Karstic submarine groundwater discharge into the Mediterranean: Radon-based nutrient fluxes in an anchialine cave and a basin-wide upscaling

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Abstract

Anchialine caves are common in Mediterranean karstic shorelines and elsewhere, delivering point-source fresh groundwater and nutrients to the coastal ocean. Here, we first quantified submarine groundwater discharge (SGD) in a typical karstic system (Zaton Bay, Croatia) receiving groundwater from anchialine caves using a radon (222Rn) mass balance model. We then combine our new observations with the literature to provide a Mediterranean-scale estimate of karstic fresh SGD nutrient fluxes. We found that SGD and related nutrient fluxes in the upper brackish layer were much higher than those in the underlying layer in Zaton Bay. In the upper brackish layer, both SGD (m d⁻¹) and associated nutrient fluxes (mmol m⁻² d⁻¹) in the wet season (SGD: 0.29–0.40; DIN: 52; DIP: 0.27) were significantly higher than those in the dry season (SGD: 0.15; DIN: 22; DIP: 0.08). Red tides were observed in the wet season but not in the dry season. Nutrient budgets imply that SGD accounted for >98% of the total dissolved inorganic nitrogen (DIN) and phosphorous (DIP) sources into Zaton Bay. These large SGD nutrient fluxes with high N/P ratios (190–320) likely trigger and sustain red tide outbreaks. Combining our results with 30 previous studies in the region revealed that point-source DIN and DIP fluxes via karstic fresh SGD may account for 8–31% and 1–4%, respectively, of riverine inputs in the Mediterranean Sea. Overall, we demonstrate the importance of karstic SGD as a source of new nutrients with high N/P ratios to the Mediterranean Sea and emphasize how SGD lagging precipitation can drive red tide outbreaks.

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1. INTRODUCTION

Submarine groundwater discharge (SGD), riverine inputs, and atmospheric deposition transport nutrients from land to coastal waters. SGD has been historically overlooked and remains as a poorly quantified source of nutrients to coastal waters worldwide (Moore, 1999; Burnett et al., 2001). The development of quantitative approaches (e.g., hydrologic models, seepage meters, geochemical tracers) to estimate SGD has helped to reveal the magnitude of SGD-derived nutrient fluxes and its effects on coastal ecosystems (Moore, 2010). These effects include

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enhanced primary productivity and red tides (Lee et al., 2010; Lecher et al., 2015; Luo and Jiao, 2016), coastal hypoxia (McCoy et al., 2011; Peterson et al., 2016), local acidification (de Weys et al., 2011; G. Wang et al., 2014), and greenhouse gas emissions to the atmosphere (O’Reilly et al., 2015; Santos et al., 2015).

SGD is defined as all flow of water on continental margins from the seabed to the coastal ocean, regardless of fluid composition or driving force, which includes fresh groundwater discharge (FGSD) and recirculated saline groundwater discharge (RSGD) (Burnett et al., 2003; Santos et al., 2012). While FGSD is a source of new water and dissolved compounds, RSGD can be a source of recycled organic matter respiring groundwaters such as nutrients and carbon to the coastal ocean (Santos et al., 2012). Previous studies have shown that coastal groundwater is often enriched in nutrients due to natural and anthropogenic sources (e.g., Slomp and Van Cappellen, 2004; X. Wang et al., 2014). As a result, even a small SGD flux may contribute large nutrient fluxes to a coastal system (Moore, 2010).

Several studies provide increasing evidence that SGD represents an important source of nutrients to coastal ecosystems, including lagoons, wetlands, bays, coral reefs and sandy beaches (Lee et al., 2009; Rodellas et al., 2014; Tovar-Sánchez et al., 2014; Sadat-Noori et al., 2016a; Chen et al., 2019). On a global scale, dissolved inorganic nitrogen (DIN) and phosphorus (DIP) fluxes via SGD could be approximately 1.4-fold and 1.6-fold of the river fluxes to the global ocean (Cho et al., 2018). SGD generally has a much higher N/P ratio when compared with Redfield ratio (16) (Slomp and Van Cappellen, 2004; Su et al., 2011; Santos et al., 2013; Chen et al., 2018a). These large nutrient fluxes with high N/P ratio via SGD can change the algal composition (Lee et al., 2010; Su et al., 2011) and primary production rates of coastal waters (G. Wang et al., 2018; X. Wang et al., 2018), which may contribute to the eutrophication of receiving water bodies and drive algal blooms (Lee et al., 2010; Su et al., 2011).

Harmful algal blooms (HABs), sometimes referred to as “red tides”, can alter the structure and function of marine ecosystems, often resulting in catastrophic impacts to aquaculture and local economies (Anderson, 1997; Richlen et al., 2010). Nutrients often limit primary production in estuaries and the coastal ocean (Howarth, 1988; Anderson et al., 2002), and large anthropogenic nitrogen inputs are often a major driver of phytoplankton production in estuarine and coastal waters (Anderson et al., 2002). Nutrient sources with high N/P ratios such as most groundwaters can shift the N-limited coastal primary production towards P-limitation as predicted from models (Slomp and Van Cappellen, 2004) and demonstrated via observations (Santos et al., 2013).

As a common occurrence along the Mediterranean karst coastline (Fleury et al., 2007; Sanfilippo et al., 2015; Gerovasileiou et al., 2016; Moosdorf and Oehler, 2017), anchialine caves can deliver point-source, nitrogen enriched groundwater to the coastal ocean. An anchialine environment is defined as a tidally-influenced subterranean estuary located within crevicular and cavernous karst and volcanic terrains that extends inland to the limit of seawater penetration (Bishop et al., 2015). Anchialine systems are characterized by sharp physical and chemical stratification and connect a marine system to a groundwater system inland. These springs have been used as drinking, bathing, irrigation, fishing, tourism, culture, or ship navigation in ancient Greece, Italy, France, Croatia, etc. (Moosdorf and Oehler, 2017; Rossi and Cukrov, 2017). Anchialine caves have variable hydrological and chemical characteristics (Bishop et al., 2015) and provide direct access to the aquifer source (Beddows et al., 2007). Moreover, anchialine caves often create steep salinity gradients in receiving waters with an overlying freshwater layer on top of saline water (Cuculic et al., 2011; Kwokal et al., 2014).

In this study, we hypothesize that Mediterranean anchialine caves are an important source of nutrients and drive the N/P ratios of receiving coastal waters. First, we use naturally occurring 222Rn to quantify SGD and associated nutrient fluxes in a highly stratified bay (Zaton Bay, Croatia). We examine if SGD is derived from the upper point-source discharging into the photic zone via anchialine sources, and if SGD contributes to seasonal outbreaks of red tides. Second, since karstic springs or caves are widely distributed along Mediterranean coastlines, we combine our results with the literature to estimate nutrient fluxes via karstic fresh SGD to the Mediterranean Sea and discuss the potential implications for regional, basin-scale nutrient budgets.

2. MATERIALS AND METHODS

2.1. Study area

Field investigations were performed in Zaton Bay, a part of the highly stratified Krka River estuary system in Croatia (Fig. 1). The Krka River estuary has typical characteristics of a Mediterranean estuary: a narrow tidal range (0.2–0.5 m), negligible tidal currents, mild, wet winters and warm, dry summers. The Krka River estuary, which is mainly cut into Upper Cretaceous and Eocene limestones, was formed during the Holocene transgression (Prohić and Kniewald, 1987; Pravdić and Juračić, 1988). Numerous anchialine caves and submarine springs occur along the Krka River estuary and there is no investigation of cavedelivered nutrients to the estuary. Marine phytoplankton blooms have been observed in the upper brackish layer of the estuary above the halocline due to the local anthropogenic nutrient inputs (Legović et al., 1994; Moreira-Turcq et al., 2001; Supraha et al., 2014). The abundance of picoplankton cells in the wet season are significantly higher than that in the dry season (Moreira-Turcq et al., 2001). Supraha et al. (2014) revealed that the blooming species was Plagioselmis cf. Prolonga.

Zaton bay is a narrow bay (2 km length, 300 m wide) with an average depth of 8 m (http://www.arctiler.com/). A large anchialine cave (Litno Cave) and related spring delivers groundwater into Zaton Bay. The outflow of water from Litno Cave is continuous through the year and the discharge of Litno Cave increases significantly in the wet season. Other smaller submarine springs are known to occur in Zaton Bay (Domínguez-Villar et al., 2018). A
recent study used temperature to trace the hydrodynamic characteristics of Litno Cave, which showed that the plume of fresh to brackish water that outflows from Litno Cave had a local effect on Zaton Bay and was more intense after precipitation events (Domínguez-Villar et al., 2018). Zaton Bay has sharp carbonate slopes. Seabed sediments are carbonate sands and muds. Although anchialine caves were considered to be the significant source for pollutants (such as toxic metals) into adjacent coastal waters (e.g., Cuculić et al., 2011; Kwokal et al., 2014), there were no previous investigations assessing the nutrient inputs supplied by anchialine caves to the Krka River estuary and Zaton Bay.

2.2. Sampling and analysis

Water samples from Litno Cave and Zaton Bay (including three vertical profiles in the stations a, b and c) were collected using Niskin bottles during April (wet season), August (dry season), and December (wet season) 2016 in Zaton Bay, respectively (Fig. 1c). The outlet from Litno Cave to Zaton Bay is located at ~1 m below the water surface, with a water discharge flow of ~45 L s⁻¹ (Domínguez-Villar et al., 2018). Water samples from Litno Cave were directly collected at the cave outlet prior to any interaction with the atmosphere. We thus assume that these samples are representative of waters in Litno Cave. ²²²Rn samples were collected into 250-mL glass bottles after overflowing and immediately analyzed using a RAD7 detector coupled with a RAD-H₂O attachment (see Chen et al., 2018a,b). To analyze ²²⁶Ra, 60 L of seawater were passed slowly (<1 L min⁻¹) through 20 g of MnO₂-impregnated acrylic fiber. These fibers were then thoroughly washed with Milli-Q water to remove particles and salts (Moore and Arnold, 1996) and sealed for >20 days and analyzed using a RAD7 detector (Kim et al., 2001; Peterson et al., 2009). Nutrient samples were collected using polyethylene bottles, stored in the dark at 20°C, then analyzed using the method of Strickland and Parsons (1972). Salinity, temperature, pH, and dissolved oxygen (DO) profiles were obtained using an in situ multi-parametric probe (Hach Lange HQ40D) and wind speed was measured by a hand-held anemometer. In addition, triplicate sediment samples were collected from station b in Zaton Bay (Fig. 1) for determining ²²²Rn diffusion from seabed sediments using a sediment equilibration experiment (Corbett et al., 1998).

2.3. ²²²Rn mass balance model

Radon mass balance models originally developed by Burnett and Dulaiova (2003) have been applied to coastal systems, such as estuaries (e.g., Swarzenski et al., 2006; Kim et al., 2010; Sadat-Noori et al., 2015), lagoons (e.g., Su et al., 2014; Rocha et al., 2016), mangroves (e.g., Chen et al., 2018a,b; Smith et al., 2016; Tait et al., 2016) and coral reefs (e.g., Santos et al., 2011; Cyronak et al., 2013, 2014).
Santos et al. (2010) modified this model to estimate SGD into both the surface and bottom layers in a stratified tropical estuary in Florida. Here, we also used this model to quantify SGD into both the upper brackish layer above the halocline and the underlying layer below the halocline in Zaton Bay. For the upper brackish layer, the $^{222}\text{Rn}$ sources include SGD input and ingrowth of dissolved $^{226}\text{Ra}$ while the sinks include atmospheric evasion, decay of $^{222}\text{Rn}$, diffusion into underlying layer and mixing loss of $^{222}\text{Rn}$ with seawater. For the underlying layer, the $^{222}\text{Rn}$ sources include SGD, ingrowth of dissolved $^{226}\text{Ra}$ and diffusion from sediment and upper brackish layer while the sinks include decay of $^{222}\text{Rn}$ and mixing loss of $^{222}\text{Rn}$ with offshore seawater in the underlying layer. A conceptual model illustrating these sources and sinks is shown in Fig. 2. Hence, assuming that the system was in steady state, the $^{222}\text{Rn}$ fluxes via SGD ($\text{Bq m}^{-2}\text{day}^{-1}$) into the upper brackish layer ($F_{\text{SGD above}}$) and the underlying layer ($F_{\text{SGD below}}$) can be separately estimated as follows:

\[
A \times F_{\text{SGD above}} = \left( V_{\text{above}} \times \frac{(222\text{Rn}_{\text{above}} - 222\text{Rn}_{\text{seawater}})}{\lambda} \right) + (A \times F_{\text{atm}}) + (A \times F_{\text{vertical}}) + (\lambda \times V_{\text{above}} \times 222\text{Rn}_{\text{above}}) - (\lambda \times V_{\text{above}} \times 226\text{Ra}_{\text{above}}) \]

where $A$ is the area of study site ($\text{m}^2$), $V_{\text{above}}$ and $V_{\text{below}}$ refer to the volume ($\text{m}^3$) of the brackish water and underlying layer, $222\text{Rn}_{\text{above}}$ and $222\text{Rn}_{\text{below}}$ are the mean $^{222}\text{Rn}$ activity ($\text{Bq m}^{-3}$) in the upper brackish layer and underlying layer, $222\text{Rn}_{\text{seawater}}$ is the $^{222}\text{Rn}$ activity ($\text{Bq m}^{-3}$) in the seawater end-member (i.e., the samples with the highest salinity in the mouth of Zaton Bay), $F_{\text{atm}}$ is $^{222}\text{Rn}$ atmospheric evasion ($\text{Bq m}^{-2}\text{day}^{-1}$), $F_{\text{vertical}}$ is the $^{222}\text{Rn}$ diffusive flux from the brackish layer into underlying layer ($\text{Bq m}^{-2}\text{day}^{-1}$), $\lambda$ is $^{222}\text{Rn}$ decay constant (0.182 day$^{-1}$), $^{226}\text{Ra}_{\text{above}}$ and $^{226}\text{Ra}_{\text{below}}$ are the $^{226}\text{Ra}$ activity ($\text{Bq m}^{-3}$) in the upper brackish layer and underlying layer, $F_{\text{mix below}}$ is the $^{222}\text{Rn}$ mixing loss ($\text{Bq m}^{-2}\text{day}^{-1}$) with offshore seawater in the underlying layer, which can be neglected due to the long water flushing time for the underlying layer (Legović, 1991) and the small difference of $^{222}\text{Rn}$ activity between the underlying water and the offshore water outside the bay, $F_{\text{sed}}$ is the $^{222}\text{Rn}$ flux dif-

\[
A \times F_{\text{SGD below}} = \left( V_{\text{below}} \times \frac{(222\text{Rn}_{\text{below}})}{\lambda} \right) + (A \times F_{\text{mix below}}) - (A \times F_{\text{sed}}) \]

Fig. 2. Schematic diagram of $^{222}\text{Rn}$ processes in the upper brackish layer above the halocline and the underlying layer below the halocline in Zaton Bay (a); the red tide only occurred in the upper brackish layer in Zaton Bay (b). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)
fused from sediments (Bq m\(^{-2}\) day\(^{-1}\)), \(T_f\) is the water flushing time (day) and described by Dyer (1973):

\[
P = \int_{H}^{0} Adz
\]

\[
T_f = \frac{V_{\text{above}} T}{(1 - b)P}
\]

where \(P\) is the tidal prism, \(z\) is the mean water depth over the tidal range (H), \(T\) is the tidal period, and \(b\) is the return flow factor, which can be estimated by a mixing model (modified by Moore et al., 2006):

\[
f_S + f_G = 1
\]

\[
f_s S_S + f_G S_G = S_H
\]

where \(f_S\) and \(f_G\) is the fraction of seawater end-member and groundwater end-member; \(S_S\), \(S_G\) and \(S_H\) are the salinity of seawater end-member, groundwater end-member and surface bay water, respectively. Here the fraction of seawater end-member is simply the return flow factor, i.e. \(b = f_S\) (Moore et al., 2006).

Since samples are not homogeneously distributed in Zaton Bay, area-weighed mean \(^{222}\text{Rn}\) activities (\(^{222}\text{Rn}\)) were calculated to estimate radon inventories and decay (Garcia-Solsona et al., 2010a; Su et al., 2011). The total area (\(A_{\text{tot}}\)) of Zaton Bay are divided into six boxes (I–VI) (Fig. 1) and \(^{222}\text{Rn}\) calculated as follow:

\[
^{222}\text{Rn} = \sum_{i=1}^{n} \left( \frac{^{222}\text{Rn}_i \times A_i}{A_{\text{tot}}} \right)
\]

where \(i\) represents the number of each box, \(n\) is the number of total boxes, \(^{222}\text{Rn}\) is the mean \(^{222}\text{Rn}\) activity measured in each box and \(A_i\) is the area of each box.

\(^{222}\text{Rn}\) atmospheric evasion (\(F_{\text{atm}}\)) depends on molecular diffusion generated by concentration gradients and turbulent transfer, which can be calculated as follows (MacIntyre et al., 1995):

\[
F_{\text{atm}} = k(C_w - xC_{\text{air}})
\]

where \(C_{\text{air}}\) and \(C_w\) are the \(^{222}\text{Rn}\) concentrations in the air and in the surface bay water, respectively (Bq m\(^{-3}\)); \(x\) is the partition coefficient, which was corrected for salinity and temperature (Schubert et al., 2012); \(k\) is the gas transfer velocity, which can be determined as follows (MacIntyre et al., 1995; Lambert and Burnett, 2003):

\[
k_{600} = \begin{cases} 
0.45u^{1.6} (S_{600})^{-0.5} & (u > 3.6 \text{ m s}^{-1}) \\
0.45u^{1.6} (S_{600})^{-0.6667} & (u \leq 3.6 \text{ m s}^{-1})
\end{cases}
\]

where \(u\) is the wind speed (m s\(^{-1}\)); \(S_{600}\) is Schmidt number for \(^{222}\text{Rn}\) at a given water temperature and calculated based on the formulations given by Pilson (1998).

The diffusive flux of \(^{222}\text{Rn}\) from brackish layer into underlying layer (\(F_{\text{vertical}}\)) (Fick’s first law) and \(^{222}\text{Rn}\) flux diffused from sediment (\(F_{\text{sed}}\)) (Peng et al., 1974; Martens et al., 1980) were calculated as:

\[
F_{\text{vertical}} = (\lambda \times D_m)^{0.5} \left( ^{222}\text{Rn}_{\text{above}} - ^{222}\text{Rn}_{\text{below}} \right)
\]

\[
F_{\text{sed}} = (\lambda \times \varphi \times D_m)^{0.5} \left( ^{222}\text{Rn}_{\text{eq}} - ^{222}\text{Rn}_{\text{below}} \right)
\]

\[
D_m = 10^{-(430/173+1.59)}
\]

where \(\varphi\) is sediment porosity. \(D_m\) is molecular diffusion coefficient, \(^{222}\text{Rn}_{\text{eq}}\) is the \(^{222}\text{Rn}\) activity in pore water that is equilibrium with that in sediment (Bq m\(^{-3}\)), \(^{222}\text{Rn}_{\text{below}}\) is the \(^{222}\text{Rn}\) activity in overlying water, and \(T\) is water temperature (\(^{\circ}\)C).

3. RESULTS

3.1. Spatial distributions in the surface layer

Temperature, salinity, pH, DO, \(^{222}\text{Rn}\), and nutrients in surface waters had clear seasonal and spatial gradients (Figs. 3–4 and Tables S1–S4). The salinity, pH and DO near the entrance of Litno Cave in each season were lower than other stations, while the highest \(^{222}\text{Rn}\) activities were measured at the entrance of Litno Cave on all surveys. Temperature and salinity in seawater were 16.2–24.9 \(^{\circ}\)C and 9.8–29.5 in summer (August), 8.2–14.7 \(^{\circ}\)C and 1.0–5.5 in winter (December), and 14.7–17.5 \(^{\circ}\)C and 1.1–13.1 in spring (April), respectively. \(^{222}\text{Rn}\) activity and DO in surface water showed opposite trends ranging from 250 to 1940 (mean: 620 ± 160) Bq m\(^{-3}\) and 5.4 to 13.0 (mean: 10.4 ± 1.4) mg L\(^{-1}\) during December, 184 to 1750 (mean: 350 ± 110) Bq m\(^{-3}\) and 7.9 to 11.1 (mean: 9.5 ± 0.9) mg L\(^{-1}\) during April, and 41 to 2040 (mean: 233 ± 77) Bq m\(^{-3}\) and 6.3 to 9.2 (mean: 8.5 ± 0.6) mg L\(^{-1}\) during August, respectively. The seasonal changes in pH were not obvious with ranges between 7.6 and 8.2 and lowest values always closer to the cave.

The highest values of nutrients (DIN and DIP) appeared near the entrance of Litno Cave except that the highest value of DIN during April 2016 occurred in inner bay (Fig. 4). The highest DIP values during April 2016 in surface waters were 77 and 740 mg L\(^{-1}\) during April and August 2016 in surface waters were 77 and 122, respectively, well above the Redfield ratio (16).
3.2. Vertical distributions

Vertical profiles of temperature, salinity, pH, DO, 222Rn, 226Ra, and nutrients revealed a highly stratified water column (Figs. 5–6, S1 and Tables S4–S7). The brackish layer occupied the upper 2.8–4.8 m with salinities ranging from 3.1 to 37.6, while the salinities in the bottom approached seawater values. Temperature was vertically homogeneous during April, decreased with depth during August, and increased with the depth during December. pH profiles showed no remarkable variation with depth. DO was higher in the upper brackish layer and lower in the underlying layer, implying respiration of sinking organic material. The 222Rn activities in the upper brackish layer (mean: 530 ± 410 Bq m$^{-3}$) were significantly higher than those in the underlying layer (mean: 117 ± 91 Bq m$^{-3}$) at these three vertical profiles. The activities of 226Ra were orders of magnitude lower than 222Rn, but showed a similar enrichment in the upper brackish layer (mean: 1.68 ± 0.66 Bq m$^{-3}$) than in the underlying layer below the halocline (mean: 0.81 ± 0.38 Bq m$^{-3}$). Based on the two observations during April and August, 2016, the DIN concentrations in the upper brackish layer (mean: 37 ± 27 μmol L$^{-1}$) were also significantly higher than those in the underlying layer (mean: 16 ± 24 μmol L$^{-1}$), while the DIP concentrations had no obvious change in the water column (mean value in the underlying layer: 0.6 ± 1.2 μmol L$^{-1}$; mean value in the underlying layer: 0.7 ± 1.0 μmol L$^{-1}$).

3.3. Anchialine cave water

Overall, 222Rn, DIN, and N/P ratios in anchialine cave water were always much higher than those in bay water, while the DIP variation between the anchialine cave water and bay water was relatively small (Fig. 7). Salinity in anchialine cave water was widely variable ranging from ~1.0 during April and December to 10.0 during August.

![Fig. 3. Horizontal distribution of temperature, salinity, pH, DO, and 222Rn in surface water of Zaton Bay during April, August, and December 2016.](image-url)
The parameters analyzed in anchialine cave water in different seasons were relatively constant, varying over a small range of 14.7–16.5 (mean: 15.4 ± 0.8) °C for temperature, 7.3–7.9 (mean: 7.6 ± 0.2) for pH, 6.3–6.8 (mean: 6.5 ± 0.2) for DO, 1580–2040 (mean: 1860 ± 170) Bq m$^{-3}$ for $^{222}$Rn, 150–180 (mean: 161 ± 14) mmol L$^{-1}$ for DIN, and 0.47–0.95 (mean: 0.65 ± 0.21) mmol L$^{-1}$ for DIN. The N/P ratio in anchialine cave water ranged from 190 to 320 (mean: 250 ± 85), which was much higher than the Redfield ratio (16).

3.4. $^{222}$Rn mass balance

To determine the $^{222}$Rn fluxes via SGD during the three seasonal observations, all $^{222}$Rn sources and sinks in both the upper brackish layer and the underlying layer were estimated (Table 1). The $^{222}$Rn mass balance model (Eq. (1)) requires SGD radon fluxes at 500 ± 170 Bq m$^{-2}$ d$^{-1}$ during April, 290 ± 100 Bq m$^{-2}$ d$^{-1}$ during August, and 630 ± 190 Bq m$^{-2}$ d$^{-1}$ during December in the upper brackish layer. Much smaller SGD-derived radon fluxes were estimated in the underlying layer (5 ± 34 Bq m$^{-2}$ d$^{-1}$ during April, 26 ± 42 Bq m$^{-2}$ d$^{-1}$ during August, and 158 ± 99 Bq m$^{-2}$ d$^{-1}$ during December). SGD-derived $^{222}$Rn fluxes in the upper brackish layer were 4–100-fold higher than those in the underlying layer (Table 1).

4. DISCUSSION

4.1. Linking SGD-derived nutrient inputs to red tide outbreaks

Selecting a proper groundwater end-member is often the main uncertainty in SGD estimates (Santos et al., 2012; Cerdà-Domènech et al., 2017; Chen et al., 2018a,b; Cook et al., 2018). Thus, the selection of groundwater end-member is very important for estimating SGD and related nutrient fluxes. Here, the $^{222}$Rn activities of the surface brackish water from Zaton bay displayed a significant negative correlation with salinity revealing mixing between high-$^{222}$Rn, low-salinity waters from the anchialine cave and low-$^{222}$Rn, high-salinity waters from the seawater end-member (Fig. 8). This implies that the anchialine cave water samples can be used as reasonable groundwater...
end-member in Zaton Bay (Peterson et al., 2009). The SGD rate (m d\(^{-1}\)) to Zaton Bay can be estimated from the \(^{222}\text{Rn}\) flux (Bq m\(^{-2}\) d\(^{-1}\)) via SGD divided by the \(^{222}\text{Rn}\) activity (Bq m\(^{-3}\)) in groundwater. By using \(^{222}\text{Rn}\) activities in the anchialine cave as groundwater end-member, we estimated that the SGD rates in the upper brackish layer of Zaton Bay were 0.29 ± 0.10 m d\(^{-1}\) during April, 0.15 ± 0.05 m d\(^{-1}\) during August, and 0.40 ± 0.12 m d\(^{-1}\) during December, respectively.

Multiplying the SGD rate of each season by the corresponding end-member nutrient concentrations in groundwater yields SGD-derived DIN fluxes of
5.2 \times 10^{-2} \text{ mol m}^{-2} \text{ d}^{-1} \) during April and \( 2.2 \times 10^{-2} \text{ mol m}^{-2} \text{ d}^{-1} \) during August, and SGD-derived DIP fluxes of \( 2.7 \times 10^{-4} \text{ mol m}^{-2} \text{ d}^{-1} \) during April and \( 0.8 \times 10^{-4} \text{ mol m}^{-2} \text{ d}^{-1} \) during August in the upper brackish layer. Assuming the same nutrients and \(^{222}\text{Rn}\) end-members for karstic-point sourced discharge from the cave and from discharge through the sediment in the bottom, SGD-derived DIN fluxes of \( 5.0 \times 10^{-5} \text{ mol m}^{-2} \text{ d}^{-1} \) during April and \( 2.0 \times 10^{-3} \text{ mol m}^{-2} \text{ d}^{-1} \) during August, and the SGD-derived DIP fluxes of \( 2.7 \times 10^{-4} \text{ mol m}^{-2} \text{ d}^{-1} \) during April and \( 6.9 \times 10^{-4} \text{ mol m}^{-2} \text{ d}^{-1} \) during August in the underlying layer. Because the SGD-derived nutrient inputs from the upper brackish layer are nearly two orders of magnitude higher than those from the underlying layer, the nutrient inputs via SGD from the underlying layer can be neglected. As expected, the SGD-derived nutrient fluxes of the upper brackish layer in the wet season were significantly higher than those in the dry season. Red tide only occurred in the upper brackish layer (Fig. 2) in the wet season when the highest SGD rates were estimated.

To better understand the impacts of SGD on the coastal ecosystem, nutrient budgets for Zaton Bay were constructed based on a box model designed by Land-Ocean Interactions in the Coastal Zone (LOICZ) program
nutrients in the Mediterranean (Markaki et al., 2010), the DIN and DIP fluxes from the atmospheric deposition in Zaton Bay were $0.68 \times 10^3$ mol d$^{-1}$ and $0.01 \times 10^2$ mol d$^{-1}$, respectively, which were two orders of magnitude lower than those from SGD (DIN: $(1.4-3.3) \times 10^4$ mol d$^{-1}$; DIP: $(0.5-1.7) \times 10^2$ mol d$^{-1}$) (Fig. 9). This is consistent with earlier estimates suggesting that the DIP input via atmospheric deposition is $<5\%$ of total DIP input into the lower Krka River (Drolc and Koncan, 2002).

Overall, the amount of nutrient inputs was significantly greater than the outputs, implying significant uptake by primary producers, consumption by secondary production and eventually deposition in sediments. We estimate that the uptake of DIN and DIP by primary productivity accounted for 76–92% and 29–79% of the total sinks, respectively (Fig. 9). Generally, tides drive freshwater-seawater mixing in most coastal areas (Chen et al., 2018a). The Zaton Bay is a microtidal environment (tidal range: 0.01–0.35 m), allowing for stratified conditions to develop and creating longer residence times. Thus, the export of nutrients offshore is restricted and allows the accumulation of nutrients in the upper brackish layer, developing phytoplankton communities and red tides in Zaton Bay. Because the DIN and DIP fluxes from SGD accounted for $>98\%$ of the total estimated sources, SGD likely controls primary productivity.

Previous studies have evaluated eutrophication or phytoplankton blooms in the Krka River estuary (e.g., Legović et al., 1994; Moreira-Turcq et al., 2001; Supraha et al., 2014). However, no studies have evaluated the impact of SGD on nutrient fluxes or budgets. The nutrient budgets in Zaton Bay suggest that other nutrient sources can be neglected compared with the nutrient input from groundwater (Fig. 9). In other coastal ecosystems such as bays, lagoons, estuaries, mangroves and coral reefs (Table 2), SGD-derived DIN and DIP fluxes ranged from $0.1 \times 10^{-3}$ to $69 \times 10^{-3}$ mol m$^{-2}$ d$^{-1}$ and $0.1 \times 10^{-5}$ to $190 \times 10^{-5}$ mol m$^{-2}$ d$^{-1}$. Although the SGD-derived DIN ($[22-52 ] \times 10^{-3}$ mol m$^{-2}$ d$^{-1}$) and DIP fluxes ($[8-27 ] \times 10^{-5}$ mol m$^{-2}$ d$^{-1}$) in Zaton Bay were within the broad range often observed in other ecosystems, the proportion of SGD-derived nutrients in the nutrient budgets of Zaton Bay ($>98\%$) is much larger than that of other ecosystems (DIN: 3.7–97 (mean: 57%); DIP: 2.8–87 (mean: 31%)) due to the lack of other significant sources in Zaton Bay (Table 2). Therefore, SGD-derived nutrient fluxes seem to be very important in this Mediterranean ecosystem.

Although there are many reasons for the frequent occurrence of red tides, they are often driven by nutrients produced by natural and anthropogenic origins entering coastal waters through many pathways (Slomp and Van Cappellen, 2004; Zhou and Yu, 2007; Garcia-Solsona et al., 2010b; Moore, 2010). Considering that there are no industrial and aquaculture activities near Zaton Bay, the high DIN concentrations (150–180 μmol L$^{-1}$) in the karst springs are presumably of natural or agricultural origin in Zaton Bay. The Krka River is a medium sized non-contaminated river with a length of about 49 km and a flow of 40–60 m$^3$ s$^{-1}$ (Bonacci et al., 2006). The water column of the Krka River estuary is oligotrophic with concentrations

![Fig. 8. $^{222}$Rn versus salinity plots of surface brackish water and anchialine cave water in Zaton Bay.](image-url)
of DIN ranging from 1.0 to 7.7 (mean: 7.7 ± 6.6) μmol L⁻¹ (Gržetić et al., 1991; Cetinić et al., 2006). DIN concentrations in Zaton Bay are significantly higher (10–114 μmol L⁻¹) than in estuarine waters, mainly as a consequence of SGD inputs (accounting for >98% of DIN inputs). The estimated SGD rate in the wet season (April and December) was higher than that in the dry season (August). Similarly, the DIN and DIP fluxes supplied by SGD were 2 and 3 times the fluxes estimated for the dry season in Zaton Bay (Fig. 10). Here, since the DIN concentrations (150–180 (mean: 161 ± 14) μmol L⁻¹) in cave water did not change significantly, we used the average nutrient concentrations in the end-member for April and August 2016 to estimate nutrient fluxes in December 2016. In our observations in 2016, red tides were visible during April and December, but not during August. The relevance of SGD as a source of nutrients to the bay, together with the agreement between the seasonal magnitude of SGD inputs and the occurrence of red tides, suggest that SGD is the main source of nutrients fueling red tide outbreaks in Zaton Bay.

Previous studies found that SGD-derived nutrients with high N/P ratio can drive red tides (e.g., Hu et al., 2006; Luo and Jiao, 2016). The N/P ratios of anchialine cave water (April: 190; August: 288) were significantly higher than those in surface water (April: 77; August: 122). The high N/P ratios (77-122) of surface water suggest that Zaton Bay would be limited by phosphorus. P-limitation may be driven by sequestration of phosphorus in calcareous sediments of karstic areas (Elser et al., 2007). The high nutrient inputs via SGD (accounting for >98% of total nutrient inputs) are delivered to Zaton Bay with a clear depletion of P (N/P ratio were 190–320 in karstic spring), which may induce or increase P-limitation and alter the structure of biological communities in Zaton Bay. Therefore, we suggest that the high nutrient fluxes via SGD, the high N/P ratio in anchialine cave water, and long residence times drive local red tide outbreaks, especially in the wet season.

Because Zaton Bay has a small tidal range of 0.01–0.35 m (microtidal environment), tides likely play a minor role in SGD (Cerdà-Domènech et al., 2017). Generally, microtidal Mediterranean coastal aquifers are highly influenced by precipitation (Garcia-Solsona et al., 2010b; Rodellas et al., 2012). A comparison between the estimated SGD rates and the local precipitation in Zaton Bay (Fig. 11) implies that SGD responds to the accumulated precipitation in the 1–2 months previous to the samplings. Similar lags between local recharge by precipitation and groundwater discharge have been observed in other Mediterranean karstic systems (Garcia-Solsona et al., 2010b; Rodellas et al., 2012). Thus, the high precipitation in the wet season (Fig. 11) may lead to the high SGD, enhancing the red tide outbreaks (Fig. 10). This suggests that lagged precipitation is probably a key driving force in controlling red tide outbreaks.

4.2. Importance of karstic SGD-derived nutrients in the Mediterranean Sea

Submarine springs or caves are widely distributed along Mediterranean coastlines (Fig. 12; Bakalowicz, 2015; Moosdorf and Oehler, 2017). More than 90% of known submarine springs in the world are located along Mediterranean coastlines (Bakalowicz, 2015). However, nutrient inputs via these point-source groundwater sources remain poorly understood. Here, we build on the existing literature to evaluate the relevance of karstic springs as a source of dissolved nutrients to the Mediterranean Sea. Several
Table 2
Contribution of SGD-derived nutrient fluxes to nutrient budgets in different coastal ecosystems.

<table>
<thead>
<tr>
<th>Study area</th>
<th>Ecosystem type</th>
<th>Tracer SGD rate</th>
<th>DIN flux</th>
<th>Percentage to total DIN sources</th>
<th>DIP flux</th>
<th>Percentage to total DIP sources</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bangdu Bay, Korea</td>
<td>Bay &amp; Shield volcano</td>
<td>$^{222}\text{Rn}$ &amp; $^{224,226}\text{Ra}$</td>
<td>33–49</td>
<td>21</td>
<td>90</td>
<td>16</td>
</tr>
<tr>
<td>Gulf of Aqaba, Israel</td>
<td>Bay</td>
<td>$^{223,224}\text{Ra}$</td>
<td>6–26</td>
<td>2.9–10</td>
<td>32–46</td>
<td>1.8–20</td>
</tr>
<tr>
<td>Masan Bay, Korea</td>
<td>Bay</td>
<td>$^{226}\text{Ra}$</td>
<td>6.1–7.1</td>
<td>7.2–8.5</td>
<td>42–45</td>
<td>51–57</td>
</tr>
<tr>
<td>Gamak Bay, Korea</td>
<td>Shellfish farming bay</td>
<td>$^{226}\text{Ra}$</td>
<td>8–12</td>
<td>8.8–12</td>
<td>85–90</td>
<td>10–23</td>
</tr>
<tr>
<td>Badum, Spain</td>
<td>Open karstic coastal area</td>
<td>$^{223,224,226,228}\text{Ra}$</td>
<td>5.5–8.9</td>
<td>1.5–8.3</td>
<td>-</td>
<td>1.9–4.0</td>
</tr>
<tr>
<td>Dor Bay, Israel</td>
<td>Bay</td>
<td>Seepage meters</td>
<td>8.1$^a$</td>
<td>26.7$^b$</td>
<td>-</td>
<td>2.4$^b$</td>
</tr>
<tr>
<td>Sanggou Bay, China</td>
<td>Bay &amp; Multi-species culture</td>
<td>$^{223,224,226,228}\text{Ra}$</td>
<td>13–14</td>
<td>18–21</td>
<td>65</td>
<td>6.3–7.5</td>
</tr>
<tr>
<td>Caboortu River estuary, Australia</td>
<td>Bay</td>
<td>$^{222}\text{Rn}$</td>
<td>26.8</td>
<td>11</td>
<td>25</td>
<td>43</td>
</tr>
<tr>
<td>Palma Beach, Spain</td>
<td>Estuary</td>
<td>$^{223,224,226,228}\text{Ra}$</td>
<td>12.8$^c$</td>
<td>1.9$^d$</td>
<td>-</td>
<td>0.016$^d$</td>
</tr>
<tr>
<td>Messiniaikos Gulf, Greece</td>
<td>Bay</td>
<td>$^{222}\text{Rn}$</td>
<td>-</td>
<td>69</td>
<td>3</td>
<td>79</td>
</tr>
<tr>
<td>Geoje Bay, Korea</td>
<td>Bay</td>
<td>$^{223,224,226,228}\text{Ra}$</td>
<td>5.4</td>
<td>3</td>
<td>3</td>
<td>89</td>
</tr>
<tr>
<td>Laoye Lagoon, China</td>
<td>Lagoon &amp; Mangrove</td>
<td>$^{222}\text{Rn} &amp; ^{223,224,226,228}\text{Si}$</td>
<td>9.4</td>
<td>3.3</td>
<td>54</td>
<td>3</td>
</tr>
<tr>
<td>Xiaohai Lagoon, China</td>
<td>Lagoon &amp; Mangrove</td>
<td>$^{223,224,226,228}\text{Ra}$</td>
<td>4.1</td>
<td>36</td>
<td>45</td>
<td>190</td>
</tr>
<tr>
<td>Kasitsna Bay, USA</td>
<td>Bay</td>
<td>$^{223,224,226,228}\text{Ra}$</td>
<td>125$^{a,c}$</td>
<td>4.3$^{b,d}$</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Beaufort Sea, USA</td>
<td>Open coastal area</td>
<td>$^{223,224,226,228}\text{Ra}$</td>
<td>12$^{a,e}$</td>
<td>1.2$^{b,d}$</td>
<td>-</td>
<td>0.04$^{b,d}$</td>
</tr>
<tr>
<td>Elson Lagoon, USA</td>
<td>Lagoon</td>
<td>$^{223,224,226,228}\text{Ra}$</td>
<td>12$^{a,e}$</td>
<td>0.5$^{b,d}$</td>
<td>-</td>
<td>0.01$^{b,d}$</td>
</tr>
<tr>
<td>Korogoro Creek, Australia</td>
<td>Estuary</td>
<td>$^{224}\text{Ra}$</td>
<td>17–77</td>
<td>1.6–8.1</td>
<td>55–66</td>
<td>45–97</td>
</tr>
<tr>
<td>Maowei Sea, China</td>
<td>Oyster aquaculture</td>
<td>$^{222}\text{Rn}$</td>
<td>36</td>
<td>33</td>
<td>50</td>
<td>39</td>
</tr>
<tr>
<td>Sanya Bay, China</td>
<td>Bay &amp; Mangrove</td>
<td>$^{223,224,226,228}\text{Ra}$</td>
<td>4.3–7.8</td>
<td>6.1–11</td>
<td>95–97</td>
<td>7.1–13</td>
</tr>
<tr>
<td>Daya Bay, China</td>
<td>Bay</td>
<td>$^{224}\text{Ra}$</td>
<td>1.18</td>
<td>0.2–0.37</td>
<td>42</td>
<td>0.8–2.3</td>
</tr>
<tr>
<td>La Palme lagoon, France</td>
<td>Karstic lagoon</td>
<td>$^{222}\text{Rn}$</td>
<td>0.1–0.5</td>
<td>0.4–1.2</td>
<td>96</td>
<td>0.5–1.5</td>
</tr>
<tr>
<td>Zaton Bay, Croatia</td>
<td>Bay &amp; Anchialine cave</td>
<td>$^{222}\text{Rn}$</td>
<td>15–40</td>
<td>22–52</td>
<td>&gt;98</td>
<td>8–27</td>
</tr>
</tbody>
</table>

$^a$ The references supply only SGD rate in the relevant study areas.
$^b$ The references supply only nutrient flux via SGD in the relevant study areas.
$^c$ Units in m$^3$ m$^{-3}$ d$^{-1}$.
$^d$ Units in mol m$^{-3}$ d$^{-1}$.  

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SGD studies have been conducted in the Mediterranean Sea (Fig. 12). We summarize DIN and DIP concentrations in groundwaters and the estimated SGD rates (Table S8).

To provide a first-order estimate of the total DIN and DIP fluxes supplied to the whole Mediterranean Sea via karstic fresh SGD, we need to estimate reasonable DIN and DIP end-member concentrations in karstic fresh groundwater and total karst SGD flowing to the Mediterranean Sea. Mediterranean karst aquifers have complex hydrological conditions and may be influenced by mixing of groundwater from different origins and are influenced by multiple driving forces (e.g., precipitation, wave setup and seasonal changes of the water table elevation) (Gilli et al., 2010; Gilli, 2015; Cerdà-Domènech et al., 2017). To determine a reasonable karstic fresh groundwater end-member, we used literature data from karstic groundwater springs with salinity < 10 (Table S8). The DIN and DIP concentration ranges (DIN: 120–440 \( \mu \text{mol L}^{-1} \); DIP: 0.18–0.72 \( \mu \text{mol L}^{-1} \)) between the first and third quartiles of the dataset were used to offer a possible range in DIN and DIP concentration in karstic fresh SGD in the Mediterranean (Rodellas et al., 2015). The fresh SGD flow to the Mediterranean Sea was estimated to be \( 0.7 \times 10^{11} \text{ m}^3 \text{ yr}^{-1} \) using hydrogeological modeling (Zektser et al., 2007). Since carbonate lithologies account for 46% of Mediterranean coastlines (Hartmann and Moosdorf, 2012; Trezzi et al., 2017), we assume that approximately half of the flux reported by Zektser et al. (2007) is discharging through carbonate areas. By combining the fresh SGD flow through carbonate areas and the range of nutrient concentrations in low-salinity karstic springs, we estimated that the total DIN and DIP fluxes via karstic fresh SGD in the Mediterranean Sea are on the order of \( (0.4–1.5) \times 10^{10} \text{ mol yr}^{-1} \) and \( (0.6–2.5) \times 10^7 \text{ mol yr}^{-1} \), respectively.

These karstic fresh SGD-derived nutrients are equivalent to approximately 8–31% and 1–4% of riverine inputs (DIN: \( \sim 5 \times 10^{10} \text{ mol yr}^{-1} \); DIP: \( \sim 6 \times 10^8 \text{ mol yr}^{-1} \)) (Ludwig et al., 2009; Rodellas et al., 2015) and 4–16% and 1–2% of atmospheric inputs (DIN: \( 9.7 \times 10^{10} \text{ mol yr}^{-1} \); DIP: \( 1.1 \times 10^9 \text{ mol yr}^{-1} \)) (Markaki et al., 2010) in the Mediterranean Sea. Our estimates imply that fresh karstic groundwater discharge is a relevant source of dissolved nutrients not only at a local scale (e.g., Zaton Bay), but also at the Mediterranean Sea scale. Whereas previous studies already suggested that total SGD (including fresh and saline groundwater) represents a major source of dissolved nutrients to the Mediterranean Sea, comparable to riverine and atmospheric inputs (Rodellas et al., 2015), we highlight the relevance of karstic groundwater inputs as a source of nutrients from a local to a basin-wide scale. Unlike saline SGD that delivers recycled nutrients and carbon from shallow sediments (Billerbeck et al., 2006; Santos et al., 2009; Seidel et al., 2014; Sadat-Noori et al., 2016b), nutrient inputs driven by karstic SGD represent a source of new nutrients into the coastal ocean. Inputs of dissolved nutrients supplied by both karstic and saline SGD should be considered in nutrients budgets of the Mediterranean basin.

The Mediterranean Sea is one of the most oligotrophic seas in the world (Béthoux et al., 1998), making it very sensitive to new external inputs of nutrients (Rodellas et al., 2015). Significant increases of nutrient levels and N/P ratios could derive changes in the coastal microalgal community composition (Harding et al., 2015) and result in ecosystem impairments, such as red tides or harmful algae blooms (Hu et al., 2006; García et al., 2011; Luo and Jiao, 2016). Karstic fresh SGD-derived nutrients with high N/P ratios (mean: 550 > Redfield ratio of 16) (n = 15 sites) in the

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**Fig. 10.** SGD rates (m d\(^{-1}\)) and related DIN fluxes (10\(^{-2}\) mol m\(^{-2}\) d\(^{-1}\)) and DIP fluxes (10\(^{-4}\) mol m\(^{-2}\) d\(^{-1}\)) during April, August and December 2016 in the upper brackish layer in Zaton Bay.

**Fig. 11.** Monthly precipitation in Sibenik City in 2016 (blue bars) and SGD rates into Zaton Bay (red dots) (monthly precipitation data from Meteorological and Hydrological Institute of Croatia: Web Interface, [http://klima.hr/klima_archiva.php](http://klima.hr/klima_archiva.php)). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)
Mediterranean Sea are 4-times greater than the N/P ratios in the saline SGD end-member (n = 10 sites) used by Rodellas et al. (2015), which could provide additional nutrient sources and force the primary production conditions to change from N-limitation to P-limitation (Slomp and Van Cappellen, 2004; Su et al., 2011). These high N/P ratios would strongly affect the primary production and nutrient structure in Mediterranean, and then may trigger and sustain algal blooms or red tide outbreaks, especially in waters near the point sources such as Zaton Bay. Therefore, point-source nutrient fluxes via fresh SGD should not be overlooked in the Mediterranean.

5. CONCLUSIONS

This study used $^{222}$Rn to quantify seasonal SGD and associated nutrient fluxes from anchialine caves or springs into a coastal ecosystem (Zaton Bay, Croatia). A $^{222}$Rn mass balance revealed that karstic SGD, which is mainly discharging to the upper brackish layer of the bay, accounts for $>98\%$ of DIN and DIP inputs to Zaton Bay. SGD-derived water and nutrient fluxes in the wet season were significantly higher than those in the dry season, coinciding with the seasonal occurrence of red tides. As major nutrient sources into Zaton Bay, the SGD-derived inputs of nutrient with high N/P ratio (190–320) may alter the nutrient structure of seawater, change the microalgal community composition, and drive red tide outbreaks.

Combining our new observations with literature data from other Mediterranean karstic springs, we estimate karstic SGD-derived DIN and DIP fluxes to the entire Mediterranean Sea (DIN: $(0.4–1.5) \times 10^{10} \text{ mol yr}^{-1}$; DIP: $(0.6–2.5) \times 10^{7} \text{ mol yr}^{-1}$). These estimated nutrient fluxes have high N/P ratio ($\sim 550$) and are equivalent to 8–31\% and 1–4\% of total riverine inputs in the Mediterranean Sea, respectively. Therefore, karstic fresh SGD seems to be a relevant external source of new nitrogen not only at a local scale, but also at the Mediterranean Sea scale.

6. RESEARCH DATA

Research data (i.e., Supplementary Information) to this article can be found online at https://doi.org/10.17632/nc26mcmgxb.2.

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