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Assessing submarine groundwater discharge (SGD) and nitrate fluxes in highly heterogeneous coastal karst aquifers: challenges and solutions

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Abstract

Groundwater discharge in coastal karst aquifers worldwide represents a substantial part of the water budget and is a main pathway for nutrient transport to the sea. Groundwater discharge to the sea manifests under different forms, making its assessment very challenging particularly in highly heterogeneous coastal systems karst systems. In this study, we present a methodology approach to identify and quantify four forms of groundwater discharge in a mixed lithology system in southern Spain (Maro-Cerro Gordo) that includes an ecologically protected coastal area comprised of karstic marble. We found that groundwater discharge to the sea occurs via: (1) groundwater-fed creeks, (2) coastal springs, (3) diffuse groundwater seepage through seabed sediments, and (4) submarine springs. We used a multi-method approach combining tracer techniques (salinity, ^{224}Ra , and ^{222}Rn) and direct measurements (seepage meters and flowmeters) to evaluate the discharge. Groundwater discharge via submarine springs was the most difficult to assess due to their depth (up to 15 m) and extensive development of the springs conduits. We

determined that the total groundwater discharge over the 16 km of shoreline of the study area was at least $11 \pm 3 \times 10^3 \text{ m}^3 \text{ d}^{-1}$ for the four types of discharge assessed. Groundwater-derived nitrate (NO_3^-) fluxes to coastal waters over ~3km (or 20%) in a highly populated and farmed section of Maro-Cerro Gordo was $641 \pm 166 \text{ mol d}^{-1}$, or ~75% of the total NO_3^- loading in the study area. We demonstrate in this study that a multi-method approach must be applied to assess all forms of SGD and derived nutrient fluxes to the sea in highly heterogeneous karst aquifer systems.

Keywords: Coastal karst aquifers, submarine groundwater discharge, nitrate fluxes, multi-method approach.

1 Introduction

Coastal karst aquifers are 46% of the Mediterranean coastline, and play a key role in regional socioeconomic, providing residents with essential water resources (Fleury et al., 2007; Bakalowicz, 2015; Arfib and Charlier, 2016; Trezzi et al., 2017). Groundwater is often the only available source as Mediterranean precipitation is scarce and sporadic, and often limited runoff due to efficient infiltration and percolation through the karst aquifers (McCormack et al., 2014).

Typically, karstified carbonate aquifers are comprised of a complex set of fractures, conduits, and cavities generating high spatial and temporal heterogeneity in groundwater flow (Worthington, 1999; Bakalowicz et al., 2005; Barberá and Andreo, 2015). This in turn results in challenging water resources management and attempts to develop water budgets and numerical models describing karst systems often fail or result in estimates with large uncertainties (Butscher and Huggenberger, 2007; Martínez -Santos and Andreu, 2010; Rapaglia et al., 2015).

When a karst system is hydraulically connected to the sea, a significant part of groundwater can flow directly to the sea in different forms (Stringfield and Legrand, 1971; Pinault et al., 2004; Custodio, 2010). Groundwater discharge to the sea can occur via submarine springs (Fleury et al., 2007; Bakalowicz et al., 2008; Dimova et al., 2011) or subaerial coastal springs near the shoreline (Aunay et al., 2003; Mejías et al., 2008; García-Solsona et al., 2010) depending on the geologic structure (Bonacci and Roje-Bonacci, 1997; Benac et al., 2003; Stamatis et al., 2011). Conduits and fractures buried under seabed sediments near the shoreline can also produce diffuse groundwater seepage (e.g. Tovar-Sánchez et al., 2014; Rodellas et al., 2012). Conversely, impervious strata can create enough hydraulic pressure for inland springs whose runoff flows to the sea as groundwater-fed creeks without experiencing infiltration (e.g. Yobbi, 1992; Katz et al., 2009). In this work, we will use the widely accepted term submarine

groundwater discharge (SGD) for the submerged forms of groundwater discharge to the sea as defined by Burnett et al. (2003) and Moore (2010).

Groundwater discharge of unconsolidated sedimentary coastal aquifers has been considered an insignificant component in water and nutrient budgets, mostly due to its relatively small (<10%) volumetric contribution compared to surface water (Burnett and Dulaiova, 2003; Moore 2010). However, in karst systems with limited runoff, SGD is a major component of the coastal aquifer water and nutrient budget. Where excess of nutrients are delivered in coastal systems, these produce ecological perturbations such as harmful algae blooms (e.g. Hallegraeff, 1993; Smith and Swarzenski, 2012), and seagrass habitat modification (e.g. Valiela et al., 1992) to mention a few.

Coastal karst SGD can have very different composition due to the wide range of groundwater residence time and complex pathways of the discharging waters (Weinstein et al., 2011; Tovar-Sánchez et al., 2014; Trezzi et al., 2016). It is therefore necessary to apply a multi-method approach to adequately identify and assess all forms of groundwater discharge when they coexist.

A number of techniques have been developed to identify and estimate groundwater discharge to coastal areas under different climatic conditions and geologic settings. For instance, naturally occurring radon and radium isotopes are effective groundwater tracers of SGD (e.g. Cable et al., 1996; García-Solsona et al., 2010; Rodellas et al., 2015; Dimova et al., 2015) as they are chemically conservative and are typically a few orders of magnitude higher concentrations in groundwater than surface waters, allowing for easy detection in receiving coastal waters (Burnett et al., 2003). Furthermore, mass balance determination of radium and radon excess in near-shore surface quantifies the magnitude of groundwater fluxes (Cable et al., 1996; Wong et al., 2013;

Tovar-Sánchez et al., 2014). Specifically, ^{222}Rn ($t_{1/2} = 3.8$ d) and ^{224}Ra ($t_{1/2} = 3.6$ d) which have relatively short half-lives, and in the time-scale range of typical coastal mixing processes can be used in combination to assess SGD (Moore, 1996; Cable et al., 1996; Burnett and Dulaiova, 2003).

Alternatively, in areas of faster groundwater flow regimes (e.g. karst and volcanic systems), salinity (e.g. Knee et al., 2010; Stieglitz et al., 2010; García -Solsona et al., 2010; Dimova et al., 2011) and thermal anomalies along the shoreline at the points of discharge are proven to be good indicators of SGD (e.g. Pluhowski, 1972; Johnson et al., 2008; Peterson et al., 2009; Mejías et al., 2012; Tamborski et al., 2015). In areas where permeable sediments are present, direct measurements of SGD using seepage meters are used in parallel with radiotracer techniques (Lee, 1977; Burnett et al., 2006; Sadat-Noori et al., 2015).

The mixed lithology Maro-Cerro Gordo coastal area is an example where identifying and quantifying all components of groundwater discharge are critical to building a comprehensive water budget that addresses adequately the existing economic and ecological demands of the adjacent coastal communities and ecosystems. Land use includes intensive agriculture with 1.3 km² of greenhouses and additional surface tropical crops, in combination with accelerating tourism in the area during the past decades. These land uses are increasingly satisfied by groundwater extractions, in this case from the Sierra Almirajara-Alberquillas Aquifer (Andreo and Carrasco, 1993), a highly fissured and karstified marble formation within the study site.

In order to assess the severity and impact of the increasing groundwater abstractions, water managers require a comprehensive water budget for the area. The current water budget based on a mass balance approach indicates total fresh water of $50 \times 10^6 \text{ m}^3 \text{ y}^{-1}$ for the Sierra Almirajara-Alberquillas Aquifer (Castillo et al., 2001). This budget was suggested to be comprised

of: (1) inland springs and intermittent creeks ($32 \times 10^6 \text{ m}^3 \text{ y}^{-1}$), (2) extraction for irrigation and consumption purposes ($12 \times 10^6 \text{ m}^3 \text{ y}^{-1}$), (3) water transfer to the Neogene-Quaternary coastal formations, and the remaining part to (4) groundwater discharge to the sea ($6 \times 10^6 \text{ m}^3 \text{ y}^{-1}$). A more recent water mass balance budget using the APLIS (A = altitude, P = slope, L = lithology, I = infiltration landforms, S = soil type) method (Andreo et al., 2008) included an infiltration coefficient of 40 - 45% and confirmed that the total budget of the Sierra Almirajara-Alberquillas Aquifer is $50 \times 10^6 \text{ m}^3 \text{ y}^{-1}$ for 2003 – 2005, which were notably dry years (Pérez-Ramos and Andreo, 2007). This assessment based on 2003-2005 data found a slightly higher natural drainage through springs ($38 \times 10^6 \text{ m}^3 \text{ y}^{-1}$) and extraction ($15 \times 10^6 \text{ m}^3 \text{ y}^{-1}$) compared to the estimate by Castillo et al. (2001), suggesting that groundwater discharge is negligible. However, more recently SGD was found to be significant at $1 \times 10^6 \text{ m}^3 \text{ y}^{-1}$ in Maro-Cerro Gordo using a combination of GIS-based approach, hydrometeorological methods, and preliminary ^{224}Ra evaluations (Andreo et al., 2017).

In this study, we performed a comprehensive assessment of the total groundwater discharge to the sea in the Maro-Cerro Gordo area through the application of a set of methods selective to each form of discharge. We used a combination of radiotracers (^{222}Rn and ^{224}Ra) and salinity mass balances, seepage meter measurements, and flowmeter measurements to: (1) identify point discharges to the sea; and (2) quantify the total groundwater discharge from the Sierra Almirajara-Alberquillas Aquifer to adjacent coastal waters. We further (3) estimated groundwater-derived nitrate (NO_3^-) fluxes to the coastal waters of Maro-Cerro Gordo and compared these NO_3^- fluxes in an ecologically protected area (with low anthropogenic activities) to unprotected zones (with intense agriculture and overpopulation). The sampling campaigns were conducted during base flow conditions to provide a conservative estimate of the total

groundwater discharge to the sea and nitrate fluxes of the Sierra Almirajara-Alberquillas Aquifer and Maro-Cerro Gordo coastal area. Finally, (4) we compared the applicability of each method to assess the forms of groundwater discharge and made recommendations for applying this approach to other karst aquifer systems worldwide.

2 Study site and hydrogeological settings

The study site, Maro-Cerro Gordo, is located along the coastal fringe between Nerja and La Herradura in the easternmost section of the Malaga Province and part of the western Granada Province (Southern Spain) along 16 km of shoreline (Fig. 1). Approximately 80% of the study area is within the environmentally protected Maro-Cerro Gordo Natural Area, which comprises 3.58 km² and 14.31 km² of terrestrial and marine surface respectively. The area is characterized by a typical Mediterranean climate with average annual precipitation of 500 mm y⁻¹ occurring almost entirely during fall and winter (Andreo and Carrasco, 1993). We have divided the area in three sections based on their predominant lithology and associated forms of discharge. From east to west these are: (1) karst section, which includes the Cerro Gordo cape from Cañuelo Beach to La Herradura; (2) schist section, confined between El Cañuelo Beach and Maro Beach; and (3) conglomerate section, which comprises the area between Maro Beach and Nerja (city) (Fig. 1).

Figure 1: Study site location and geological map showing water table contour lines (from Pérez-Ramos and Andreo, 2007), groundwater flow direction, important wells and piezometers, sampling points, and terrestrial springs. Groundwater discharge to the sea (TGD) is represented in purple and is based on this study. Coastal springs are represented as CS, groundwater-fed creeks as GC, diffuse groundwater seepage as GS, and submarine springs as SS. The study area is divided in

three sections: conglomerate section, schist section, and karst section. The distribution of seagrass beds are based on Bañares-España et al. (2002), and Aranda and Otero (2014).

2.1 Alberquillas Aquifer Unit

The main aquifer formation in the study area is the Alberquillas Aquifer Unit, a telogenetic karst formation that underlines the southeast sector of the Sierra Almirajara Aquifer unit and is comprised of highly fissured and karstified Triassic marble (Andreo and Carrasco, 1993). The lithology varies from dolomitic to calcitic marble over the 600 m maximum thickness from basement to the surface (Andreo et al., 1993). In general, the primary porosity of this unit is negligible and the degree of karstification is locally higher in the lower portion, with the exception of Nerja Cave, which is a $3 \times 10^5 \text{ m}^3$ cavity located 158 m above sea level and 930 m from the shoreline (Durán, 1996; Andreo et al., 1993; Jordá et al., 2011).

The Alberquillas Aquifer Unit exhibits an elongated shape towards the southeast and a total surface of 60 km^2 , and is directly in contact with the Mediterranean Sea only along the karst section (Fig. 1). The two aquifer units (Alberquillas and Almirajara Aquifer units) are hydraulically connected, constituting the Sierra Almirajara-Alberquillas Aquifer (142 km^2), which recharges from local precipitation (Carrasco et al., 1998). Conceptual hydrogeological models developed for the Sierra Almirajara-Alberquillas Aquifer suggest that groundwater generally flows from north to south, and SGD occurs mainly in eastern Cerro Gordo (Andreo and Carrasco 1993; Carrasco et al., 1998; Pérez-Ramos and Andreo, 2007).

The first attempt to locate SGD in Maro-Cerro Gordo was performed by Espejo et al. (1988) via airborne infrared thermal (IRT) remote sensing. Two thermal anomalies were detected during this survey, one in the Maro area (conglomerate section), and one in the vicinity of Cerro

Gordo and Cantarrijan (karst section); these were also confirmed by lower surface seawater salinity (Espejo et al., 1988).

A cluster of three submarine caves with active springs (Cantarrijan Caves) were identified at water depths of about 7 m near the Cantarrijan Beach (Fig. 1) during SCUBA diving explorations in the karst section during this study. The vents of these springs are located at the same depth and only 2 – 3 m away from each other. Thus, in our assessments the flux of these three springs was treated as a single discharge point. We identified the vents of two additional submarine springs at water depths of 12 m (Palomas Cave) and 15 m (Sifon Cave) in anchialine caves with up to 10 m of horizontal development (Fig. 1). These caves, together with the three small Cantarrijan Cave springs, represent the deep SGD of Sierra Almirajara-Alberquillas Aquifer in the karst section. From SCUBA diving observations, we found that all three discharge points are related to highly-developed karstic conduits at depth. We found during this study that they were active even during droughts (Fig. 2), showing base flow conditions of Sierra Almirajara-Alberquillas Aquifer water budget drainage.

2.2 Schist formation

Alberquillas Aquifer Unit is overlaying a concordant Paleozoic schist formation along most of its extension and is tectonically in contact through a set of faults (Andreo et al., 1993). Metamorphosed during the Alpine Orogeny it presents a maximum thickness of 500 m and very low hydraulic conductivity (Andreo et al., 1993). Outcrops of the schist formation can be found almost along the entire schist section (Fig. 1). The schist formation serves as a hydrogeological barrier for SGD in this area (Andreo and Carrasco, 1993), and groundwater discharge to the sea in this section manifests as four small-size creeks and one coastal spring. The four creeks include: Tierras Nuevas Creek which emanates from a soil layer on the schist formation; the

Colmenarejos Creek which was dry over the sampling campaigns; Miel Creek which is of particular interest as it is solely fed by permanently discharging springs located along the Sierra Almijara-Alberquillas Aquifer in the sea (Andreo and Carrasco, 1993). The Maro Stream was observed to be produced by irrigation excess from abundant agriculture located nearby.

Lastly, the Alberquillas coastal spring, located 20 m from the shore at the Alberquillas Beach at the contact between the highly permeable Alberquillas Aquifer Unit karstic marble and impermeable schist, was found to have a perennial flow regime.

2.3 Conglomerate, breccia, and travertine formations

Pliocene conglomerate and breccia deposits with a maximum thickness of 60 m, form ~ 90% of the conglomerate section of the study area, representing the second most important permeable formation in the study site (Fourniguet, 1975; Andreo et al., 1993; Guerra-Merchán and Serrano, 1993). This formation is comprised of marble fragments cemented by a red matrix, showing signs of dissolution in the upper portion due to its calcite composition. Its hydraulic conductivity permits limited groundwater flow mainly due to primary porosity and the slight presence of fractures (Andreo and Carrasco, 1993). In the coastline comprised of this formation, groundwater discharge can be identified visually as two coastal springs, the Doncellas and Barranco Maro Spring and the groundwater-fed creek (Caleta Creek) which originates from a spring located near the town of Maro (Fig. 1). On the easternmost sector of the conglomerate section, south from the town of Maro, a 30 m thick highly porous and permeable quaternary travertine is present in direct contact with the sea at Maro Cliff to the south (Jordá, 1988). The two small coastal springs of Huerto Romero and Maro Beach are present in this formation along with the intermittent groundwater-fed creek of Maro Creek. We have observed that excess water from the Maro Spring located approximately 1 km to the north of Maro Cliff, flows as Maro

Creek and discharges to the sea from the travertine cliff as a waterfall that is intermittently active depending on irrigation times. The Maro Sprig is well-known and it was included in the Sierra Almijara-Alberquillas Aquifer water budget, and it is utilized for drinking and irrigation purposes (Liñán et al., 2000). The Sanguino Creek remained dry throughout this study.

Figure 2: Average monthly precipitation and sea level change during 2010, 2015, and 2016. Error bars show the monthly rainfall variability during this study. In December of 2015 slight precipitation occurred only during the first week, however, abundant rainfall took place during September-November. Sea level showed lower values during January-May and higher during August-December. Sampling campaigns were conducted during May-July (dry periods) and December (wet periods).

3 Methods

Water fluxes to the sea from karstic submarine springs were quantified using (1) ^{224}Ra and (2) salinity mass balances, groundwater seepage was quantified using both (3) a ^{222}Rn box model mass balance and (4) seepage meter deployments in the locations where radon anomalies were observed. Subaerial groundwater discharge from coastal springs and groundwater-fed creeks was measured directly using a flowmeter (5).

3.1 Tracer techniques

3.1.1 ^{224}Ra distribution and submarine springs discharge assessment

A total of 38 discrete ^{224}Ra samples of 60 L each were collected in September of 2006 and 2010 to survey the schist and karst sections (Fig. 1). All seawater samples were collected at a depth of 0.3 m, with the exception of SW- 7 and SW-21 that were collected at the submarine springs at 8 m and 15 m respectively. Seawater (n = 30) and groundwater (n = 8) samples were

obtained using a submersible pump, and were later passed through a PVC column filled with about 25 g of MnO₂-coated-fibers (Mn-fibers) at a flow rate of approximately 1 L min⁻¹ to allow for a quantitative absorption of ²²⁴Ra (Moore, 1976; 2008). Mn-fibers were then transferred to the lab, rinsed with Ra-free water, and partially dried (Sun and Torgersen, 1998). Activities of ²²⁴Ra were measured using a Radium Delayed Coincidence Counter (RaDeCC) system (Moore and Arnold, 1996; García-Solsona et al., 2008). The Mn-fibers were counted twice, with the first time immediately after collection to assess the total ²²⁴Ra in the water, and a second time after a month to evaluate the supported ²²⁴Ra in equilibrium with ²²⁸Th. The excess of ²²⁴Ra was used to construct a ²²⁴Ra mass balance following Charette et al. (2001), which assumes that the ²²⁴Ra excess in coastal waters is the result of groundwater inputs (Eq. 1). This approach was applied to assess water fluxes (F_{SGD} , m³ d⁻¹) originated from the three submarine springs present in the karst section of the study site (Fig 1):

$$F_{SGD} = \frac{\frac{(Ra_{sw} - Ra_{ow}) \times V}{t} + Ra_{sw} \times V \times \lambda}{Ra_{SGD}} \quad (1)$$

where Ra_{sw} is the ²²⁴Ra activity in coastal waters, i.e. the surface water end-member (dpm m⁻³); Ra_{ow} is the offshore ²²⁴Ra activity in open waters (dpm m⁻³); Ra_{SGD} is the activity of the groundwater end-member (dpm m⁻³); t is the coastal water residence time (d); V is the volume (m³) of coastal water affected by each submarine spring (SGD plume; and λ is the ²²⁴Ra decay constant (0.1894 d⁻¹).

Because this area is greatly exposed to prevailing west winds, large waves, and intensive mixing, we assumed that the residence time (t) of the water in this high energy coastline must be no more than one day. Thus, we used the one-day value in our mass balance model. The volume affected by SGD (V) was constrained using the surface area of the salinity anomaly created by the spring plume and corresponding water depths, obtained from the Andalusia Council of

Environment bathymetry database: <http://www.juntadeandalucia.es/medioambiente/site/rediam>.

To obtain the ^{224}Ra activity (Ra_{sw}) surface water end-member representative of the whole water column, average values of water samples collected from the surface and at the depth of the spring discharge were used.

3.1.2 Salinity anomalies and submarine spring discharge evaluation

To identify and quantify submarine springs discharge following the 1-meter isobath parallel to the shoreline, three salinity boat surveys were performed in May, July, and December of 2015 along the entire stretch of the studied coastline. Electrical conductivity (EC) and temperature (T , $^{\circ}\text{C}$) were measured continuously at a constant depth of 0.3 m with accuracies of $\pm 20 \mu\text{S cm}^{-1}$ and $\pm 0.1^{\circ}\text{C}$ by towing a conductivity-temperature-depth sensor (CTD, Solinst[®]) from boat at a speed of about 2 km h^{-1} . Seawater salinity values were obtained from EC using the conversion method 2520B (Standard Methods for the Examination of Water and Wastewater, APHA, 1999). Data were recorded in 2 min intervals concurrently with precise GPS boat positioning recorded in 30-sec intervals (Garmin Etrex[®] 20x) with an accuracy of $\pm 3 \text{ m}$. Electrical conductivity and temperature of groundwater samples were measured using a Pro2030 (YSI Inc.) handheld instrument with accuracies of $\pm 1 \mu\text{S cm}^{-1}$, and $\pm 0.3^{\circ}\text{C}$. Before sampling, the CTD sensor and handheld instrument (YSI) were calibrated using two conductivity solutions (Oakton[®]): $1413 \mu\text{S cm}^{-1}$ and $12,880 \mu\text{S cm}^{-1}$, measured at 25°C . Temperature correction for EC was automatically performed using linear compensations of $2\% ^{\circ}\text{C}^{-1}$ and $1.91\% ^{\circ}\text{C}^{-1}$ for the CTD sensor and the handheld instrument respectively.

To compare data points from all surveys and identify consistent spatial salinity variations (i.e. permanent groundwater fluxes) independent of seasonal fluctuations, salinity values from each survey were normalized based on their total average. Salinity anomalies were defined as

positive when salinity is higher than average and negative when it is lower than the average value.

A salinity mass balance based on the salinity anomalies generated by submarine springs inputs was constructed to determine groundwater fluxes (F_{SGD} , $m^3 d^{-1}$) in the karst section using Eq. 2 and following Crusius et al. (2005) and Knee et al. (2010). To calculate the fresh water fraction of the spring discharge, we used the approach described in Knee et al. (2010), which indirectly defines the groundwater salinity end-member (Sal_{SGD}) to be zero (Eq. 2):

$$F_{SGD} = \frac{(Sal_{ow} - Sal_{sw}) \times V}{t \times Sal_{ow}} \quad (2)$$

where, Sal_{ow} and Sal_{sw} represent salinity values of open water and coastal surface waters. As in Eq. 1, V is the volume of coastal water affected by SGD (m^3); and t is the coastal water residence time (d). We used the same end-member values as in the ^{224}Ra mass balance. Note that this mass balance assumes a groundwater salinity end-member (Sal_{SGD}) of zero in order to quantify only the fresh component of SGD (Knee et al., 2010).

3.1.3 ^{222}Rn surveys and groundwater seepage assessment

Seawater ^{222}Rn concentrations were measured in surface coastal waters (at about 0.3 m depth) in July, December of 2015, and July of 2016 along all sections using a RAD AQUA set up (Durrige Co., Inc.) as described in Dulaiova et al. (2005) and further improved by Dimova et al. (2009). To obtain radon-in-water concentrations, the measured radon-in-air was corrected using the temperature-dependent Ostwald's solubility coefficient (Macintyre et al., 1995) (Eq. 3):

$$\alpha = 0.105 + 0.405e^{(-0.05027 \times T)} \quad (3)$$

where T ($^{\circ}C$) is the water temperature, measured in 2 min intervals using a temperature data logger (HOBO[®], Onset[®] Inc.). Analytical uncertainties of ^{222}Rn in water were most of the time lower to 10%. The RAD AQUA system was run stationary for at least 20 min at the beginning of

all surveys to achieve water/air and radioactive equilibrium (Dimova et al., 2009), and set up to measure in 10 min intervals while moving at boat speed of 2 km h⁻¹ to allow for detection of rapid ²²²Rn changes. These data were coupled with GPS coordinates to be mapped later.

Diffuse groundwater seepage was quantified using a ²²²Rn mass balance (box model) as described in Burnett and Dulaiova (2003) during July of 2015 and 2016, and December of 2016. To evaluate diffuse groundwater seepage using a ²²²Rn mass balance (Eq. 4), ²²²Rn time-series (1 - 2 days long) were conducted in the Maro Cliff and Cantarrijan Beach seepage area. For this study, this mass balance was modified to account for radon inputs to the sea from a small groundwater-fed waterfall (Maro Creek) (Fig. 1). Radon fluxes (F_{GW}) (dpm m⁻² h⁻¹) from groundwater discharge were determined using mass balance equation where total ²²²Rn inputs to the water column are balanced by radon:

$$F_{GW} = F_{Atm} + F_{Mix} - F_{Waterfall} - C_{Ra} - F_{Diff} \quad (4)$$

where F_{Atm} is the ²²²Rn atmospheric evasion fluxes through the water/air interphase; F_{Mix} are mixing losses due to tidal variations and horizontal mixing; $F_{waterfall}$ are fluxes of ²²²Rn into the system from a groundwater-fed waterfall present in Maro Cliff; C_{Ra} is the production of ²²²Rn from ²²⁶Ra decay within the water column; and F_{Diff} is ²²²Rn diffusion flux from seabed sediments.

To assess the contribution of ²²²Rn from Maro Creek the radon flux from the creek ($F_{waterfall}$) was calculated by multiplying the average creek radon concentration by the water flux which was based of flowmeter measurements and specific area of discharge. This correction was only done during Creek flow regime. Corrections for the production of ²²²Rn from dissolved ²²⁶Ra (i.e. supported radon) in coastal waters (C_{Ra}) were done utilizing the Mn-fiber collected in September of 2006 (one sample) and in July of 2016 (two samples) in Maro Cliff

and Cantarrijan Beach at the time series stations. The average concentration (September 2006 and July 2016) was applied in the ^{222}Rn mass balance. The procedure follows the technique described in details in (Charette et al., 2001). The ^{226}Ra equilibrated samples were counted via gamma spectrometry (HPGe well detector, Canberra GCW3522) using the ^{214}Pb peak at 352 keV. Atmospheric evasion of ^{222}Rn (F_{Atm}) was calculated based on the water/air interphase ^{222}Rn concentration gradient (dpm m^{-3}), ^{222}Rn Ostwald solubility coefficient, and ^{222}Rn gas transfer velocity (k , m h^{-1}). The gas transfer velocity (m h^{-1}) was calculated using Eq. 5 as described in Macintyre et al. (1995):

$$k(600) = 0.45 \times u_{10}^{1.6} \left(\frac{S_c}{600} \right)^{-b} \quad (5)$$

where u_{10} is wind velocity at 10 m above sea level (m s^{-1}) acquired from an internet web service (<http://www.wunderground.com/>), S_c is the Schmidt number, and b is a factor that ranges from $\frac{1}{2}$ ($u_{10} < 3.6 \text{ m s}^{-1}$) to $\frac{2}{3}$ ($u_{10} > 3.6 \text{ m s}^{-1}$).

During high wind conditions (July of 2015), we used Eq. 6 (all terms are defined in Eq. 5) designed in Kremer et al. (2003) for shallow waters and a wide range of wind speeds (Cockenpot et al., 2015):

$$k(600) = 1.65 \times e^{(u_{10})} \left(\frac{S_c}{600} \right)^{-b} \quad (6)$$

Molecular diffusion flux of ^{222}Rn from seabed sediments (F_{Diff}) was determined using the approach described in Martens et al. (1980).

After all corrections were made, negative fluxes were considered mixing losses (F_{Mix}). The pore water ^{222}Rn concentration and porosity of sediments were determined based on the procedure reported in Corbett et al. (1998). Groundwater seepage velocity (SGD , cm d^{-1}) was then calculated (Eq. 7) by dividing SGD -derived ^{222}Rn fluxes by the representative groundwater ^{222}Rn concentration end-member (Rn_{SGD} , dpm m^{-3}) (Burnett and Dulaiova, 2003).

The groundwater end-member (Rn_{SGD}) was assessed in groundwater collected from a small cavity in the travertine cliff located 1 m a.s.l. in Maro Cliff, and GW-Well in Cantarrijan Beach (Fig.1). Groundwater ^{222}Rn concentrations were analyzed with a RAD7 using a RAD H_2O set up in duplicate 250 mL samples.

$$SGD = \frac{F_{GW}}{Rn_{SGD}} \quad (7)$$

In order to calculate groundwater fluxes (F_{SGD} , $\text{m}^3 \text{d}^{-1}$), the obtained seepage velocities were multiplied by the total area through which SGD occurs using Eq. 8:

$$F_{SGD} = SGD \times A \quad (8)$$

where SGD represents seepage velocity (cm d^{-1}), and A is the seepage area (m^2). To constrain the seepage area (A) at the beach face, we conducted a high-resolution ^{222}Rn survey by manually moving a small boat at a speed of 15 m h^{-1} . For more precise results, during this survey, the RAD AQUA system was let to equilibrate for 20 min every 2 - 10 m of shoreline. The high-resolution ^{222}Rn survey data was mapped using a linear ordinary kriging interpolation method (ArcGIS 10), each concentration interval was then contoured (using the ArcGIS 10 contour spatial analyst) to obtain ^{222}Rn concentration isolines. The seepage area (A) was delineated by creating a polygon that followed the $35 \times 10^3 \text{ dpm m}^{-3}$ isoline as a threshold in Maro Cliff and $6 \times 10^3 \text{ dpm m}^{-3}$ in Cantarrijan Beach. The seepage area (m^2) was obtained by calculating the polygon geometry based on the ETRS 1989 UTM Zone 30N projected coordinate system.

3.1.4 Fresh SGD assessment in diffuse seepage

As defined by Taniguchi et al. (2002), diffuse groundwater seepage is comprised of two components: (1) a fresh (meteoric) groundwater component and (2) a recirculated seawater component. To calculate the fresh water component in seepage areas of the study site (e.g. in Cantarrijan Beach), we applied a salinity mixing model (Eqs. 9 and 10) as described in

Taniguchi et al., (2005) and used by many others (e.g. Charette et al., 2007; Taniguchi et al., 2008; Santos et al., 2009). The approach relies on two basic equations:

$$f_{\text{FSGD}} + f_{\text{RSGD}} = 1 \quad (9)$$

$$\text{Sal}_{\text{FSGD}} \times f_{\text{FSGD}} + \text{Sal}_{\text{RSGD}} \times f_{\text{RSGD}} = \text{Sal}_{\text{SGD}} \times f_{\text{SGD}} \quad (10)$$

where f_{FSGD} and f_{RSGD} represent the fresh and recirculated fractions of SGD, and Sal_{FSGD} and Sal_{RSGD} are the salinity values measured in fresh groundwater (GW-Well) and maximum recirculated salinity (GW-PZ-4).

3.2 Direct groundwater flow measurements

3.2.1 Flowmeter measurements of coastal springs and creeks

The location of coastal springs and inland springs feeding groundwater-fed creeks were identified via field observations. The discharge from the identified coastal springs (Doncellas, Barranco Maro, Huerto Romero, Maro Beach, and Alberquillas) and groundwater-fed creeks (Caleta Creek, Tierras Nuevas Creek, and Miel Creek) entering the sea, were measured using a flowmeter (OTT C2, OTT Hydromet GmbH) with an accuracy of $\pm 10\%$. Channel widths were between 10 cm and 140 cm and depths were below 30 cm in all springs and creeks. Flow velocity measurements at the average water depths were recorded in 10 cm intervals across the stream cross section right before discharge into the sea. Water fluxes were calculated for each interval multiplying width (10 cm) and depth by flow velocity. Total water flux ($\text{m}^3 \text{d}^{-1}$) was then calculated by adding water fluxes in all intervals. To observe differences between dry and wet periods measurements were conducted during July and December of 2016.

3.2.2 Seepage meter measurements of diffuse seepage

To verify ^{222}Rn -based SGD estimates, we deployed multiple seepage meters in July of 2016. Lee-type seepage meters, built following the procedure described in Lee (1977) were

deployed near the ^{222}Rn time series station in areas of active groundwater seepage (Maro Cliff and Cantarrijan Beach) during July of 2016. Four seepage meters were deployed in Maro Cliff and nine in Cantarrijan Beach to obtain a representative evaluation of the seepage area. These were made of a bottomless 60 L plastic drum with an area of 0.12 m^2 with a plastic bag attached to a two-way valve (Isiorho and Meyer, 1999; Schincariol and McNeil, 2002; Rosenberry, 2008). The seepage meters were submerged and slowly inserted in the sediments leaving 2 cm of space between the sediments and the drum interior top. The seepage meter was positioned inclined in order to leave the valve side slightly higher allowing any gas to escape before plastic bag attachment; the water volume entering the plastic bag and time elapsed were then recorded (Lee, 1977). Seepage velocities (SGD , cm d^{-1}) were calculated using Eq. 11 modified from Lee (1977):

$$\text{SGD} = \frac{68.79 \times V}{t} \quad (11)$$

where V is volume of water entering the plastic bag (mL); t is the time elapsed (s), and 68.79 is a unit conversion factor specific to the 0.12 m^2 flow area to obtain seepage velocity in cm d^{-1} . Groundwater discharge ($\text{m}^3 \text{ d}^{-1}$) was calculated using Eq. 8.

3.3 Groundwater chemistry, stable isotopic composition, and NO_3^- fluxes

During July and December of 2015, and in July of 2016 water stable isotopes ($\delta^2\text{H}$ and $\delta^{18}\text{O}$), NO_3^- and SO_4^{2-} were measured in all points of groundwater discharge to the sea, Maro Spring, and a well located in the conglomerate section (Nerja Cave) (Fig. 1). A total of 23 samples were collected in Maro Cliff and Cantarrijan Beach (GW-Well) ($n = 4$), all subaerial coastal springs (Doncellas, Barranco Maro, Huerto Romero, Maro Beach, and Alberquillas, $n = 14$), and groundwater-fed creeks (Maro Creek and Miel Creek, $n = 5$) during all sampling campaigns.

Water samples were collected for analysis in 150 mL bottles and stored at 4°C until measurement, diluted to 1 mS cm⁻¹, and filtered before analysis. NO₃⁻ and SO₄²⁻ concentrations were analyzed at the CEHIUMA (Center of Hydrogeology of the University of Malaga) laboratory via ionic chromatography (Metrohm 881 Compact IC Pro) with an accuracy of ± 2%. Water stable isotopes (δ²H and δ¹⁸O) were also analyzed at the CEHIUMA using a Laser Cavity Ring-Down Spectrometer (Picarro CRDS L2120-i) with accuracies of ± 1‰ and ± 0.1‰ for δ²H and δ¹⁸O respectively. Isotopic ratios were calculated using the Vienna Standard Mean Ocean Water (VSMOW, in ‰). Nitrate fluxes ($F_{NO_3^-}$, mmol d⁻¹) to the sea were calculated by multiplying NO₃⁻ concentrations at each point of discharge during each sampling campaign by corresponding measured groundwater flux (Eq. 12):

$$F_{NO_3^-} = F_{SGD} \times [NO_3^-] \quad (12)$$

where $[NO_3^-]$ represents nitrate concentrations (mmol m⁻³), and F_{SGD} is the groundwater flux (m³ d⁻¹)

4 Results

4.1 Detecting submarine spring discharge using ²²⁴Ra and salinity

4.1.1 ²²⁴Ra activities in seawater and groundwater

During the ²²⁴Ra sampling campaign in September of 2010, the average ²²⁴Ra concentrations in surface waters along the study area was 17 ± 2 dpm m⁻³ (n=30) ranging from 56 ± 4 dpm m⁻³ to 8 ± 1 dpm m⁻³ (Fig. 3; Supplementary material Table A.1). In general, ²²⁴Ra values along the schist and karst sections of the study area were lower compared to other Mediterranean regions (e.g. Moore, 2006; García-Solsona et al., 2010; Rodellas et al., 2014). However, two distinctive ²²⁴Ra-high anomalies in coastal surface waters were identified during

this survey; these were associated with water inputs with average salinity of 0.8 from the groundwater-fed Miel Creek ($56 \pm 4 \text{ dpm m}^{-3}$), and the three clustered submarine springs discharging from Cantarrijan Caves ($51 \pm 4 \text{ dpm m}^{-3}$) located in the Cantarrijan area (Fig. 3). Miel Creek (average salinity anomaly = 0.3), which flows through the marble formation of Alberquillas Aquifer Unit for a total length of approximately 5 km, has a perennial flow, a firm indication that it is fed by groundwater (Fig. 3). Indeed, a set of springs located predominantly in the southernmost section of the Creek at the marble-schist contact have been observed to maintain the constant creek flow regime all year long. The second peak of ^{224}Ra was located right above the three submarine springs (Cantarrijan Caves) near Cantarrijan Beach. Average ^{224}Ra values significantly higher ($20 \pm 7 \text{ dpm m}^{-3}$) than offshore background activity ($8 \pm 1 \text{ dpm m}^{-3}$) were detected also along the karst section from Cantarrijan to Cerro Gordo, where Alberquillas Aquifer Unit is directly in contact with the sea (Fig. 3).

Figure 3: Interpolated ^{224}Ra activity concentrations in September of 2010 along the schist and karst sections. Two areas of high ^{224}Ra in coastal waters were identified in the schist section near groundwater-fed Miel Creek ($56 \pm 4 \text{ dpm m}^{-3}$), and the three clustered submarine springs discharging from Cantarrijan Caves ($51 \pm 4 \text{ dpm m}^{-3}$) located in the Cantarrijan area (karst section).

Radium-224 in groundwater in Cantarrijan Beach varied from $660 \pm 30 \text{ dpm m}^{-3}$ (salinity anomaly = 1.6) in a shallow well (GW-Well, Supplementary material Table A.1) to $5500 \pm 430 \text{ dpm m}^{-3}$ (salinity = 31.1) in five piezometers installed on the shore (GW-Pz-1-5, Supplementary material Table A.1). Activity of ^{224}Ra in groundwater collected from two wells in the karstic marble (GW-CG-1 and GW-CG-2, Supplementary material Table A.1) showed similar activities,

1260 $\pm$ 90 dpm m⁻³ and 1020 $\pm$ 80 dpm m⁻³ with salinities of 2.2 and 0.6 respectively. The variation of ²²⁴Ra concentrations in GW-Well and Pz-1-5 (Fig 5c) can be explained by the seawater recirculation in the beach sediments. Radium concentration in fresh waters is very low due to adsorption onto particles. However, in pore water with higher ionic strength (i.e. brackish and salt water) radium desorbs due to cation exchange. This process increases dissolved ²²⁴Ra concentration (Webster et al., 1995).

4.1.2 Salinity anomalies

The average salinity in coastal waters of the study site during continuous measurements in September of 2010 was 36.4 $\pm$ 0.2, during May of 2015 was 36.6 $\pm$ 4.0, in July 2015 was 37.2 $\pm$ 1.2, and in December of 2015 was 34.5 $\pm$ 1.7. A negative salinity anomaly of -1.2 to -1.7 was observed during all sampling campaigns in the conglomerate section in the vicinity of multiple coastal springs (Doncellas, Barranco Maro, Huerto Romero, and Maro Beach) and two groundwater-fed creeks (Caleta Creek, and Tierras Nuevas Creek) (Fig. 4). However, in the schist section where Alberquillas coastal spring enters the sea, salinity was generally similar to the average throughout the coastline with a value of 36.3 in September of 2010, 37.1 in May of 2015, 37.1 in July of 2015, and 34.4 in December of 2015. Similarly, small salinity variation (Fig. 4) associated with high ²²⁴Ra (Fig. 3) was observed near the outlet of the groundwater-fed Miel Creek.

Figure 4: Salinity anomaly map showing combined results from May, July, and December of 2015. Two areas of negative salinity anomalies were found in the conglomerate (salinity anomaly = -1.2 to -1.7) and karst (salinity anomaly = -0.3 to -1.0) sections almost perfectly aligned with their delineated extent.

In the karst section (Fig. 1), where the karstic marble formation is in contact with the sea, negative salinity anomalies (-0.3 to -1.0) coincided with previously observed high ^{224}Ra concentrations in coastal waters near the Palomas and Sifon Caves submarine springs. The largest salinity anomaly (-1.0) in the karst section was found in Cantarrijan Beach, which could be related to Cantarrijan Caves springs. However, the lowest values are distributed along the beach area, slightly deviated to the East off Cantarrijan Caves, where groundwater seepage through marine sediments can, therefore, also be occurring.

4.2 Evaluating submarine spring discharge using ^{224}Ra and salinity

4.2.1 ^{224}Ra mass balance

To assess groundwater discharge in the areas of high ^{224}Ra ($12 - 51 \text{ dpm m}^{-3}$) and negative salinity anomalies (-0.3 to -1.0), i.e. the areas of Cantarrijan Caves, Palomas Cave, and Sifon Cave submarine springs (Figs. 2 and 3), we used a ^{224}Ra mass balance following Moore (1996) and Charette et al. (2001; Eq.1). The main assumption in this approach is that the ^{224}Ra excess in the karst section is considered to be originated solely by submarine springs.

SGD through Cantarrijan Caves was quantified using the ^{224}Ra coastal water end-member measured in SW-6, SW-7, SW-13 and SW-24 ($Ra_{sw} = 25 \pm 2 \text{ dpm m}^{-3}$, $n = 4$), where SW-7 was collected at the depth of discharge (8 m). Average offshore background activity ($8 \pm 1 \text{ dpm m}^{-3}$) measured in SW-23, SW-27, SW-29, and SW-30 was used as the open water end-member (Ra_{ow}) (Supplementary material Table A.1). Groundwater samples collected from well GW-CG-1 (Fig.1), which is the closest well to the submarine springs and is representative of the marble aquifer formation, was used as the groundwater end-member ($1260 \pm 90 \text{ dpm m}^{-3}$, salinity = 2.2). Following the same approach, SGD was also evaluated in the area of Palomas Cave using SW-SW-20, SW-21, and SW-25 ($Ra_{sw} = 18 \pm 2 \text{ dpm m}^{-3}$, $n = 3$), where SW-21 was collected at 15 m

depth of discharge. In Sifon Cave samples SW-14, SW-22, and SW-26 were used as the coastal water end-member. The same open water (Ra_{ow}) and groundwater (Ra_{SGD}) end-members were used: 1260 ± 90 dpm m^{-3} and 8 ± 1 dpm m^{-3} respectively (Fig. 3; Table 1).

The estimated groundwater fluxes (F_{SGD}) through Cantarrijan Caves was $4.7 \pm 0.5 \times 10^3$ m^3 d^{-1} , at Palomas cave was $4.3 \pm 0.5 \times 10^3$ m^3 d^{-1} , and for Sifon Cave was $3.7 \pm 0.4 \times 10^3$ m^3 d^{-1} . This represents a total flux of $12.8 \pm 1.4 \times 10^3$ m^3 d^{-1} via submarine springs, where reported errors are based on analytical uncertainties of ^{224}Ra measurements.

4.2.2 Salinity mass balance

The salinity anomaly created by the Cantarrijan, Palomas, and Sifon Caves in the karst section (Fig. 4, Table 1) allowed us to construct individual mas-balances at each location and calculate SGD independently of the ^{224}Ra approach. Considering that the salinity of groundwater discharge of these springs is the same value of the endmember used for the ^{224}Ra method (Table 1), and applying Eq. 2 we calculated a total groundwater flux of $0.8 \pm 0.1 \times 10^3$ m^3 d^{-1} in Cantarrijan Caves, $0.9 \pm 0.1 \times 10^3$ m^3 d^{-1} in Palomas Cave, and $0.5 \pm 0.1 \times 10^3$ m^3 d^{-1} through Sifon Cave; representing a total of $2.3 \pm 0.2 \times 10^3$ m^3 d^{-1} .

4.3 Assessing diffuse groundwater seepage using a ^{222}Rn mass balance and seepage meter measurements

4.3.1 ^{222}Rn distribution in seawater

High ^{222}Rn concentrations were measured in two distinct areas in the Maro Cliff area (conglomerate section) and Cantarrijan Beach (karst section) with maximum concentrations of $44 \pm 3 \times 10^3$ dpm m^{-3} and $30 \pm 2 \times 10^3$ dpm m^{-3} respectively (Fig. 5). In general, along the conglomerate section, ^{222}Rn activities were within background levels ($1.9 \pm 0.6 \times 10^3$ dpm m^{-3}) with the mentioned exception of a cove in the Maro Cliff area where the travertine formation is

in contact with the sea. In this location, a 15-m travertine cliff ends in coarse seabed sand through which groundwater seepage was identified underlying a 1.5-m water column. In the karst section, high ^{222}Rn was detected only along the Cantarrijan Beach where a steep ravine, formed in the marble formation, ends in a big opening comprised of coarse sand, pebbles, cobbles, and even boulders suggesting flash flooding events in the ravine after significant precipitations.

Figure 5: Radon-222 distribution map based on surveys during July and December of 2015, and July of 2016. Two radon peaks were in found in Maro Cliff (conglomerate section) and Cantarrijan Beach (karst section) with maximum concentrations of $44 \pm 3 \times 10^3 \text{ dpm m}^{-3}$ and $30 \pm 2 \times 10^3 \text{ dpm m}^{-3}$ respectively.

4.3.2 Groundwater discharge assessments in the conglomerate section (Maro Cliff)

Diffuse groundwater seepage was identified in this area during all ^{222}Rn surveys (July and December of 2015, and July of 2016) suggesting the seepage is maintained by base groundwater flow (Fig. 6a). We calculated that ^{222}Rn contribution from the waterfall (i.e., $F_{\text{Waterfall}}$) was on average $16 \pm 6 \text{ dpm m}^{-2} \text{ d}^{-1}$ (Table 2). To account for the production of ^{222}Rn from ^{226}Ra dissolved in coastal waters (C_{Ra}), we used the averaged concentration ($280 \pm 50 \text{ dpm m}^{-3}$, $n = 3$) measured in September of 2006 ($306 \pm 40 \text{ dpm m}^{-3}$, $n = 1$) and July of 2016 ($260 \pm 50 \text{ dpm m}^{-3}$, $n = 2$) at the time series station (Table 2, Fig. 6b). Atmospheric evasion (F_{Atm}) was calculated using Eq 8 except in July of 2015, when wind speed was much higher (8 m s^{-1}) and we used Eq. 6 instead. Diffusive flux of ^{222}Rn from seabed sediments (F_{Diff}) was $619 \pm 57 \text{ dpm m}^{-2} \text{ d}^{-1}$ accounting for only 0.2 – 0.5% of total ^{222}Rn fluxes (Fig. 7). As one would expect in coastal

waters with little protection against wind and waves, mixing losses in this study represent the main ^{222}Rn loss in the model (Fig. 7).

Figure 6: (a) Groundwater seepage velocity averaging results from radon mass balance and seepage meters in areas of diffuse seepage (Maro Cliff and Cantarrijan Beach). Radon distribution in (b) Maro Cliff (conglomerate section) and (c) Cantarrijan Beach (karst section) where cylinder symbols represent seepage meter locations and the star radon time series stations.

The ^{222}Rn concentrations in groundwater end-members (Rn_{SGD}) were $350 \pm 50 \times 10^3$ dpm m^{-3} , $440 \pm 60 \times 10^3$ dpm m^{-3} , and $320 \pm 30 \times 10^3$ dpm m^{-3} during July, December of 2015, and July of 2016 respectively, with an average value of $370 \pm 50 \times 10^3$ dpm m^{-3} . Based on these estimates (Table 2) and applying Eq. 4, we obtained average seepage velocities of 39 ± 10 cm d^{-1} ($n = 43$) in July 2015, 40 ± 11 cm d^{-1} ($n = 78$) in December of 2015, and 38 ± 10 cm d^{-1} ($n = 90$) during July of 2016. Reported SGD uncertainties are calculated based on ^{222}Rn variations from all samples collected in the area to obtain the groundwater end-members (Rn_{SGD}) (Burnett et al., 2007); which ranged from $320 \pm 30 \times 10^3$ dpm m^{-3} to $690 \pm 50 \times 10^3$ dpm m^{-3} ($n = 8$) during this study.

Utilizing Eq. 8 we estimated total groundwater fluxes based on the ^{222}Rn box model to be $3.0 \pm 0.8 \times 10^3$ m^3 d^{-1} during July of 2015, $3.1 \pm 0.8 \times 10^3$ m^3 d^{-1} in December of 2015, and $2.9 \pm 0.7 \times 10^3$ m^3 d^{-1} in July of 2016 (Table 2). Using Eq. 11 an average seepage velocity of 28 ± 6 cm d^{-1} (Table 3) was calculated. This assessment is in good agreement with the average ^{222}Rn -based value of 38 ± 10 cm d^{-1} . Using Eq. 8 and a seepage area of 7.7×10^3 m^2 based on the radon concentration (Fig. 6b), we calculated a groundwater flux of $2.1 \pm 0.4 \times 10^3$ m^3 d^{-1} in July of 2016 (Table 3).

4.3.3 Groundwater fluxes in the karst section (Cantarrijan Beach)

Multiple radon surveys in this area (July and December of 2015, and July of 2016) indicated a strong seasonality in seawater ^{222}Rn concentrations, with an average of $75 \pm 3 \times 10^3 \text{ dpm m}^{-3}$ in December and $11 \pm 2 \times 10^3 \text{ dpm m}^{-3}$ in July, suggesting higher SGD during the wet period. The average ^{226}Ra concentration (C_{Ra}) was $170 \pm 40 \text{ dpm m}^{-3}$ measured in September of 2006 ($169 \pm 30 \text{ dpm m}^{-3}$, $n = 1$) and July of 2016 ($170 \pm 40 \text{ dpm m}^{-3}$, $n = 2$) (Table 2). The variation of the groundwater ^{222}Rn end-member ($240 \pm 60 \times 10^3 \text{ dpm m}^{-3}$ to $350 \pm 40 \times 10^3 \text{ dpm m}^{-3}$, $n = 6$) was used to calculate the final groundwater discharge flux uncertainties. Seepage velocities in December and July were on average $52 \pm 8 \text{ cm d}^{-1}$ ($n = 61$) and $22 \pm 3 \text{ cm d}^{-1}$ ($n = 115$) respectively (Table 3).

We found that groundwater seepage occurs only in the westernmost sector at the end of the Cantarrijan Ravine (Fig. 6c). Seepage velocities, determined from all seepage meters deployed along the beach, show that groundwater seepage ceases exactly at the location where seepage meter SM-4 was deployed (Fig. 6c). We used this as a criterion to define the seepage face and decided to use the ^{222}Rn contour line of $6 \pm 1 \times 10^3 \text{ dpm m}^{-3}$ to calculate the seepage area, and averaged SM-1-4 to determine a seepage velocity of $23 \pm 7 \text{ cm d}^{-1}$. Using the ^{222}Rn method we found that the total diffuse groundwater seepage in the Cantarrijan Beach area ranged from $2.3 \pm 0.3 \times 10^3 \text{ m}^3 \text{ d}^{-1}$ during the wet period to $0.9 \pm 0.1 \times 10^3 \text{ m}^3 \text{ d}^{-1}$ during dry conditions; whereas seepage meter measurements resulted in $0.9 \pm 0.2 \times 10^3 \text{ m}^3 \text{ d}^{-1}$.

Figure 7: Radon fluxes result of each component of the mass balance box model during all sampling campaigns in Maro Cliff (conglomerate section) and Cantarrijan Beach (karst section). The largest tracer losses occurred via mixing due to the high exposure of both areas to waves and currents.

Greater difference in SGD-²²²Rn fluxes was found between wet periods (December) and dry periods (July) in Cantarrijan Beach compared to Maro Cliff.

During all sampling campaigns, the groundwater sampled from the shallow well at Cantarrijan Beach (GW-Well, Fig.1) always had salinity values of 1.6 – 3.2. During September of 2010, salinities of 6.6 – 31.1 were also observed in pore water samples collected in all five piezometers installed on the beach (GW-PZ-1-5, Fig 1). Based on the salinity mixing model (using Eqs. 9 and 10) we calculated that the fresh fraction of SGD at this site was 48% of the total groundwater seepage. Therefore, when constructing the Sierra Almirajara-Alberquillas Aquifer freshwater water budget for July of 2016, only $0.4 \pm 0.1 \times 10^3 \text{ m}^3 \text{ d}^{-1}$ (representative of the 48% freshwater component) should be taken into account.

4.4 Groundwater contribution from coastal springs and groundwater-fed creeks

Groundwater discharge to the sea during dry conditions calculated using flowmeter measurements in July of 2016 from coastal spring Huerto Romero was $37 \pm 3 \text{ m}^3 \text{ d}^{-1}$, from Maro Beach was $26 \pm 2 \text{ m}^3 \text{ d}^{-1}$, from Barranco Maro was $17 \pm 1 \text{ m}^3 \text{ d}^{-1}$, from Doncellas was $460 \pm 40 \text{ m}^3 \text{ d}^{-1}$, and from Alberquillas was $1060 \pm 90 \text{ m}^3 \text{ d}^{-1}$ (Supplementary material Table A.2). The discharge from groundwater-fed creek Miel Creek was $1230 \pm 110 \text{ m}^3 \text{ d}^{-1}$, from Caleta Creek $160 \pm 10 \text{ m}^3 \text{ d}^{-1}$, and from Tierras Nuevas Creek was $110 \pm 10 \text{ m}^3 \text{ d}^{-1}$. The total discharge from all creeks was $3100 \pm 280 \text{ m}^3 \text{ d}^{-1}$; which represents 33% of the total groundwater discharge in the study area.

In December of 2016, during high flow conditions, discharge from coastal springs Huerto Romero was $100 \pm 9 \text{ m}^3 \text{ d}^{-1}$, from Maro Beach was $43 \pm 4 \text{ m}^3 \text{ d}^{-1}$, from Barranco Maro was $69 \pm 6 \text{ m}^3 \text{ d}^{-1}$, from Doncellas was $530 \pm 50 \text{ m}^3 \text{ d}^{-1}$, and from Alberquillas was $1590 \pm 140 \text{ m}^3 \text{ d}^{-1}$. Discharge via groundwater-fed Miel Creek was $1820 \pm 160 \text{ m}^3 \text{ d}^{-1}$, from Caleta Creek was $220 \pm$

20 m³ d⁻¹, and from Tierras Nuevas Creek was 190 ± 20 m³ d⁻¹; which constitutes 4580 ± 60 m³ d⁻¹ or 37% of the total discharge in the study area (Supplementary material Table A.2).

4.5 Groundwater isotopic composition, water chemistry, and nitrate fluxes

Isotopic values are widely scattered along a linear trend (Local Groundwater Line, LGL) with a slope of 6.06, with averages of -42‰ and -7.1‰ for δ²H and δ¹⁸O respectively (Figs. 8a and 8b). All samples fall between the Global Meteoric Water Line (GMWL; Craig, 1961) and the Western Mediterranean Meteoric Water Line (WMMWL; Gat and Garmi, 1970), samples collected in or derived from Maro Spring are situated slightly above the WMMWL. Deuterium values ranged from -33 ± 1‰ to -46 ± 1‰, while δ¹⁸O were between -5.6 ± 0.1‰ and -7.8 ± 0.1‰ (Supplementary material Table A.2). We observed that groundwater collected from Maro Spring (conglomerate section) has the lightest isotopic signature of -46‰ and -7.7‰ for δ²H and δ¹⁸O respectively. Samples collected in the conglomerate section from coastal springs Barranco Maro, Huerto Romero, Maro Beach, and groundwater-fed Maro Creek showed values that ranged from -45 and -7.6 to -43‰ and -7.2‰. At the point of seepage discharge in the sea, Maro Cliff showed slightly higher values of -44‰ and -7.4‰ for δ²H and δ¹⁸O. Coastal springs Doncellas, Alberquillas, and groundwater-fed Miel Creek all located in the schist section, are grouped together with Nerja Cave (conglomerate section), showing average values of -33‰ and -5.5‰ for δ²H and δ¹⁸O. Samples collected from GW-Well (Cantarrijan Beach), have the highest values in the study area with averages of -22‰ and -3.8‰ for δ²H and δ¹⁸O.

Figure 8: (a) Isotopic composition (δ¹⁸O, δ²H) of water samples collected during all sampling campaigns. Local Groundwater Line (LGL) represents the linear trend based on all groundwater samples collected in the study area. Global Meteoric Water Line (GMWL) is based on Craig, (1961)

and the Western Mediterranean Meteoric Water Line (WMMWL) on Gat and Garmi, (1970). White color represents points of discharge in conglomerate and breccia lithology, while light grey are in travertine (conglomerate section); dark grey shows points in schist (schist section); and black color show locations in karstic marble (karst section). Maro Spring and Nerja Cave well (not points of discharge to the sea) are represented with a black and white star respectively. Water samples collected at each section (conglomerate section, schist section, and karst section) are grouped in dashed squares. (b) Isotopic composition of samples collected from points of discharge from the travertine formation in the conglomerate section. The two groundwater end-members (Maro Spring and irrigation waters) are circled, while diffuse seepage in Maro Cliff is represented with squares.

Groundwater sulphate (SO_4^{2-}) concentrations ranged from $500 \pm 10 \text{ mmol m}^{-3}$ in Alberquillas coastal spring to $3220 \pm 64 \text{ mmol m}^{-3}$ in Cantarrijan Beach ($n = 23$) (Supplementary material Table A.2). Samples collected in the conglomerate section from coastal springs Doncellas, Barranco Maro, Huerto Romero, Maro Beach; groundwater-fed Maro Creek, and diffuse seepage in Maro Cliff had similar SO_4^{2-} concentrations ranging between 1500 and 3000 mmol m^{-3} . All samples (including Maro Spring) collected from Sierra Almijara-Alberquillas Aquifer in this area fall within a SO_4^{2-} concentration range of 1700 – 2600 mmol m^{-3} . Miel Creek and coastal spring Alberquillas (schist section) showed lower values ranging from 500 ± 10 to $710 \pm 14 \text{ mmol m}^{-3}$. Water collected in Cantarrijan Beach had the highest concentration in the study area, with an average of $3030 \pm 60 \text{ mmol m}^{-3}$ (Supplementary material Table A.2).

Nitrate (NO_3^-) concentrations were highest in coastal springs of the conglomerate section including Doncellas, Barranco Maro, Huerto Romero, and Maro Beach with an average of $446 \pm$

50 mmol m⁻³ (n = 6). Water samples that were directly derived from Maro Spring (Maro spring, Maro Creek) and did not experience infiltration (i.e. had no fertilizer added), showed NO₃⁻ concentration of 5 – 21 mmol m⁻³. NO₃⁻ concentrations in diffuse groundwater seepage in Maro Cliff were consistently near 130 ± 3 mmol m⁻³ (n = 2). Samples collected in the schist section from groundwater-fed Miel Creek and coastal spring Alberquillas, and in the karst section from Cantarrijan Beach, showed levels of NO₃⁻ ranging from 55 mmol m⁻³ in Miel Creek to 168 mmol m⁻³ in Cantarrijan Beach (n = 5) (Supplementary material Table A.2).

Nitrate fluxes were unevenly distributed in the three sections of the study site (Table 4). The combination of high NO₃⁻ in coastal springs and high flow groundwater seepage results in NO₃⁻ fluxes in the conglomerate section of 550 ± 140 mol d⁻¹ and 730 ± 190 mol d⁻¹. During this study, NO₃⁻ fluxes in the schist and karst section together were 150 ± 20 mol d⁻¹ during dry and 250 ± 40 mol d⁻¹ during wet periods (Table 4).

5 Discussion

5.1 Method selection and assessment of each form of groundwater discharge to the sea

Submarine springs: Quantifying submarine springs discharge in the karst section was found to be the most difficult part of this study. None of the data collected during the three ²²²Rn boat surveys along the coastline showed tracer anomalies in the areas of submarine spring discharge (Fig. 5). However, we were able to detect ²²⁴Ra and salinity anomalies produced by the three submarine springs discharging from Cantarrijan, Palomas, and Sifon Caves (Fig. 3 and 4). Concentrations of ²²⁴Ra were on average four times higher (20 ± 7 dpm m⁻³, n = 10) compared to offshore waters (8 ± 1 dpm m⁻³, n = 4) in locations where no ²²²Rn signal was detected.

Considering that ^{224}Ra and ^{222}Rn have similar half-lives and experience similar mixing, we hypothesize that the lower ^{222}Rn concentrations in coastal waters of the karst section must be due to degassing. Similar effects on dissolved ^{222}Rn and ^{224}Ra have been observed in coastal waters by Dulaiova and Burnett (2006) and Stieglitz et al. (2010). As found in this study site, both studies showed a strong correlation between ^{222}Rn concentration and salinity or ^{222}Rn and ^{224}Ra , trends that are consistent with a ^{222}Rn deficiency due to atmospheric evasion (Stieglitz et al, 2010). Furthermore, when combining the ^{222}Rn concentration data with salinity anomalies from all boat surveys along the entire shoreline, we observe that ^{222}Rn concentrations decrease at a faster rate than salinity when closer to the groundwater source (Fig. 9a, b). If wind conditions are constant during the surveys (which there were), following the 1st Fick's Law, degassing due to molecular diffusion through the water-atmosphere interphase must be enhanced when seawater ^{222}Rn concentration is higher (the concentration gradient is higher). Thus, this effect is most likely created because the water column-atmosphere concentration gradient in areas close to the groundwater source is at its highest, favoring atmospheric evasion.

Figure 9: Mixing plots of ^{224}Ra (a) and ^{222}Rn versus salinity (b) showing best fit linear and exponential mixing lines, respectively, during surface water surveys along the coastline in September of 2010, July and December of 2015.

Based on these findings, we concluded that ^{224}Ra (Eq. 1) and salinity (Eq. 2) mass balances are the two methods better suited to evaluate groundwater discharge from submarine springs of the ones utilized in this study. However, we found a significant difference between the springs discharge assessments obtained using these two tracers; the flux based on the ^{224}Ra mass balance was $12.8 \pm 1.4 \times 10^3 \text{ m}^3 \text{ d}^{-1}$, whereas using the salinity mass balance we calculated a

discharge of $2.3 \pm 0.2 \times 10^3 \text{ m}^3 \text{ d}^{-1}$. We suggest that the difference could be explained by selection of the end-member in the mixing model, which has been previously described by others as a factor in correct determination of groundwater discharge (e.g. Peterson et al., 2008; Moore, 1996; Cerdà-Domènech et al., 2017). A critical component in any tracer study is the selection of a representative groundwater end-member (Ra_{SGD} and Sal_{SGD}) collected at the point of discharge.

All submarine springs described here are located in submarine caves (Cantarrijan, Palomas, and Sifon Caves) with vents parallel to the surface (i.e. horizontal geometry) at depths of 8 – 15 m below sea level. The springs discharge occurs parallel to the land surface at about 5 – 10 m landward from the caves entrance. SCUBA diving to the springs vents for representative groundwater/spring water end-member was challenging, thus the presented estimates of spring discharge are based on groundwater from the closest located well (GW-CG-1, Fig. 1) with a ^{224}Ra concentration of $1260 \pm 90 \text{ dpm m}^{-3}$ and salinity of 2.2 ± 0.1 .

Because springs conduits are subject to seawater intrusion, we suggest that the salinity of the discharging spring water could be slightly to significantly higher than groundwater salinity sampled from the inland well (GW-CG-1) which we used as the groundwater end-member (Ra_{SGD} and Sal_{SGD}). While in fresh water, radium is mostly attached to particles and its dissolved concentration is very low, in brackish spring water radium would be mostly dissolved and we would have observed higher ^{224}Ra in the end-member waters (Burnett et al., 2006; Cerdà-Domènech et al., 2017). Based on the correlation between salinity and ^{224}Ra desorption, a salinity increase of 5 to the groundwater end-member (GW-CG-1) would produce an extrapolated ^{224}Ra increase of 60 dpm m^{-3} , resulting in a decrease spring flux of about 65%, which is closer to the salinity mass balance estimation. A salinity of 5 in submarine springs seems reasonable as it is similar to those found by García-Solsona et al. (2010) in a coastal karst

aquifer in eastern Spain, where annual average salinity of outflowing brackish submarine springs was 6.8. Furthermore, in well GW-CG-1 located 500 m inland from the submarine springs in the karstic marble, a salinity value of 2.2 was measured, also indicating that a value of 5 was plausible.

The salinity mass balance method estimates only the fresh water fraction of the spring discharge. In this way, the difference in discharge estimation using a ^{224}Ra and a salinity mass balance is found because the ^{224}Ra method estimates the total (brackish) discharge, while the salinity method accounts only for the fresh portion. Therefore, only the spring discharge based on the salinity model should be used in the water budget of Sierra Almirajara-Alberquillas Aquifer.

Diffuse groundwater seepage through seabed sediments: In contrast to the case of submarine spring discharge, we found that groundwater seepage through seabed sediments (Maro Cliff, conglomerate section; and Cantarrijan Beach, karst section) was most adequately detectable using ^{222}Rn as a tracer and direct measurements (i.e. seepage meters). The observed ^{222}Rn concentrations in receiving surface waters were as high as $44 \pm 3 \times 10^3 \text{ dpm m}^{-3}$ at both groundwater seepage areas, i.e. Maro Cliff and Cantarrijan Beach (Fig. 4).

Although, we also observed high ^{224}Ra concentrations in samples collected near Cantarrijan Beach (Fig. 3), these were associated with nearby discharge from the Cantarrijan Caves submarine spring (Fig. 3, sampling points SW-6, SW-7, and SW-13). Indeed, during one of the dry period sampling events (July of 2016), we did not detect any ^{224}Rn in coastal waters of Cantarrijan Beach giving us confidence that the previously observed signals (September 2010) were from the springs and not from the diffuse seepage. For the same reason, salinity could not be used as a tracer in either of the seepage areas (Maro Cliff and Cantarrijan Beach) because

salinity anomalies were also created mostly by nearby coastal and submarine springs respectively, overwhelming the salinity signal that is only due to diffuse seepage.

In this complex scenario, ^{222}Rn was the only groundwater tracer able to uniquely identify diffuse groundwater seepage to the sea and a ^{222}Rn mass balance was thus used to quantify groundwater seepage fluxes. Based on this mass balance in the Maro Cliff area, we calculated a discharge of $2.9 \pm 0.8 \times 10^3 \text{ m}^3 \text{ d}^{-1}$ (Table 2), whereas using seepage meter deployments ($n = 4$) the discharge was $2.1 \pm 0.4 \times 10^3 \text{ m}^3 \text{ d}^{-1}$. In the Cantarrijan Beach we found very similar seepage flux estimates using the ^{222}Rn approach ($0.9 \pm 0.1 \times 10^3 \text{ m}^3 \text{ d}^{-1}$) and using seepage meters ($0.8 \pm 0.2 \times 10^3 \text{ m}^3 \text{ d}^{-1}$) with a total of 9 deployments (Table 2). While the two methods agree very well, we recommend using the ^{222}Rn method over seepage meters. The main advantages of the ^{222}Rn technique are (1) fully automatic data collection with very little field efforts, (2) temporal and spatially integrated SGD estimates, which allow capturing small hydraulic conductivity variations over large areas of diffuse seepage (Burnett et al., 2001).

Subaerial forms of groundwater discharge to the sea (coastal springs and groundwater-fed creeks): Coastal springs, and creeks that are primarily groundwater sustained, were only present at the conglomerate and schist sections of the study site that are comprised of conglomerate and schist, where permeabilities are lower than in the marble formation (karst section). During boat surveys ^{222}Rn activity levels in coastal waters of these two sections were always within background offshore values ($1.0 \pm 0.2 \times 10^3 \text{ dpm m}^{-3}$, Fig. 5) even at the points of coastal springs and groundwater-fed creeks discharge that were visually identified. We attributed the observed low ^{222}Rn concentrations to degassing and radioactive decay during groundwater transit from land to the ocean. For instance, ^{222}Rn concentration at the point of the groundwater-fed Maro Creek origin (Maro Spring, $250 \pm 90 \text{ dpm m}^{-3}$) was significantly higher than at the

point of the Creek entrance to the sea (Maro Creek 3, $16 \pm 7 \text{ dpm m}^{-3}$) (Fig. 1; Supplementary material Table A.2). However, we were able to find groundwater signature of the Miel Creek and the Alberquillas coastal spring in coastal waters of the schist section using ^{224}Ra concentration anomalies; radium was $56 \pm 4 \text{ dpm m}^{-3}$ and $12 \pm 2 \text{ dpm m}^{-3}$ respectively at their point of entry to the sea (Fig. 1). While coastal springs were easily located visually, additional field efforts were usually required to determine whether the creeks were solely fed by groundwater inputs from the karst aquifer in order to be considered (or not) in the total groundwater budget of Sierra Almijara-Alberquillas Aquifer.

Total groundwater discharge to Maro-Cerro Gordo coastal area: Combining all groundwater fluxes to the sea in Maro-Cerro Gordo, we estimate a daily groundwater discharge that ranged between $9 \pm 2 \times 10^3 \text{ m}^3 \text{ d}^{-1}$ during dry periods and $12 \pm 3 \times 10^3 \text{ m}^3 \text{ d}^{-1}$ during wet periods, with an average of $11 \pm 3 \times 10^3 \text{ m}^3 \text{ d}^{-1}$. This combined discharge is composed of: $3.6 - 4.0 \times 10^3 \text{ m}^3 \text{ d}^{-1}$ in the conglomerate section, $2.4 - 3.6 \times 10^3 \text{ m}^3 \text{ d}^{-1}$ in the schist section, and $3.3 - 4.7 \times 10^3 \text{ m}^3 \text{ d}^{-1}$ in the karst section (Supplementary material Table A.2). As described above, differences in the geologic settings in each section, have defined the form of groundwater flow to the sea (Fig. 10, Table 4).

Figure 10: Total groundwater discharge (TGD) in the study area divided in forms of discharge (GS: groundwater diffuse seepage, CS: coastal springs, GC: groundwater-fed creeks, SS: submarine springs), showing maximum and minimum flux during wet and dry periods.

In the conglomerate section, most of the groundwater flow takes place preferentially through the travertine formation as groundwater seepage and it is 25 - 31% of the total discharge in the study area, whereas small coastal springs dispersed along the section contribute to 5 - 6%,

and groundwater-fed creeks for 1 – 2%. The ubiquitous presence of a schist formation in the schist section impedes direct submarine flow and groundwater discharge converges in two points: groundwater-fed Miel Creek, and Alberquillas coastal spring which account for 25 – 30% of the total discharge. In the karst section, where Sierra Almirajara-Alberquillas Aquifer is in direct connection with the sea, SGD takes place as groundwater seepage through marine sediments in Cantarrijan Beach assessed to account for 10 - 18%. Karstic submarine springs in Cantarrijan Caves, Palomas Cave, and Sifon Cave represent 19 - 25% of the total groundwater discharge to the sea.

5.2 Complexity of Sierra Almirajara-Alberquillas karst aquifer hydrodynamics

The large spatial variations in the different forms of groundwater discharge in this coastal karst aquifer were also reflected in the seasonal variability of discharge during contrasting periods (Fig. 2). For instance, in Maro Cliff (conglomerate section, Fig. 1) we expected higher seepage rates in December during the wet period (Fig. 2). However, the discharge estimations for the dry period (July) and the wet period (December) were statistically identical: groundwater seepage in Maro Cliff during the dry period was $2.9 \pm 0.8 \times 10^3 \text{ m}^3 \text{ d}^{-1}$ and $3.0 \pm 0.8 \times 10^3 \text{ m}^3 \text{ d}^{-1}$ during the wet period.

There are two hypotheses that attempt to explain the observed lack of seasonal variation of groundwater discharge in Maro Cliff. The first hypothesis suggests that the observed steady flow is maintained by continuous infiltration of agricultural irrigation water used by the adjacent greenhouse fields. A second hypothesis, proposed by Espejo et al. (1988) and Castillo et al. (2001) suggests that the surplus of groundwater that maintains the base flow during the dry season originates from the Sierra Almirajara-Alberquillas Aquifer. The authors propose that groundwater is transferred from the Sierra Almirajara-Alberquillas Aquifer to the coast through the

adjacent conglomerate unit and travertines near the small town of Maro. These two hydrogeologic units are indeed in immediate contact with the sea (Fig. 1). To test both hypotheses we used two common geochemical approaches.

We first differentiated between heavier isotopic ($\delta^2\text{H}$ and $\delta^{18}\text{O}$) compositions (more positive values), associated with evaporation processes or mixing with seawater (Gat, 1971). The isotopic composition of groundwater collected from Maro Spring (i.e. in the conglomerate section) showed the most negative values (-46‰, -7.7‰) on the local groundwater line (LWL) in this area (Fig. 8b). These values correspond to the composition of deep groundwater flow in Sierra Almirajara-Alberquillas Aquifer (Liñán et al., 2000). Groundwater seepage in Maro Cliff presents average isotopic values (-44‰ and -7.4‰) that are similar but slightly higher than Maro Spring, suggesting that water transfer from the marble formation is a plausible option.

To differentiate between irrigation water and water transferred from the Sierra Almirajara-Alberquillas Aquifer to the travertines, the water stable isotopes end-members have to be very different than the deep/spring groundwater which has a negative composition compared to more positive values of evaporated irrigation water. We know that the water used for irrigation is withdrawn by farmers from Maro Spring. However, once extracted and in contact with the atmosphere, the water isotopic composition changes to more positive isotopic values. We also found that the collected spring water utilized for irrigation is typically stored in holding tanks and used when needed. During this holding time and in the process of irrigation, the water experiences further evaporation, and as a result, it should result in even more positive isotopic signature such as the waters of the coastal spring Barranco Maro (up to -43 and -7.3). The isotopic signature of irrigation water is thus, very different from the original Maro Spring water, allowing us to define a two-end-member system where coastal spring Huerto Romero represents

the most evaporated irrigation water (Fig. 8b). Based on a mixing model using these end-members we found that seeping groundwater at Maro Cliff is indeed composed mostly from infiltrating irrigation water. We also found that the ratio of Maro Spring water to irrigation changes depending on the season with highest percentage (up to 82%) of irrigation water during the dry period compared to the wet period (74%).

To further confirm these finding, we utilized water quality parameters, such as sulfate (SO_4^{2-}) and nitrate (NO_3^-) concentrations, to differentiate between these two water sources. Infiltrated irrigation water should have much higher NO_3^- concentrations and constant SO_4^{2-} , whereas deep groundwater should natural concentrations of NO_3^- . Thus, NO_3^- content can be used as an indication of irrigation origin. The isotopic composition of Sierra Almijara-Alberquillas Aquifer in this area fall within a narrow SO_4^{2-} concentration range (1700 – 2600 mmol m^{-3}) (Fig. 11), being naturally high in Maro Spring groundwater (Liñán et al., 2000). When plotting SO_4^{2-} and NO_3^- concentrations in water, all water samples derived from Maro Spring before infiltration showed low NO_3^- concentration (5 – 21 mmol m^{-3}) and naturally high levels of SO_4^{2-} (Fig. 11). All samples collected from coastal springs that discharge to the sea (Doncellas, Barranco Maro, Huerto Romero, and Maro Beach coastal springs), showed levels of SO_4^{2-} typical of Sierra Almijara-Alberquillas Aquifer and high levels of NO_3^- (more than 350 mmol m^{-3}) indicating fertilizer inputs. On the other hand, samples collected at the area of seepage through seabed sediments in the Maro Cliff, showed NO_3^- concentrations (130 mmol m^{-3}) that are closer to the observed background levels of Sierra Almijara-Alberquillas groundwater representative (5 – 21 mmol m^{-3}) than to the contaminated infiltrated water (Fig. 11).

Figure 11: Groundwater ionic relationship between NO_3^- and SO_4^{2-} where groundwater samples with similar composition are grouped in dashed squares. Symbols are presented as in Fig. 8 based

on the section and lithology they are located. In the conglomerate section Maro Spring, Nerja Cave, and Maro Creek show similar SO_4^{2-} concentration with low NO_3^- , while Doncellas, Barranco Maro, Huerto Romero, and Maro Beach present NO_3^- contamination. Samples from the schist section (Miel and Alberquillas) present a distinctive signal with low NO_3^- and SO_4^{2-} concentrations. Groundwater collected in Cantarrijan Beach (karst section) shows seawater influence from saltwater recirculation in beach sediments. Arrows indicate the geochemical change before irrigation and after fertilizers application (NO_3^-), where Maro cliff (diffuse seepage) shows mixing between both groups.

Therefore, we are confident that groundwater seepage to the sea observed and quantified in Maro Cliff is mostly generated as a result of infiltrated irrigation water. We found uniform groundwater flux (independently of rainfall) in this area throughout the year (Fig. 6a) supporting this hypothesis. Irrigation occurs constantly throughout the year, and infiltration through the highly porous travertine constitutes a constant source of water that flows towards the coast and ultimately discharges into the sea as groundwater seepage. Irrigation water from greenhouse farming is collected from the Maro Spring and thus SGD in the Maro Cliff should not be added to the total budget of the aquifer system as it has been already accounted as groundwater from Maro Spring on land. This is a significant new finding and should be considered when compiling the total water budget of the Sierra Almirajara-Alberquillas Aquifer.

In contrast to the groundwater seepage dynamics in Maro Cliff (conglomerate section), the seepage rates in the Cantarrijan Beach (karst section) were seasonally modulated; the groundwater flux that the Cantarrijan Beach area received in the dry period was $0.9 \pm 0.1 \times 10^3 \text{ m}^3 \text{ d}^{-1}$ which was half of its wet period discharge ($2.3 \pm 0.3 \times 10^3 \text{ m}^3 \text{ d}^{-1}$). Differences in aquifer recharge and sea level variations between the dry and wet periods have control on the

magnitude of SGD (Carrasco et al, 1998; Santos et al., 2009). During dry periods precipitation was absent for up to two months, decreasing the recharge from infiltrated meteoric water in Sierra Almijara-Alberquillas Aquifer. Although during December of 2015 the area did not receive any rainfall, rain events occurred during September-November contributed to the recharge of Sierra Almijara-Alberquillas Aquifer, deriving in higher seepage fluxes in Cantarrijan Beach (Fig. 2). Additionally, the mean sea level measured during 2010-2016 near the study area (Permanent Service for Mean Sea Level, <http://www.psmsl.org/data/obtaining/stations/1940.php>) showed seasonal fluctuations, with lower sea levels during January-May compared to higher levels during August-December (Fig. 2). The observed moderate increase of 15 cm during the dry periods has contributed to the observed higher salinity of groundwater in Cantarrijan Beach, as well as the overall lower groundwater seepage rates during the dry periods.

Based on the salinity mixing model (Eqs. 9 and 10), we calculated that the fresh fraction of SGD was 48% of the total groundwater seepage, which means that during July of 2016, only $0.4 \pm 0.1 \times 10^3 \text{ m}^3 \text{ d}^{-1}$ should be taken into account as part of the Sierra Almijara-Alberquillas Aquifer water budget.

The salinity gradient observed from GW-Well to GW-Pz-4 is an indication that there is saltwater recirculation in the beach sediments and with the ^{222}Rn approach we have captured both the fresh and recirculated SGD (Fig. 6c). We did not repeat these measurements during the wet period, but we can hypothesize that this percentage was very similar based on the salinity measured in GW-Well during December of 2015 (Supplementary material Table A.2).

5.3 Importance of groundwater discharge for the water budget of Sierra Almijara-Alberquillas Aquifer and nitrate loading to Maro-Cerro Gordo coastal area

To estimate the portion of the annual fresh groundwater discharge to the sea from Sierra Almirajara-Alberquillas Aquifer water budget, we extrapolated average daily fluxes to obtain an annual range for the wet and dry periods (Table 4). During this study, we found that the total groundwater discharge to the sea was $1.9 \pm 0.5 \times 10^6 \text{ m}^3 \text{ y}^{-1}$ during the dry period, and $2.6 \pm 0.8 \times 10^6 \text{ m}^3 \text{ y}^{-1}$ wet period (Table 4). Based on Pérez-Ramos and Andreo (2007) and Castillo et al. (2001) the total annual groundwater budget of the Sierra Almirajara-Alberquillas Aquifer is $50 \times 10^6 \text{ m}^3 \text{ y}^{-1}$, and thus the flux we estimated represents 4 - 5% of the water resources of this karst system. This is a conservative estimate and should be considered as groundwater flow at base conditions because sampling campaigns were purposely not conducted after big rain events (Fig. 2).

In these calculations, we do not account for groundwater seepage in Maro Cliff (conglomerate section), coastal springs Doncellas, Barranco Maro, Huerto Romero, and Maro Beach, and groundwater-fed Tierras Nuevas Creek as they are originated from irrigation water that has been already accounted as outputs from Maro Spring.

Based on the groundwater discharge to the sea, NO_3^- fluxes per unit of shore length in the conglomerate section were $205 \pm 90 \text{ mmol m}^{-1} \text{ d}^{-1}$, while the schist and karst sections together receive between $15 \pm 3 \text{ mmol m}^{-1} \text{ d}^{-1}$ on average. When normalized by shore length, NO_3^- discharge in the conglomerate section is $3.5 \text{ mmol m}^{-2} \text{ d}^{-1}$, which compared to other anthropogenically impacted sites of coastal karst aquifers in the Mediterranean, is very similar. For example, García-Solsona et al. (2010) estimated a nitrate flux of $8.3 - 1.5 \text{ mmol m}^{-2} \text{ d}^{-1}$ in eastern Spain, and Rodellas et al. (2014) found $0.97 \text{ mmol m}^{-2} \text{ d}^{-1}$ in Majorca Island (Balearic Islands), whereas in a site in Menorca Island the flux was $18 \text{ mmol m}^{-2} \text{ d}^{-1}$ (García-Solsona et al., 2010b). It is important to note that while it only represents 20% (or 3 km) of the total shoreline

length (16 km), the conglomerate section receives about 75% of the total NO_3^- delivered to Maro-Cerro Gordo coastal waters (Supplementary material Table A.2).

Since 1989 the Maro-Cerro Gordo Natural Area (schist and karst sections), has been protected due to the presence of endemic and endangered flora and fauna by the Council of Environment of Andalusia. The European Commission designated the area as a Special Protection Area (SPA), Specially Protected Area of Mediterranean Importance (SPAMI), Site of Community Importance (SCI), and Special Area of Conservation (SAC) (Aranda and Otero, 2014). Specifically, the conservation area hosts three species of marine phanerogams (*Zostera marina*, *Posidonia oceanica*, and *Cymodocea nodosa*), included in the IUCN Red List of Threatened Species. Seagrass provides a unique habitat for a wide range of species (Hughes et al., 2009); including the largest bivalve in the Mediterranean *Pinna nobilis* (Theodorou et al., 2015), endangered fish *Epinephelus marginatus* (Gallego et al., 2015), and marine turtle *Caretta caretta* (Tomas et al., 2001) among others. As other studies have demonstrated, nitrate surplus loading often alters the primary producers community (Rapport and Whitford, 1999), and fast growing micro and macroalgae can proliferate preventing seagrasses *Zostera marina* and *Posidonia oceanica* from having enough sunlight and space (Hauxwell et al., 2001; Deegan et al., 2002). For example, Valiela et al. (2002) demonstrated that seagrass production could decrease up to 90% when nitrogen inputs are higher than $500 \text{ kg N ha}^{-1} \text{ y}^{-1}$. Only in the groundwater seepage area of Maro Cliff we have found that nitrogen fluxes (as nitrate) was about $2500 \text{ kg N ha}^{-1} \text{ y}^{-1}$, which is five times higher than the Valiela et al.'s assessment and should be a major concern for the ecological status of the marine system in the conglomerate section (Fig. 1). However, to further understand the implications of nutrients fluxes to the sea on

the marine ecosystem (particularly on endemic seagrass and fauna), additional investigation in the area must be conducted.

5.4 Sensitivity analysis of methods applied

To further compare the applicability of methodologies utilized in the presented multi-method approach, we constructed a sensitivity analysis including each method's main assumptions.

5.4.1 Parameter sensitivity of ^{224}Ra and salinity mass balance methods for determining discharge of submarine springs

Three terms represent the major source of uncertainty in the ^{224}Ra and salinity mass balances we used to calculate submarine spring discharge, including (1) the residence time of the receiving coastal waters (t), (2) the volume of the SGD plume (V), and (3) the uncertainty in the determination of groundwater end-member (Ra_{SGD}) (Table 5).

The largest uncertainty in this model is given by the assumption of a one day residence time (t). A common technique for assessing water ages of coastal waters is based on short-lived radium isotopes, ^{223}Ra and ^{224}Ra (Moore, 2000). However, during this study we could not measure both radium isotopes and we were unable to apply this method. The karst section of Maro-Cerro Gordo displays rocky cliff areas spread across the geographically exposed to prevailing west winds coastline which reflects the influence of high energy waves. The karst aquifer has very high secondary porosity and permeability which provides the opportunity for extensive groundwater-surface water exchange. The estimate of a one day residence time for this study is based on a comparison to similar high-energy coastal environments that are typical for the Mediterranean coastline. Under similar hydrogeological conditions in eastern Spain, using the methodology presented in Moore (2000), García-Solsona et al. (2010) assessed residence

time (t) between 1.1 d and 2.7 d, whereas Tovar-Sánchez et al. (2014) found residence times of 1.7, and 1.2 days in three coves in a karst system in the eastern shore of the Majorca Island. Considering these studies and specifics of this study site, we suggest using residence times of 0.25, 0.5, 1.0, and 3.0 days in the sensitivity analysis.

To determine the volume ($V = \text{plume area} \times \text{depth}$) of the SGD plume, we used areas of salinity sea surface anomalies created by the submarine springs discharge at Maro-Cerro Gordo. Specifically, we utilized salinity anomalies of -0.3, 0.0, 0.3, and 0.6 isolines. For vertical scale we use water depths acquired from the bathymetry database of the Andalusia Council of Environment (<http://www.juntadeandalucia.es/medioambiente/site/rediam>) assuming a well-mixed water column. However, Garcia-Solsona et al. (2010) found in eastern Spain that although complete mixing in the water column could be found near the karst springs vents, the salinity anomaly measured in surface waters was limited to the 0.5 m upper most layer. Similar settings are possible in Maro-Cerro Gordo; thus, we also calculated V based on the 0.0 salinity anomaly isoline and considering a depth of 0.5 m (Table 5)

There are only two groundwater wells in the karst section of Maro-Cerro Gordo, (GW-CG-1 and GW-CG-2). For the sensitivity analysis we used ^{224}Ra concentration in GW-CG-1 ($1260 \pm 90 \text{ dpm m}^{-3}$) and GW-CG-2 ($1020 \pm 80 \text{ dpm m}^{-3}$) as end-members, both sampled in September of 2006.

After tabulating these parameters, both the ^{224}Ra and salinity mass balance models showed the highest sensitivity to variations in the volume affected by SGD (V). We found that the total discharge from submarine springs decreases by 80% when using salinity isolines of 0.6 to -0.3 in a well-mixed water column; however, if the fresh plume is limited to the 0.5 m top layer of the water column, the decrease is up to 97%. Residence time (t) was the second most

important variable affecting the variability of discharge from submarine springs, increasing by 92% when changing the residence time from 0.25 to 3.0 days (Table 5). The ^{224}Ra mass balance showed limited sensitivity to varying groundwater end-member values (Ra_{SGD}), when using the GW-CG-2 value instead of GW-CG-1, all estimations increased only by 20%. The maximum variation utilizing the three variables simultaneously in the ^{224}Ra mass balance was 100% with a total discharge of $0.2 - 90.5 \times 10^3 \text{ m}^3 \text{ d}^{-1}$. The salinity mass balance presented a total variation of 100% to changing t and V , with a total discharge of $0.03 - 13.5 \times 10^3 \text{ m}^3 \text{ d}^{-1}$, which represents the purely fresh discharge (Table 5).

5.4.2 Parameter sensitivity of the ^{222}Rn mass balance and seepage meters measurements in determining diffuse seepage

In the ^{222}Rn model, we considered that only the seepage area (A) could be subject to ambiguity because all terms in the model (including the groundwater end-member) have been carefully measured. To delineate the size of the seepage face we used the following ^{222}Rn concentration isolines: for the Cantarrijan Beach we used the 10, 8, 6, and 5 dpm m^{-3} , while in Maro Cliff we used the 25, 30, 35, and 45 dpm m^{-3} (Table 5). For comparison reasons, were used the same seepage areas to calculate SGD when using the seepage meters approach. Using the $25 \times 10^3 \text{ dpm m}^{-3}$ ^{222}Rn concentration isoline in Maro Cliff produces 86% higher for both dry and wet periods, compared to seepage area based on the $45 \times 10^3 \text{ dpm m}^{-3}$ isoline. The discharge ranged from $0.9 - 6.7 \times 10^3 \text{ m}^3 \text{ d}^{-1}$ and $0.9 - 7.5 \times 10^3 \text{ m}^3 \text{ d}^{-1}$ during dry and wet periods respectively. In Cantarrijan Beach we found an increase of 82%, with a discharge estimation that ranged between $0.2 - 1.2 \times 10^3 \text{ m}^3 \text{ d}^{-1}$ and $0.5 - 2.9 \times 10^3 \text{ m}^3 \text{ d}^{-1}$ during dry and wet periods. The radon method showed higher sensitivity (89%) than the seepage meter assessments (87%) (Table 5).

5.4.3 Implications for the water budget of Sierra Almirajara-Alberquillas

Aquifer

Using the presented ranges of fluxes of each methodology, we calculated a total groundwater discharge to the sea of $4.3 - 105.1 \times 10^3 \text{ m}^3 \text{ d}^{-1}$ from all forms of discharge (Table 6). The fresh water component of the total discharge can be obtained from the salinity mass balance in submarine springs, ^{222}Rn mass balance and seepage meters for diffuse seepage in Cantarrijan Beach (47% fresh, based on the salinity mixing model), Caleta and Miel Creeks, and Alberquillas Spring (see sections 5.2 and 5.3). Applying a residence time of 0.25 d, the lowest estimated volumes affected by the SGD plume (V) at each submarine spring ($0.2 \times 10^5 \text{ m}^3$, $0.18 \times 10^5 \text{ m}^3$, $0.19 \times 10^5 \text{ m}^3$) derived from a 0.5 m water column, and the largest estimates for seepage face in Cantarrijan Beach ($A = 1.0 \times 10^3 \text{ m}^2$) for the ^{222}Rn model and seepage meter methods, the minimum fresh groundwater discharge is $0.9 \times 10^6 \text{ m}^3 \text{ y}^{-1}$. Applying the assumption of a 3-days residence time, the largest V at each submarine spring ($4.6 \times 10^5 \text{ m}^3$, $8.7 \times 10^5 \text{ m}^3$, $7.1 \times 10^5 \text{ m}^3$), and the largest A in cantarrijan Beach ($5.7 \times 10^3 \text{ m}^2$) for the ^{222}Rn model and seepage meter methods, the maximum fresh groundwater discharge from Sierra Almirajara-Alberquillas Aquifer is $6.8 \times 10^6 \text{ m}^3 \text{ y}^{-1}$. A total groundwater discharge of $6.8 \times 10^6 \text{ m}^3 \text{ y}^{-1}$ seems plausible but unlikely during base flow conditions when compared to the total water budget of Sierra Almirajara-Alberquillas ($50 \times 10^6 \text{ m}^3 \text{ y}^{-1}$). However, a residence time of 1 day seems more realistic based on other studies conducted in similar areas. The application of this sensitivity analysis including all terms and applying a 1-day residence time gives a total discharge of $1.0 - 3.5 \times 10^6 \text{ m}^3 \text{ y}^{-1}$.

5.5 Global applicability of the presented methodology approach

The modes of discharge found in Maro-Cerro Gordo are commonly observed in other areas worldwide independent of climate. About half of the Mediterranean and Adriatic coastline is comprised of karst aquifers and hydrogeological settings similar to Maro-Cerro Gordo can be expected (Fleury et al., 2007, 2005; Surić et al., 2015). In most scenarios authors often point out that groundwater discharge was not quantified due to the complex settings where at least two forms of discharge occur in multiple locations (e.g. Fleury et al., 2007; Burnett et al., 2008). Similar problems are encountered in karst coastlines in the Yucatan Peninsula (Mexico), a karst platform located in the Caribbean Sea. Gonneea et al. (2014) assumed that submarine springs were representative of the total SGD in the study area, but pointed out that diffuse discharge away from springs was not measured. Null et al. (2014) assessed SGD in the eastern shore of the Yucatan Peninsula where submarine springs and diffuse seepage are present. Due to the lack of a field method to quantify groundwater seepage, they used analytical calculations to establish a first order approximation of SGD. Furthermore, SGD in volcanic systems, although geologically different than karst, have comparable dynamics due to the similar intrinsic porosity and permeability (Burnett et al, 2008; Johnson et al., 2008; Peterson et al, 2009, Dimova et al, 2012).

Common characteristics of these sites include (1) simultaneous groundwater discharge to the sea occurring in two or more forms due to highly heterogeneous geological settings, (2) high infiltration rates resulting in negligible riverine freshwater inputs, and (3) significant groundwater inputs.

6 Conclusions

Work presented here demonstrates that determining total groundwater discharge to the ocean from coastal karst aquifers is not trivial and it requires a very good understanding of the

geology and groundwater origin to constrain an adequate water budget. Specifically, as a result of the complex geology of Maro-Cerro Gordo coastal area and highly heterogeneous Sierra Almijara-Alberquillas coastal karst aquifer, we found that groundwater discharge manifests in four different forms: (1) groundwater-fed creeks, (2) coastal springs, (3) groundwater seepage through seabed sediments, and (4) submarine springs. These expressions of discharge are typical for karst systems and should be expected in similar geological settings elsewhere including volcanic systems, which although having different rock composition, behave hydrologically very similar. We found that only the application of a set of methods specific for each form of discharge adequately characterizes and gives a realistic evaluation of groundwater discharge to the sea and thus recommend the following approaches (Table 6).

Continuous ^{222}Rn measurements in coastal waters via boat surveys proved to be the most reliable method for detecting diffuse groundwater seepage through seabed sediments. The technique complements well with a ^{222}Rn mass balance model based on time-series measurements performed with the same instrumentation. We found that this method gives similar results to direct measurements carried out from Lee-type seepage meters.

The presence of submarine springs was reliably detected using continuous salinity measurements and discrete ^{224}Ra sampling. However, because negative salinity anomalies in coastal waters could be the result of discharge of other freshwater inputs (e.g. groundwater-fed creeks and coastal springs) which are likely to occur in karst systems, salinity alone is not a reliable tracer for SGD in coastal karst systems. We were able to confirm the presence of submerged springs only when combined with high concentrations of ^{224}Ra concentrations and direct observations via SCUBA diving. Direct flowmeter measurements or applying the ^{222}Rn

method would have been technically and economically challenging, given the springs depth and their lateral vent geometry.

Subaerial coastal springs and groundwater-fed creeks are easily detectable visually in the field. However, we found that tracer surveys are helpful to identify sources of springs and assessing the total discharge from both forms of subaerial groundwater discharge.

We found that the combination of hydrochemistry (SO_4^{2-} and NO_3^-) and water stable isotopes ($\delta^2\text{H}$ and $\delta^{18}\text{O}$) was ideal to decipher the origin of each point of groundwater discharge to the sea.

Nitrate fluxes, in an area where endemic and protected seagrasses *Zostera marina*, *Posidonia oceanica* are present, were found to be comparable with other coastal karst aquifers environmentally impacted by anthropogenic activities in the Mediterranean.

Based on our experience, we strongly recommend the application of the described methodology approach in coastal karst systems to assess total groundwater discharge to the sea and associated nutrients fluxes.

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1519 Table 6: Applicability comparison of all methods utilized to detect and quantify different modes of
1520 groundwater discharge to the sea. Flux ranges are based on maxima and minima estimations obtained in

1521 the sensitivity analysis. Daily fluxes are shown for each form of discharge and method, and annual water
1522 budget (fresh) of Sierra Almijara-Alberquillas (SAA).

	Radium (1) mass balance			Salinity mass balance (2)			V ($\times 10^5 \text{ m}^3$)	F _{SGD} (1) ($\times 10^3 \text{ m}^3 \text{ d}^{-1}$)	F _{SGD} (2)
	Ra _{sw}	Ra _{SGD} (dpm m ⁻³)	Ra _{ow}	Sal _{sw}	Sal _{SGD}	Sal _{ow}			
Cantarrijan	25 ± 2	1260 ± 90	8 ± 1	36.3 ± 0.1	0.0	36.5	2.67	4.7 ± 0.5	0.8 ± 0.1
Palomas	18 ± 2	1260 ± 90	8 ± 1	36.4 ± 0.1	0.0	36.5	4.04	4.3 ± 0.5	0.9 ± 0.1
Sifon	17 ± 2	1260 ± 90	8 ± 1	36.4 ± 0.1	0.0	36.5	3.72	3.7 ± 0.4	0.5 ± 0.1
Total flux								12.8 ± 1.4	2.3 ± 0.2

Table 1

		Rn_{SGD} ($\times 10^3 \text{ dpm m}^{-3}$)	$F_{\text{Waterfall}}$ ($\times 10^3 \text{ dpm m}^{-2} \text{ d}^{-1}$)	C_{Ra} (dpm m^{-3})	F_{Diff} ($\text{dpm m}^{-2} \text{ d}^{-1}$)	F_{Mix} ($\times 10^3 \text{ dpm m}^{-2} \text{ d}^{-1}$)	F_{Atm}	Seepage Area ($\times 10^3 \text{ m}^2$)	SGD (cm d^{-1})	F_{SGD} ($\times 10^3 \text{ m}^3 \text{ d}^{-1}$)
Maro Cliff	Jul-15	350 ± 50	16 ± 6	280 ± 50	619 ± 57	149 ± 40	33 ± 9	7.7	39 ± 10	3.0 ± 0.8
	Dec-15	440 ± 60	21 ± 8	280 ± 50	619 ± 57	238 ± 64	11 ± 3	7.7	40 ± 11	3.1 ± 0.8
	Jul-16	320 ± 30	10 ± 5	280 ± 50	619 ± 57	160 ± 43	25 ± 7	7.7	38 ± 10	2.9 ± 0.7
Cantarrijan Beach	Jul-15	310 ± 70	N/A	170 ± 40	455 ± 51	-		4.3	-	-
	Dec-15	240 ± 60	N/A	170 ± 40	455 ± 51	84 ± 13	30 ± 5	4.3	52 ± 8	2.3 ± 0.3
	Jul-16	350 ± 40	N/A	170 ± 40	455 ± 51	115 ± 18	27 ± 4	4.3	22 ± 3	0.9 ± 0.1

Table 2

	SGD seepage rate (cm d ⁻¹)	
	Maro Cliff	Cantarrijan Beach
Radon model	38 ± 10	22 ± 3
Seepage meters	28 ± 7	23 ± 7
SM-1	19	13
SM-2	32	32
SM-3	37	26
SM-4	25	20
SM-5		0
SM-6		1
SM-7		0
SM-8		0
SM-9		1

Table 3

	TGD	CS	GC	GS	SS	Fresh TGD from SAA	Annual budget SAA	Agricultural area	Relative agricultural area	N-TGD
	($\times 10^3 \text{ m}^3 \text{ d}^{-1}$)		($\times 10^3 \text{ m}^3 \text{ d}^{-1}$)			($\times 10^3 \text{ m}^3 \text{ d}^{-1}$)	($\times 10^6 \text{ m}^3 \text{ y}^{-1}$)	(km^2)	(%)	(mol d^{-1})
Conglomerate section	3.5 – 4.0	0.5 – 0.8	0.1 – 0.2	2.9 – 3.0	0	0.1 – 0.2	0.06 – 0.08	204	95	550 - 732
Schist section	2.4 – 3.6	1.1 – 1.6	1.3 – 2.0	0	0	2.3 – 3.4	0.8 – 1.2	103	7	136 – 204
Karst section	3.0 – 4.8	0	0	0.9 – 2.3	2.1 – 2.5	2.5 – 3.6	1.0 – 1.3	0	0	18 – 53

Table 4

Method/Form of discharge	Model parameters										Final SGD estimate (x 10 m ³ d ⁻¹)	Percentage difference between min and max estimate
	Residence time (days)	²²⁴ Ra gw end-member (dpm m ⁻³)	Salinity isoline	Volume SGD plume (x 10 ⁵ m ³)			²²² Rn isoline (x 10 ³ dpm m ⁻³)		Seepage area (x 10 ³ m ²)			
				Cantarrijan	Palomas	Sifon	Maro Cliff	Cantarrijan Beach	Maro Cliff	Cantarrijan Beach		
Salinity mass balance/Submarine springs	0.25	N/A	-0.3	0.9	1.5	1.1	N/A	N/A	N/A	N/A	0.2 - 90.5	100%
	0.50	N/A	0.0	2.6	4.0	3.7	N/A	N/A	N/A	N/A		
	1.00	N/A	0.3	2.8	5.4	4.7	N/A	N/A	N/A	N/A		
	3.00	N/A	0.6	4.6	8.7	7.1	N/A	N/A	N/A	N/A		
	0.5 m water column		0.0	0.20	0.18	0.19	N/A	N/A	N/A	N/A		
²²⁴ Ra mass balance/Submarine springs	0.25	1020 ± 80	-0.3	0.9	1.5	1.1	N/A	N/A	N/A	N/A	0.03 - 13.5	100%
	0.50		0.0	2.6	4.0	3.7	N/A	N/A	N/A	N/A		
	1.00	1260 ± 90	0.3	2.8	5.4	4.7	N/A	N/A	N/A	N/A		
	3.00		0.6	4.6	8.7	7.1	N/A	N/A	N/A	N/A		
	0.5 m water column		0.0	0.20	0.18	0.19	N/A	N/A	N/A	N/A		
²²² Rn mass balance/Diffuse seepage	N/A	N/A	N/A	N/A	N/A	N/A	25	5	2.4	1.0	1.1 - 10.0	89%
	N/A	N/A	N/A	N/A	N/A	N/A	30	6	7.7	3.2		
	N/A	N/A	N/A	N/A	N/A	N/A	35	8	10.6	4.3		
	N/A	N/A	N/A	N/A	N/A	N/A	45	10	17.8	5.7		
Seepage meters/Diffuse seepage	N/A	N/A	N/A	N/A	N/A	N/A	25	5	2.4	1.0	1.2 - 9.1	87%
	N/A	N/A	N/A	N/A	N/A	N/A	30	6	7.7	3.2		
	N/A	N/A	N/A	N/A	N/A	N/A	35	8	10.6	4.3		
	N/A	N/A	N/A	N/A	N/A	N/A	45	10	17.8	5.7		

Table 5

Mode of groundwater (GW) discharge / site name	²²⁴ Ra method		²²² Rn method		Salinity method		Seepage meter method		Flow meter method
	Obs. anomaly in seawater	Flux ($\times 10^3 \text{ m}^3 \text{ d}^{-1}$)	Obs. anomaly in seawater	Flux ($\times 10^3 \text{ m}^3 \text{ d}^{-1}$)	Obs. anomaly in seawater	Flux ($\times 10^3 \text{ m}^3 \text{ d}^{-1}$)	Obs. anomaly in seawater	Flux ($\times 10^3 \text{ m}^3 \text{ d}^{-1}$)	Flux ($\times 10^3 \text{ m}^3 \text{ d}^{-1}$)
GW-fed creeks									
Caleta	✓	N/A	×	N/A	✓	N/A	×	N/A	1.4 – 2.2
Tierras Nuevas									
Miel									
Coastal springs									
Doncellas									
Barranco Maro	×	N/A	×	N/A	✓	N/A	×	N/A	1.6 – 2.4
Huerto Romero									
Maro Beach									
Alberquillas									
Submarine springs									
Cantarrijan	✓	0.2 – 90.5	×	N/A	✓	0.03 – 13.5	×	N/A	N/A
Palomas									
Sifon									
Diffused seepage									
Maro Cliff	×	N/A	✓	1.1 – 10.0	✓	N/A	✓	1.2 – 9.1	N/A
Cantarrijan Beach									

Table 6

List of figures

Figure 1: Study site location and geological map showing water table contour lines (from Pérez-Ramos and Andreo, 2007), groundwater flow direction, important wells and piezometers, sampling points, and terrestrial springs. Groundwater discharge to the sea (TGD) is represented in purple and is based on this study. Coastal springs are represented as CS, groundwater-fed creeks as GC, diffuse groundwater seepage as GS, and submarine springs as SS. The study area is divided in three sections: conglomerate section, schist section, and karst section. The distribution of seagrass beds are based on Bañares-España et al. (2002), and Aranda and Otero (2014).

Figure 2: Average monthly precipitation and sea level change during 2010, 2015, and 2016. Error bars show the monthly rainfall variability during this study. In December of 2015 slight precipitation occurred only during the first week, however, abundant rainfall took place during September-November. Sea level showed minima values during January-May and maxima during August-December. Sampling campaigns were conducted during May-July (dry periods) and December (wet periods).

Figure 3: Interpolated ^{224}Ra activity concentrations in September of 2010 along the schist and karst sections. Two areas of high ^{224}Ra in coastal waters were identified in the schist section near groundwater-fed Miel Creek ($56 \pm 4 \text{ dpm m}^{-3}$), and the three clustered submarine springs discharging from Cantarrijan Caves ($51 \pm 4 \text{ dpm m}^{-3}$) located in the Cantarrijan area (karst section).

Figure 4: Salinity anomaly map showing combined results from May, July, and December of 2015. Two areas of negative salinity anomalies were found in the conglomerate (salinity anomaly = -1.2 to -1.7) and karst (salinity anomaly = -0.3 to -1.0) sections almost perfectly aligned with their delineated extent.

Figure 5: Radon-222 distribution map based on surveys during July and December of 2015, and July of 2016. Two radon peaks were found in Maro Cliff (conglomerate section) and Cantarrijan Beach (karst section) with maximum concentrations of $44 \pm 3 \times 10^3$ dpm m⁻³ and $30 \pm 2 \times 10^3$ dpm m⁻³ respectively.

Figure 6: (a) Groundwater seepage velocity averaging results from radon mass balance and seepage meters in areas of diffuse seepage (Maro Cliff and Cantarrijan Beach). Radon distribution in (b) Maro Cliff (conglomerate section) and (c) Cantarrijan Beach (karst section) where cylinder symbols represent seepage meter locations and the star radon time series stations.

Figure 7: Radon fluxes result of each component of the mass balance box model during all sampling campaigns in Maro Cliff (conglomerate section) and Cantarrijan Beach (karst section). The largest tracer losses occurred via mixing due to the high exposure of both areas to waves and currents. Greater difference in SGD-²²²Rn fluxes was found between wet periods (December) and dry periods (July) in Cantarrijan Beach compared to Maro Cliff.

Figure 8: (a) Isotopic composition ($\delta^{18}\text{O}$, $\delta^2\text{H}$) of water samples collected during all sampling campaigns. Local Groundwater Line (LGL) represents the linear trend based on all groundwater

samples collected in the study area. Global Meteoric Water Line (GMWL) is based on Craig, (1961) and the Western Mediterranean Meteoric Water Line (WMMWL) on Gat and Garmi, (1970). White color represents points of discharge in conglomerate and breccia lithology, while light grey are in travertine (conglomerate section); dark grey shows points in schist (schist section); and black color show locations in karstic marble (karst section). Maro Spring and Nerja Cave well (not points of discharge to the sea) are represented with a black and white star respectively. Water samples collected at each section (conglomerate section, schist section, and karst section) are grouped in dashed squares. (b) Isotopic composition of samples collected from points of discharge from the travertine formation in the conglomerate section. The two groundwater end-members (Maro Spring and irrigation waters) are circled, while diffuse seepage in Maro Cliff is represented with squares.

Figure 9: Mixing plots of ^{224}Ra (a) and ^{222}Rn versus salinity (b) showing best fit linear and exponential mixing lines, respectively, during surface water surveys along the coastline in September of 2010, July and December of 2015.

Figure 10: Total groundwater discharge (TGD) in the study area divided in forms of discharge (GS: groundwater diffuse seepage, CS: coastal springs, GC: groundwater-fed creeks, SS: submarine springs), showing maximum and minimum flux during wet and dry periods.

Figure 11: Groundwater ionic relationship between NO_3^- and SO_4^{2-} where groundwater samples with similar composition are grouped in dashed squares. Symbols are presented as in Fig. 8 based on the section and lithology they are located. In the conglomerate section Maro Spring,

71 Nerja Cave, and Maro Creek show similar SO_4^{2-} concentration with low NO_3^- , while Doncellas,
72 Barranco Maro, Huerto Romero, and Maro Beach present NO_3^- contamination. Samples from the
73 schist section (Miel and Alberquillas) present a distinctive signal with low NO_3^- and SO_4^{2-}
74 concentrations. Groundwater collected in Cantarrijan Beach (karst section) shows seawater
75 influence from saltwater recirculation in beach sediments. Arrows indicate the geochemical
76 change before irrigation and after fertilizers application (NO_3^-), where Maro cliff (diffuse
77 seepage) shows mixing between both groups.

3°51'0"W

3°49'30"W

3°46'0"W

3°43'30"W

36°46'30"N

36°45'30"N

36°43'30"N