioturbation, bioirrigation, shear flow or flow-topography interactions, among others, recirculates seawater through surficial sediments and has been shown to enhance the fluxes of dissolved compounds to overlying waters (Huettel and Rusch, 2000; Precht and Huettel, 2003; Santos et al., 2012; Rao et al., 2012). Seawater entering the sediments carries oxygen and organic matter that fuel biogeochemical reactions within the sediments, resulting in pore fluids highly enriched in many dissolved constituents relative to overlying waters (chiefly, dissolved inorganic carbon and nutrients). In addition, in some coastal systems, the sediments themselves are considerably enriched in nutrients and other chemicals, which can be remobilized by these recirculation processes (Stieglitz et al., 2013; Trezzi et al., 2016).

Inputs of solutes (particularly, nutrients) driven by SGD and porewater exchange may have profound implications for coastal ecosystems, such as modulating the dynamics and structure of microbial communities, triggering algal blooms, promoting eutrophication or facilitating hypoxia events in poorly renewed water bodies (Hwang et al., 2005; Hu et al., 2006). However, the chemical composition of these water fluxes across the sediment–water interface may be considerably different (Weinstein et al., 2011; Cai et al., 2015), requiring the discrimination of SGD and porewater exchange to better characterize the sources of dissolved constituents to coastal systems and their ecological implications. In addition, when SGD is mainly composed of fresh groundwater, this differentiation allows a better characterization of water budgets of both aquifers and coastal water bodies, as well as improved understanding of density-driven circulation in coastal systems (Moore, 2010).

Water fluxes across the sediment–water interface are commonly a mixture of several components and may be highly heterogeneous both in space and time (Burnett et al., 2006). Thus, it can be challenging to differentiate advective fluxes into groundwater components, which commonly have resided in the aquifer for relatively long periods, and exchange of porewater, which often spends comparatively shorter times in contact with sediments. Although radium (Ra) isotopes (^{224}Ra $T_{1/2} = 3.66$ d; ^{223}Ra $T_{1/2} = 11.4$ d; ^{228}Ra $T_{1/2} = 5.75$ y; ^{226}Ra $T_{1/2} = 1600$ y) have been commonly applied to estimate total SGD flows (e.g. Moore, 2006; Charette et al., 2013; Rodellas et al., 2015a), the radium quartet can also represent a powerful set of tracers to distinguish SGD and porewater exchange provided that these processes have a different residence time within the solid matrix (i.e. the coastal aquifer or permeable sediments). Ra isotopes are continuously produced by the decay of their thorium parents, which are bound onto the aquifer solids or sediments. While Ra is mainly adsorbed onto particle surfaces in freshwater environments, it is much more soluble in brackish-saline waters and it is rapidly desorbed mainly due to ion exchange competition with the major cations in seawater (Webster et al., 1995; Gonneea et al., 2008; Kiro et al., 2012). As a consequence, Ra isotopes are highly enriched in both brackish groundwater and porewater relative to coastal seawater and they are geochemically conservative once released into saline waters. Given that the production of Ra isotopes is governed by their decay constants, shallow recirculation of seawater through sediments, which occurs over short time scales (from hours to few months), does not allow a significant ingrowth of the long-lived Ra isotopes. This results in porewater exchange fluxes much more enriched in short-lived Ra isotopes (^{224}Ra and ^{223}Ra) relative to the long-lived ones (^{228}Ra and ^{226}Ra) (Gleeson et al., 2013). In contrast, the relatively long flow paths of groundwater from regional aquifers and large recirculation cells commonly result in SGD inputs being also enriched in long-lived Ra isotopes.

The current study was conducted to test the appropriateness of Ra isotopes to distinguish and quantify groundwater and porewater exchange fluxes into the same system. This work was conducted at Alfacs Bay (NW Mediterranean Sea), a shallow micro-tidal semi-enclosed embayment with a high ecological and economical significance, because it hosts one of the most valuable aquaculture zones in the NW Mediterranean (Delgado et al., 1990). The high productivity of this area has been traditionally explained by the combination of the nutrient supply from land and the semi-enclosed geomorphology of the bay that favors the retention of the produced biomass (Delgado and Camp, 1987). However, recurrent harmful algal blooms (HABs) threaten farming activities (Delgado et al., 1990; Fernández-Tejedor et al., 2008). Previous research in the area indicate that the dynamics of phytoplankton, and of certain HABs in particular, exhibit a marked seasonal variability largely controlled by physical forcings, chiefly, estuarine circulation and wind forcing (Solé et al., 2009; Llebot et al., 2011, 2014; Artigas et al., 2014). Many uncertainties remain concerning the role of nutrient sources in the phytoplankton and HABs dynamics. Inputs from irrigation channels used in rice cultivation has been traditionally