**Biogeosciences
Discussions**

Groundwater and nutrient discharge through karstic coastal springs (Castelló, Spain)

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Abstract

Discharge of groundwater and associated chemical compounds into coastal karstic regions, which are abundant in the Mediterranean basin, is envisaged to be significant. In this study, we evaluate the groundwater discharge and its nutrient load to the open karstic site of Badum (Castelló, East Spain). Salinity profiles evidenced that groundwater discharge from coastal brackish springs causes a buoyant fresher layer, as identified with thermal infrared images. Chemical tracers (radium isotopes, dissolved inorganic silicate and seawater major elements) have been used to determine a brackish groundwater proportion in coastal waters of 36% in October 2006 and 44% in June 2007. Based on a radium-derived residence time of 2.7 days in October 2006 and 2.0 days in June 2007, total SGD fluxes have been estimated in 71 500 and 187 000 $m^3 d^{-1}$, respectively, with fresh-SGD contributions representing 71% and 85%. The calculated SGD-associated nutrient fluxes, most likely of natural origin, were 1500 and 8300 $\mu mol\, m^{-2} d^{-1}$ of DIN and 19 and 40 $\mu mol\, m^{-2} d^{-1}$ of DIP in October 2006 and June 2007, respectively. These inputs may actually lead to or enhance P limitation, thereby altering the structure of biological communities in the area.

1 Introduction

All aquifers with a hydraulic connection to the sea may discharge to coastal environments (Burnett et al., 2003) and are susceptible to be affected by seawater intrusion (Bear et al., 1999). Indeed, the interface between freshwater and seawater has been termed as a "mixing zone" of fresh and salty waters (Price and Herman, 1991). Many aquifers are conformed by detritic materials where the discharge seepage is produced by diffusive processes and seawater recirculation through the sediments may constitute a major component of submarine groundwater discharge (SGD) (Burnett et al., 2006). Conversely, in karst geological formations, fresh groundwater is channelized through preferential pathways created from limestone dissolution, being the main constituent

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when discharging to the sea. In the coastal zone of the Mediterranean basin there are very heterogeneous and disrupted mountain chains, some of them with extended development of carbonate formations (especially limestones and dolomites) that are responsible for the creation of karst configurations. In fact, Mediterranean karstic ar-
5 eas border 60% of the coastline and are estimated to contribute around 75% of the total freshwater input to the sea: much of it must be via SGD (UNESCO, 2004). In the Mediterranean Sea, a widespread existence of SGD via submarine springs has been discovered along the coasts of Turkey, Syria, Lebanon, Israel, Greece, Italy, France, Spain, Algeria, Tunisia, Libya (Mijatovic, 2007). However, there are only a few local or
10 regional studies on the quantification of karstic SGD fluxes in the Mediterranean carbonate basin, carried out in coastal areas of Italy (Moore, 2006a), Turkey (Bakalowicz et al., 2008), Israel (Swarzenski et al., 2006) and Spain (Garcia-Solsona et al., 2009).

SGD is a potential source of chemical compounds, such as nutrients, metals and pollutants, which may imply major ecological impacts in these coasts. The transfer
15 of these substances to coastal areas via SGD has been recognized of enormous significance since these fluxes may modify biogeochemical cycles (Boehm et al., 2004; Corbett et al., 2000; Moore, 1996; Paytan et al., 2006) and could alter the ecological status of the water bodies. For example, dissolved nutrient inputs through SGD, which have natural and anthropogenic origins, have been shown to be a factor in algal
20 growth dynamics (Johannes, 1980; Kinney and Roman, 1998; Sewell, 1982), hydrological modification of coastal ecosystems (McClelland et al., 1997; Short and Burdick, 1996; Valiela et al., 1992) and eutrophication processes including harmful algal blooms (Basterretxea et al., 2009; Giblin and Gaines, 1990; Gobler and Sañudo-Wilhelmy, 2001; Laroche et al., 1997). Among these nutrients, nitrogen has been particularly
25 important because represents a limiting nutrient for primary production in most of the world's oceans (Borum, 1996; Nixon and Pilson, 1983). However, the Mediterranean is considered to be P limited (Krom et al., 1991).

Karstic formations are highly susceptible to be contaminated from urban, industrial and agricultural wastewaters (Tapia González et al., 2008) and may constitute a rapid pathway of nutrients and pollutants to the sea due to the low filtration in the aquifer. The groundwater dynamics in karst regions leads the coupled coastal ecosystems to

5 be particularly vulnerable to ecological disturbances (Young et al., 2008). In addition, the Mediterranean basin is affected by an intense demand of its water resources due to the increase of population and tourism. Then, the contamination of its aquifers, and especially the karstic ones, could represent an important reverse in the water resource management and ecological status. Like the SGD water fluxes, the analyses of nutri-

10 ent discharges throughout this pathway in Mediterranean karstic formations are scarce though required to establish the ecological status of the subterranean aquifers and the coastal environments. For example, phytoplankton and harmful algal blooms (HABs) are frequent in Mediterranean coastal regions (Basterretxea et al., 2005; Garcés et al., 1999; Giacobbe et al., 2007; Honsell et al., 1995; Vila et al., 2001) and there are insuf-

15 ficient studies evaluating the potential SGD role in such phenomena (Garcia-Solsona et al., 2009).

Since the last 15 years, several techniques are being used to estimate submarine groundwater discharge fluxes to coastal areas. One of the successful tools to evaluate the total SGD (fresh groundwater plus recirculated seawater) is the radium isotopic

20 quartet (^{223,224,226,228}Ra). The approach is based on the groundwater enrichment in radium and the detection of the excess radium in coastal waters (Moore, 1996). Other elements may be enough enriched or diluted in groundwater (e.g. dissolved inorganic silicate – Hwang et al., 2005a – and seawater major elements, respectively) that enable us to estimate the groundwater fraction in coastal waters. Yet, coastal waters residence

25 time is required to quantify SGD fluxes, and this value can be only derived from radium isotopes, owing to their different half-lives (from 3.7 d to 1600 yr).

The aim of this study is to determine the karstic springs' groundwater proportion in the Badum coastal area (Peníscola, Castelló), at the Eastern Spanish Mediterranean coastline, by mass balances of i) radium isotopes, ii) dissolved inorganic silicate and

iii) seawater major elements. Radium isotopes will be then used to estimate the water residence time and the total SGD flux. Also, we endeavor to quantify the input of dissolved inorganic nutrients via SGD in order to advance in the understanding of the ecological status in the area.

2 Study area

The Badum study site, in Peníscola (Castelló, Spain), is an open coastal area corresponding to a well developed karstic structure with high permeability by fissuration and karstification processes (Mejías et al., 2008). The geologic formation that constitutes the littoral aquifer sits at grand depths (Jurassic aquifer of El Maestrat) but it outcrops in the proximity of the coast. The aquifer conditions are excellent near the shoreline, with transmissivity ranging from 1000 to 4000 $m^2 d^{-1}$ (Ballesteros, 1989) and average exploitation rates between 50 and 100 $L s^{-1}$. A mathematical model developed for the Irta Mountains area (Fig. 1) (Serrano et al., 1995) showed even higher transmissivity values (from 9000 to 15 000 $m^2 d^{-1}$), consistent with the strong karstification that presents the aquifer in that region.

Annual precipitation typically ranges from 400–650 mm, with wet and dry seasons typical of the Mediterranean regions. As many other karstic areas, precipitation penetrates the ground resulting in negligible surface runoff (excepting in cases of torrential runoff) and no permanent rivers in the area. The immediate seabed of the coastal aquifer is basically composed of coarse sands since the absence of rivers prevents the arrival of fine sediments in the vicinity. Also, strong winds support coastal waters mixing with open sea at short time scales.

Hydrological models were used to provide first estimates of SGD from coastal springs of the Irta Mountains, deriving fluxes in the range of 80–175×10^6 $m^3 y^{-1}$ (Ballesteros, 1989; IGME, 1988; IGME-IRYDA, 1977). Posterior studies, based on a reinterpretation of the geological model, on research drillings (Serrano et al., 1995) and a mathematical modeling of the coastal aquifer sector, refined the estimation of the groundwater discharge in 64×10^6 $m^3 yr^{-1}$.

The deep Maestrat Jurassic aquifer is the single hydrogeological region potentially contributing groundwater discharge to the Irta Mountains shoreline, i. e., through the coastal springs identified in Alcossebre, Peníscola and Badum. Thermal infrared aerial images allowed identifying Badum as the main area affected by SGD from coastal springs (Fig. 1; Antón-Pacheco et al., 2007).

3 Sampling and methods

Two sampling surveys at Badum coastal area were carried out in October 2006 and June 2007 (Fig. 2). Water samples were obtained for Ra isotopes (^{223}Ra, ^{224}Ra, ^{226}Ra and ^{228}Ra) (50 L), dissolved inorganic nutrients (PO_4^{3-}, NH_4^+, NO_2^-, NO_3^- and SIO_4^{4-}) (60 ml) and dissolved major elements (S, Cl, K, Ca, Br, Sr and Ba) (60 ml). Water samples were collected at 20 cm depth, although three stations were also sampled at 50 cm depth. Temperature and salinity profiles with depth were also obtained from several stations using a portable salinometer (YSI 660XLM).

Groundwater from two coastal brackish springs was also collected with a small submersible pump (~25 L) during both surveys. In addition, one of these springs (SP1) was monitored monthly from March 2007 to February 2008 measuring salinity, temperature, Ra and nutrients.

The radium isotopes were extracted from water samples using acrylic fiber impregnated with manganese oxide, Mn-fiber. The water samples were passed in the field through columns (at <1 L min^{-1}) containing Mn-fiber (25 g-dry), which quantitatively removed the radium (Moore, 1976). A Radium Delayed Coincidence Counter (RaDeCC) was used to determine the short-lived radium activities, ^{223}Ra and ^{224}Ra (Garcia-Solsona et al., 2008; Moore and Arnold, 1996). Activities of the long-lived isotopes, ^{226}Ra and ^{228}Ra, were determined by measuring the ashed Mn-fibers with a well-shaped germanium gamma detector.

Dissolved inorganic nutrients were collected in polypropylene bottles and kept frozen until analysis, which were carried out using an auto-analyzer (Grasshoff et al., 1999). For this study, DIN is defined as the sum of NO_3^-, NO_2^- and NH_4^+, DIP as PO_4^{3-} and DSi as SiO_4. Water for the determination of major elements (S, Cl, K, Ca, Br and Sr) was sampled in the same way and analyzed by X-Ray fluorescence.

4 Results

4.1 Salinity and radium distribution

The thermal infrared image taken in June 2006 (Fig. 1) showed the existence of a plume of colder water moving offshore from identified coastal springs (total shoreline of aprox. 600 m long). This observation was confirmed by the temperature and salinity measurements during both sampling campaigns (Table 1). Surface water salinities in the autumn and summer periods ranged from 23.5 to 33.0 and from 14.5 to 37.0, respectively. The high salinies at stations A7 (38.2) in autumn and S16 (37.8) in summer indicated that they were out of the fresher plume. A strong salinity and temperature vertical stratification was observed in June 2007 from water column profiles carried out at stations S11 and S16 (150 m and 350 m offshore, respectively). This fresher layer corresponds to the SGD plume moving offshore and forming a layer of 40 cm thickness (Fig. 3).

Surface radium activities in coastal waters are given in Table 1. On average, radium activities in October 2006 sampling were slightly higher than in June 2007 (1.2–1.4 times). The saltiest samples (A7 and S16, in October and June, respectively) showed significantly lower radium activities, indicating a minimal influence of SGD.

Short-lived radium activities in brackish groundwater from the springs ranged from 3 to 21 dpm 100 L^{-1} for ^{223}Ra and from 164 to 284 dpm 100 L^{-1} for ^{224}Ra, thus evidencing a clear radium enrichment (Tables 1 and 2). The highest activities in these brackish coastal springs were measured in spring and autumn. Monthly salinities within the springs ranged from 5.0 to 13.7 (Tables 1 and 2).

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Strong positive linear correlations among radium isotopes in all surface samples are observed, pointing to coastal sea and the brackish springs as the endmembers (Fig. 4). The same pattern is shown for Ra activities and salinity (Fig. 5), with linear correspondences pointing to the brackish springs as the main contributor of radium.

4.2 Nutrients

Concentrations of dissolved inorganic nutrients in all the stations are summarized in Table 1. Concentrations of NO_3^-, but also DIP and DSi, were significantly elevated in the fresher surface waters relative to the waters at 50 cm depth (t-test $p<0.003$, <0.001 and <0.0001, respectively; Table 1). In contrast, NH_4^+ was higher below the fresher layer and NO_2^- showed no clear trends with either salinity or depth. Our data can be compared to nutrient measurements in the NW Mediterranean Sea platform areas, either influenced or not by riverine inputs of nutrients (Segura, 2007): DIP concentrations in our study were lower than average concentrations in surface waters in the continental shelf of the NW Mediterranean Sea (0.37 µM). Dissolved NO_3, NH_4 and DSi concentrations were higher than in surface waters in the continental shelves (0.95, 1.00 and 5.00 µM, respectively).

The concentrations of DIN and DSi in October 2006 versus June 2007 were not statistically different (t-test $p<0.064$ and <0.352, respectively), unlike DIP, which was significantly higher in June 2007 than in October 2006 ($p<10^{-10}$). DIP was correlated with surface radium activities in October 2006 ($R^2=0.77-0.86$), but less so in June 2007 ($R^2=0.54-0.68$). Conversely, we only observed good correlations of DIN and Ra during June 2007 ($R^2=0.92-0.95$). DSi concentrations and all radium isotopes in surface waters showed clear positive correlations (Fig. 6) during both sampling periods, pointing to a conservative behavior of DSi in these coastal waters. This confirms the potential of DSi as a tracer of SGD (Hwang et al., 2005a, b).

4.3 Major elements in seawater

Concentrations of major elements in samples A7 and S16 (located out of the fresher water plume) are typical of seawater (Moe, 1982). Strong negative linear correlations of Cl, S, Ca, K, Br and Sr with radium isotopes and salinity were obtained (Fig. 7), indicating conservative behavior of major elements in seawater when diluted by spring groundwater discharge.

5 Discussion

Submarine groundwater discharge forming a thin and fresher plume in the Badum coastal area was recognized by chemical tracer enrichments (Ra isotopes and DSi) and lower salinity and temperature at all coastal stations relative to the open sea. In areas with well defined seepage faces, SGD has been reported to behave following an exponential decrease offshore (Bokuniewicz et al., 2004; Lee, 1977). However, this conventional function, in the form SGD$=A \cdot e^{-cx}$ (where A and c are constants, and x is the distance offshore; Bokuniewicz et al., 2004), does not govern the SGD flow in karstic areas, primarily due to the heterogeneity in boundary conditions at the shoreline. Fissuration and karstification processes at the Badum coastline (Fig. 8) lead to channelized discharge through brackish springs. Since it is an open site, the shape of the SGD plume at short time scales can be easily modified due to the prevailing currents and winds. As show above (Fig. 5), a good correlation between radium concentrations and salinity was obtained in coastal plume waters, i.e., radium activities were enriched in the fresher SGD plume compared to out of plume waters.

The estimation of SGD using the radium quartet requires identifying the possible sources of Ra in the coastal area. The strong linear correlations among radium isotopes in coastal plume waters, seawater and coastal brackish springs (Fig. 4) suggested that the two main endmembers that explain radium activities in the coastal area are seawater and brackish springs. Thereby, any other potential input of Ra

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(from sediments or possible deep springs) in surface coastal waters is negligible. Since dissolved inorganic silica and several major elements also showed strong linear correlations with all radium isotopes, it can be inferred that they experienced a similar conservative binary mixing pattern. While the distribution of DSi was found to be like that of radium (dilution from the enriched brackish springs to offshore; Fig. 6), major elements (Cl, S, Ca, K, Br and Sr) showed the inverse relation, i. e., seawater is diluted by mixing with brackish groundwater. In addition, the low radium activities measured in water samples below the fresher layer confirm that the only input of Ra is the terrestrial source of brackish water via coastal springs.

The SGD flux ($m^3 d^{-1}$) to the Badum area can be estimated as described in Eq. (1):

$$SGD = \frac{f_{gw} \cdot V}{T_r} \qquad (1)$$

where f_{gw} is the groundwater fraction in coastal waters, V is the volume affected by SGD (m^3) and T_r is the coastal waters residence time (days). These terms are established in the next sub-sections.

5.1 Groundwater fraction (f_{gw})

A simple two-endmember mixing model can be built, as described by Eqs. (2), (3) and (4).

$$f_{sw} + f_{gw} = 1 \qquad (2)$$

$$^{226}Ra_{sw} \cdot f_{sw} + {}^{226}Ra_{gw} \cdot f_{gw} = {}^{226}Ra_{std} \qquad (3)$$

$$^{228}Ra_{sw} \cdot f_{sw} + {}^{228}Ra_{gw} \cdot f_{gw} = {}^{228}Ra_{std} \qquad (4)$$

where f_{sw} is the seawater fraction in coastal waters, and $^{226,228}Ra_{sw}$, $^{226,228}Ra_{spring}$ and $^{226,228}Ra_{std}$ are the average activities in seawater, spring groundwater and coastal waters of Badum, respectively. A common assumption made when using Ra as a tracer

of SGD is that radium activities in the groundwater endmember are temporally and spatially constant (Hougham et al., 2008). Therefore, any change in the average surface water excess Ra activity, after correction for the residence time, is assigned to changes in SGD flux. This is why groundwater activities measured concurrently with coastal water activities have been used to estimate the autumn 2006 and June 2007 SGD fluxes.

Because of the conservative behavior of DSi and major elements, the same equations may be applied using these compounds instead of radium isotopes to estimate the groundwater fraction. The results obtained from the combination of two equations, always imposing that the sum of seawater and SGD fractions must be 1 (Eq. 2), are summarized in Table 3. All the estimates of seawater and groundwater fractions are in close agreement, with an average of 0.36±0.03 for October 2006 and 0.44±0.03 for June 2007, evidencing that surface waters in June contained about 22% more brackish groundwater than in October.

5.2 Volume of water column influenced by SGD (V)

The total volume under study was calculated by multiplying the thickness of the water column influenced by SGD (H) by the fresher plume area (A). From water column profiles of salinity at depth, water stratification was evidenced showing significantly fresher salinities from the surface down to only 40 cm depth (Fig. 3). Therefore, we define the model for the first 40 cm.

The extension of the fresher SGD plume was determined from the salinity gridding (kriging method) considering the area delimited by the salinity contour of 36. Thereby, the extension of the plume was determined to be of 2.1 km^2 in June 2007 and 1.3 km^2 in October 2006 (Fig. 9).

The resulted values for the coastal water volume affected by SGD were of approximately 540 000 m^3 in October 2006 and 850 000 m^3 in June 2007.

5.3 Coastal waters residence time (T_r)

Considering that the studied karstic system is an open coastal area, a short coastal water residence time is expected. This led us to apply the distribution of short-lived radium isotopes to estimate the water residence time.

Figure 10 depicts ^{224}Ra versus ^{223}Ra activities for surface water samples in both seasons and the coastal spring endmembers. Best-fit lines produce a ^{224}Ra / ^{223}Ra activity ratio for springs (AR_{spring}) of 18.5±0.3. For surface waters, the derived activity ratios (AR_{std}) would be 13.1±0.2 (October 2006) and 14.2±0.1 (June 2007). We then can use the difference between AR_{spring} and AR_{std} to estimate the apparent age or water residence time of plume waters (Moore, 2006b):

$$T_r(d) = \frac{\text{Ln}\left(\frac{AR_{spring}}{AR_{std}}\right)}{0.129} \tag{5}$$

Equation (5) takes into account the more rapid decay of ^{224}Ra relative to ^{223}Ra, with the 0.129 d^{-1} value accounting for the difference in the ^{224}Ra and ^{223}Ra decay constants. Applying Eq. (5), an average residence time of 2.7±0.2 days for water sampled in October is obtained, which is slightly higher than the estimated surface water residence time in June, of 2.0±0.1 d.

5.4 Determination of the SGD fluxes

Once all the necessary terms have been estimated, SGD fluxes were derived from Eq. (1), resulting in 71 500 m^3 d^{-1} in October 2006 and 187 000 m^3 d^{-1} in June 2007. Given the salinities of the coastal springs in October 2006 (average of 11.2) and June 2007 (average of 5.5), the fresh SGD portion can be estimated for both periods: 50 500 m^3 d^{-1} in October 2006 and 159 400 m^3 d^{-1} in June 2007. These fluxes for the Badum site would account for 29% to 91% of the hydrologically estimated SGD flux for the three main coastal areas of the Irta Mountains, i.e., Badum, Peníscola and Alcossebre (~175 000 m^3 d^{-1}; Serrano et al., 1995).

5.5 Variability in SGD estimates

Changes in rainfall constitute an important element responsible for seasonal variability observed in SGD, as recharge rates directly affect hydraulically-driven groundwater flow. In addition, the seasonality in precipitation will also influence the recirculated part of SGD, since migrations of the saltwater/freshwater interface with time in the "subterranean estuary" are controlled by seasonal changes in water table elevation (Michael et al., 2005).

Data on precipitation in the Maestrat Aquifer region was obtained from the pluviometric stations of the Spanish Meteorological Agency (AEMET) at Alcalá de Chivert ($40°\,17'$ N; $0°\,15'$ E, 200 m a.s.l.) and Vilafranca del Cid ($40°\,26'$ N; $0°\,15'$ W, 1130 m a.s.l.). Considering a 40 yr period (1965/66–2007/08), the average precipitation was 518 L m^{-2}, with important differences in precipitation between wet and dry years (a minimum of 315 L m^{-2} was recorded in 1993/94 and a maximum of 1003 L m^{-2} in 1971/72). More precisely, 2006 was an intermediate year (568 L m^{-2}) while 2007 was a relatively wet year (725 L m^{-2}). The monthly distribution of rainfall for 2006 and 2007 is shown in Fig. 11. Unlike June 2007, the October 2006 sampling was immediately preceded by a rainy month (Fig. 11). However, the fresh-SGD flux estimated in October 2006 was only a 32% of the flux calculated for the June 2007 period, revealing that SGD fluxes may not respond rapidly to precipitation. Conversely, the higher SGD estimate in June 2007 likely reflects the strong precipitation occurred in April of the same year (Fig. 11). By calculating the accumulated precipitation during several months previous to sampling, we obtained that the 2007/2006 precipitation ratio (3.2) agrees the 2007/2006 fresh-SGD ratio (3.2) when integrating three months (Table 4). This suggests that the estimated fresh-SGD fluxes respond the actual amount of freshwater infiltrated in the precedent ~3 months. This lag of approximately three months is somewhat shorter than the accounted values from other studies in non-karstic aquifers, which determined up to semi-annual lag effects when directly comparing SGD fluxes with precipitation maxima (Hu et al., 2006; Michael et al., 2005; Smith et al., 2008).

Regarding the SGD endmember temporal variability, we observed that coastal springs generally presented higher salinities in autumn than in summer months (Table 2). This points to a general weaker proportion of fresh SGD in autumn months due to a lower water table pressure (in response to dry summers), in addition to a smaller total SGD flux. Accordingly, spring's groundwater salinities were positive linearly correlated with short-lived radium activities (R^2=0.83 with p<0.0001 for [224]Ra and R^2=0.63 with p=0.002 for [223]Ra, figure not shown), i.e., higher radium activities in coastal springs were measured when lower SGD rates were estimated, which potentially allow a higher enrichment in radium activities.

5.6 Nutrient inputs via SGD

The fluxes of dissolved inorganic nutrients can be calculated by multiplying the SGD flux by the concentration of nutrients in the groundwater endmember. This method is strictly correct only in those instances when the sampled SGD endmember is located close to the water edge (as it is the case here), so that no further biogeochemical modifications of nutrient species occur in the subterranean estuary. The resulting total (new+recirculated) SGD-associated nutrient flows were 1500 and 8300 μmol m^{-2} d^{-1} of DIN and 19 and 40 μmol m^{-2} d^{-1} of DIP in the October 2006 and June 2007, respectively.

Given that basically rural areas without significant presence of intense farming and cattle activities surround Badum, no large anthropogenic pollutant load is expected in groundwater. Therefore, the estimated inputs of nutrients are presumably of mainly natural origin. Our calculated rate of DIP fits within the low part of the reported range in different regions (9–900 μM m^{-2} d^{-1}; Slomp and Van Cappellen, 2004), while the estimated DIN flux is consistent with the upper limit or even higher than other accounted natural inputs (160–2400 μM m^{-2} d^{-1}; Slomp and Van Cappellen, 2004).

DIN concentrations showed strong correlation with radium activities in the summer period (e.g., with ^{226}Ra: R^2=0.87, Fig. 13), in contrast with the situation in autumn (R^2=0.32, Fig. 13). The contrary trend is observed for DIP measurements, with a strong correlation in autumn (R^2=0.91) and a notably lower relationship in summer, R^2=0.62 (Fig. 13). This may suggest that physical mixing of SGD with seawater, rather than biological uptake or chemical reactions, is the prevailing process determining the nitrogen distribution in coastal waters in the summer survey. This is also in accordance with the shorter coastal water residence time in summer. The lower SGD flow estimated in autumn may allow incomplete denitrification reactions, given that the proportion of NO_2 (produced as intermediate compound) to NO_3 is higher (Uchiyama et al., 2000). The inverse behavior of DIP probably indicates that these concentrations in surface waters in the autumn period are entirely explained by seawater-groundwater mixing. In the summer time, phosphorus data are more scattered, potentially implying active biological uptake by phytoplankton communities in coastal waters, a process that is indeed activated by higher temperatures in that season. However, detailed investigations should be conducted to determine which mechanisms are actually responsible of the dissolved inorganic nutrient distributions in coastal waters.

According to the Redfield ratio (Si:N:P=16:16:1), the stoichiometric limitation criteria set by Justic et al. (1995) suggest that the Badum coastal waters would be limited by phosphorus (Si:N:P=16:12:0.2; Fig. 12), similar to other coastal areas in the NW Mediterranean region (Diaz et al., 2001). In karstic areas, P limitation may be driven by sequestration of P in calcareous sediments (Elser et al., 2007). Phosphorus has been reported as potentially having greater regulatory importance than nitrogen in several coastal areas (Bonin et al., 1989; Heiskanen et al., 1996; Mahoney, 1989). The estimated SGD associated fluxes of nutrients could indeed alter the nutrient equilibrium of the Badum biological community since coastal stations barely influenced by SGD (A7 in October 2006 and S16 in June 2007) presented Si:N:P ratios with higher N and P with respect to Si (i.e., 16:25:0.9 and 16:58:3.3, respectively) than all the other stations inside the fresher SGD plume (average of 16:22:0.1 in October and 16:23:0.3 in

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June). The latter are in turn more similar to those nutrient ratios in spring groundwater (16:7:0.09 in October and 16:31:0.16 in June). In addition, N:P ratios out of plume coastal waters (average of 16:0.6 in October and 16:0.9 in June) were closer to Redfield than coastal plume waters affected by SGD (average of 16:0.07 in October and 16:0.2 in June), which actually pointed to P limitation.

6 Conclusions

Radium isotopes have been used, together with DSi and major elements distribution, to investigate SGD through karstic springs into the coastal area of Badum (Castelló, Spain) in two different periods: October 2006 and June 2007. Salinity profiles evidenced a strong density gradient with a fresher surface layer of 40 cm produced by SGD. This fresher plume was recorded by thermal infrared images in June 2006, and resulted to be similar in size than the plume estimated from salinity measurements in June 2007 ($2.1\,\mathrm{km}^2$) while the area influenced by SGD was of about $1.3\,\mathrm{km}^2$ in October 2006. Short-lived radium isotopes have been used to estimate water apparent ages for the study site, resulting in 2.7 d in October and 2.0 d in June. By applying a mass balance model for radium, DSi and major elements in the coastal area, the brackish groundwater fraction of the plume waters averaged 36±3% in October 2006 and 44±3% in June 2007. These estimates allowed us to calculate a total SGD flux of $71\,400\,\mathrm{m}^3\,\mathrm{d}^{-1}$ in October 2006 and $186\,500\,\mathrm{m}^3\,\mathrm{d}^{-1}$ in June 2007, the respective fresh-SGD proportions being 71% and 85%. The higher SGD rate calculated in summer is in agreement with the elevated precipitation occurred in the preceding months. Indeed, SGD can be related to the precipitation occurred during the three months preceding each sampling. This lag between coastal groundwater discharge and precipitation events suggest that the mean residence times of fresh groundwater in the aquifer would be of the same order. The SGD fluxes are also used to estimate the associated input of DIN and DIP to the coastal area, which turned out to be around 1500 and $8300\,\mathrm{mM\,m}^{-2}\,\mathrm{d}^{-1}$ of DIN and 19 and $40\,\mathrm{mM\,m}^{-2}\,\mathrm{d}^{-1}$ of DIP in the autumn and summer

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periods, respectively. These, presumably natural, inputs of nutrients are delivered to the sea with a clear depletion of P (Si:N:P in brackish spring groundwater of 16:7:0.09 in October and 16:31:0.16 in June), which may induce or increase P limitation in the coastal waters and, therefore, alter the structure of biological communities in the region.

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Table 1. Temperature, salinity, radium activities and nutrient concentrations for all the stations samples in October 2006 and June 2007.

Station number	T (°C)	Sal	Ra activity (dpm $100\,\mathrm{L}^{-1}$)				Nutrient concentration (µM)		
			^{223}Ra	^{224}Ra	^{226}Ra	^{228}Ra	DIN	DIP	DSi
Oct sampling (24 Oct 2006)									
Surface coastal waters									
A1	20.4	27.1	10.1±1.1	111±7	130±2	91±2	23.77	0.13	25.3
A2	20.2	25.3	10.2±1.7	132±7	142±2	100±2	37.60	0.17	32.67
A3	20.0	23.5	10.5±0.8	156±7	142±6	114±3	34.50	0.18	35.75
A4	21.1	30.2	7.6±0.9	90±6	104±5	69±2	20.76	0.11	18.59
A5	20.8	28.6	8.1±1.4	105±5	121±5	87±2	24.94	0.13	19.25
A6	21.3	32.0	4.6±0.5	76±3	87±4	57±2	26.36	0.11	14.19
A8	21.3	33.0	4.4±0.4	73±3	71±3	50±2	28.18	0.08	13.09
Average coastal waters									
	20.7	28.5	8±2	106±30	114±27	81±23	28.0	0.13	22.7
Springs									
A-SP1	19.4	13.7	13.2±1.2	227±11	254.1±1.5	185±4	28.48	0.36	66.22
A-SP2	19.1	8.7	21.5±1.6	253±12	261.5±1.7	212±4			
Seawater: out of the fresher plume water									
A7	21.8	38.2	2.2±0.4	19.0±1.6	32±2	8.7±1.7	2.30	0.08	1.46
Jun Sampling (4–6 Jun 2007)									
Surface coastal waters									
S1	20.1	28.3	4.8±0.3	54±2	64.9±1.4	42.8±1.7	24.22	0.29	20.79
S2	21.2	32.2	3.8±0.2	53.3±1.8	52±2	34.4±1.7	19.57	0.39	13.53
S3	20.1	18.9	6.2±0.7	98±3	119±5	87±3	38.08	0.34	21.12
S4	21.7	28.0	4.7±1.1	63±9	73±3	56.2±1.9	20.83	0.44	16.83
S5	21.8	33.8	2.8±0.2	32±2	37.8±1.8	25.6±1.1	13.69	0.35	10.56
S6b	19.0	16.8	5.1±0.6	124±4	137±6	104±3	56.34	0.39	36.63
S7	19.8	26.9	4.1±1.0	74±10	63.8±1.5	46.3±1.7	34.25	0.38	30.69
S8	19.1	21.7	6.0±0.4	95±3	113.2±1.8	79.6±1.7	50.94	0.4	36.85
S9	19.5	16.6	8.8±0.5	108±4	118±6	96±3	69.55	0.44	46.64
S10	19.2	22.3	6.1±0.7	80±3	109±5	79±2	46.35	0.36	32.89
S11	19.1	21.0	7.2±1.8	92±13	77.7±1.7	74±3	50.80	0.39	35.75
S12	19.6	27.7	4.4±0.4	57±2	55±3	58±3	32.07	0.34	26.07
S13	19.0	19.3	7.0±0.4	117±3	119±5	91±2	44.06	0.37	31.79
S14	18.8	14.5	8.7±1.0	127±4	154±7	105±3	59.47	0.43	42.9
S15	20.9	37.0	1.6±0.4	23±7	20.5±1.3	15.0±1.5	7.30	0.23	3.18
S17	21.4	27.0	4.2±0.3	67±2	66.0±1.2	49.7±1.2	27.33	0.27	22.88
S18	20.2	23.3	4.9±0.3	96±3	75.5±1.8	66±2	38.70	0.32	28.27
Average coastal waters									
	20.0	24.4	6±2	86±40	85±40	63±29	37.3	0.36	26.9
Coastal waters at 50 cm depth									
S8 −50	36.3	20.4	2.5±0.3	32.3±1.3	22.1±1.6	15.0±1.4	10.36	0.27	8.14
S11 −50	36.0	20.6	2.3±0.2	29.9±1.0	25.0±0.7	16.1±1.0	9.00	0.25	9.57
S13 −50	36.0	21.1	2.2±0.2	31.0±1.1	23.1±0.7	14.8±1.0	9.61	0.26	5.52
Springs									
S-SP1	18.4	5.5	9.6±1.3	158±8	189±9	140±4	114.10	0.53	57.09
S-SP2	18.2	5.5	3.1±1.0	175±25	157±3	139±5	74.74	0.38	36.19
Seawater: out of the fresher plume water									
S16	21.6	37.8	0.9±0.2	6.9±0.6	16.1±0.6	7.6±0.7	4.02	0.23	1.11

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Table 2. Temperature, salinity, radium activities and nutrient concentrations for the monthly collected brackish springs.

monthly springs	T (°C)	Sal	Ra activity (dpm 100 L^{-1})		Nutrient concentration (µM) (±0.01)		
			^{223}Ra	^{224}Ra	DIN	DIP	DSi
2007							
Mar	18.9	9.4	14.2±1.6	284±22	69.37	0.16	47.74
Apr	17.5	6.9	12.3±1.4	233±18	55.32	0.37	41.14
May	18.1	5.0	10.1±1.3	177±12	52.49	0.44	44.55
Jun	18.2	5.5	9.6±1.3	158±8	74.74	0.38	36.19
Jul	18.2	5.6	9.1±1.3	164±9	72.08	0.34	44.33
Aug	18.3	6.4	12.7±1.5	217±14	58.88	0.68	90.31
Oct	19.1	8.4	11.7±1.0	261±15	87.25	0.28	39.27
Nov	18.9	8.0	11.4±1.1	265±24	59.05	0.28	47.96
Dec	18.7	8.8	14.4±1.6	263±14	100.53	0.54	63.25
2008							
Jan	17.7	5.2	9.4±0.8	183±9	97.59	0.45	77.22
Feb	18.1	5.5	9.2±0.8	195±9	59.61	0.49	70.84

Table 3. Coastal plume water fractions of brackish groundwater (f_{gw}) and seawater (f_{cs}) derived from the mixing models with the set of tracers.

Equations	Oct 2006		Jun 2007	
	f_{gw}	f_{cs}	f_{gw}	f_{cs}
^{226}Ra	0.36	0.64	0.44	0.56
^{228}Ra	0.38	0.62	0.44	0.56
DSi	0.33	0.67	0.51	0.49
Cl	0.37	0.63	0.41	0.59
S	0.37	0.63	0.42	0.58
Ca	0.31	0.69	0.44	0.56
K	0.32	0.68	0.41	0.59
Br	0.36	0.64	0.43	0.57
Sr	0.39	0.61	0.43	0.57
f_{gw} average	0.36±0.03		0.44±0.03	

Table 4. Accumulated precipitation during the previous months before sampling in October 2006 and June 2007 and ratios between samplings.

| | Accumulated precipitation in previous to sampling months ($L\,m^{-2}$) | | | | |
	2 months	3 months	4 months	5 months	6 months
Oct 2006	79	92	108	144	157
Jun 2007	238	300	320	361	368
2007/2006 ratio	3.0	3.2	3.0	2.5	2.3
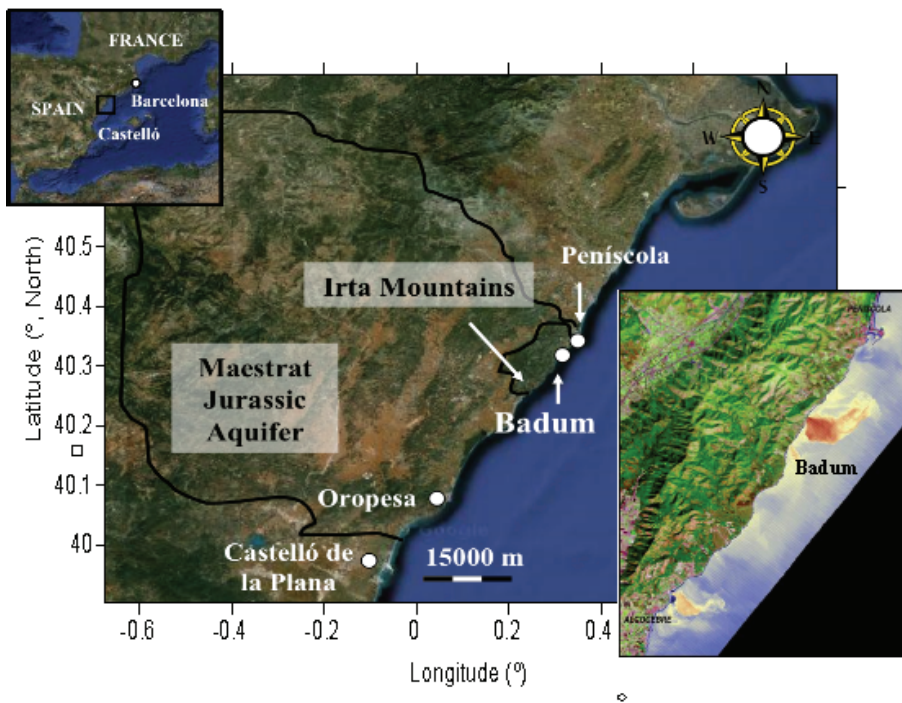
Fig. 1. Location map of the Badum coastal area, which resides inside a natural protected region (Irta Mountains). The extension of the main carbonate Maestrat aquifer is also delimited. The down-right inset shows the thermal infrared image of the area taken on June 2006 (from Antón-Pacheco et al., 2007).
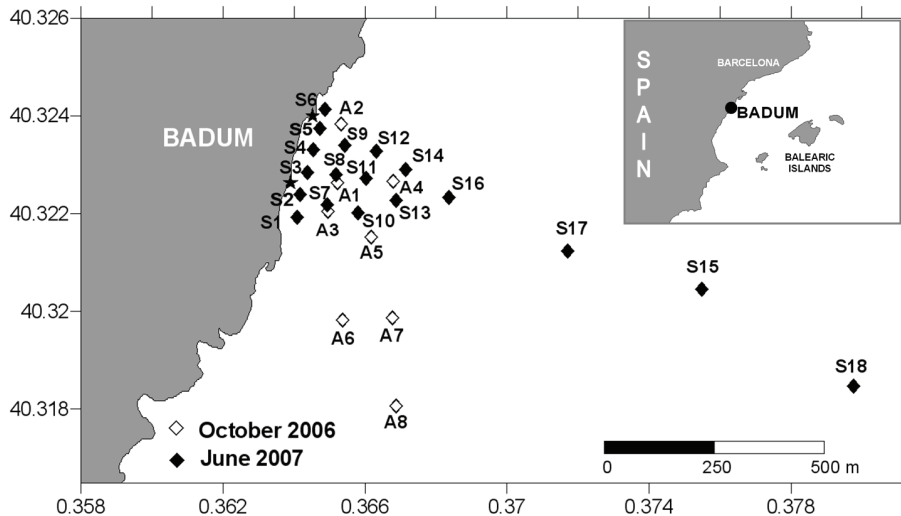
Fig. 2. Water stations in the Badum coastal area corresponding to October 2006 (open diamonds) and June 2007 samplings (solid diamonds). The stars indicate the sampled coastal springs.
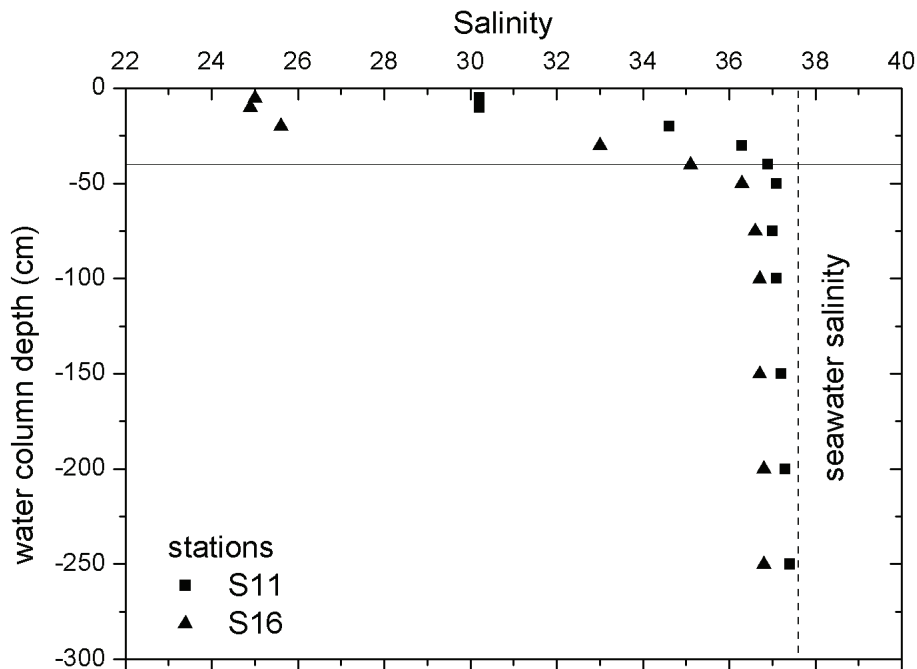
Fig. 3. Salinity profiles evidencing a fresher, less dense layer of 40 cm in June 2007.
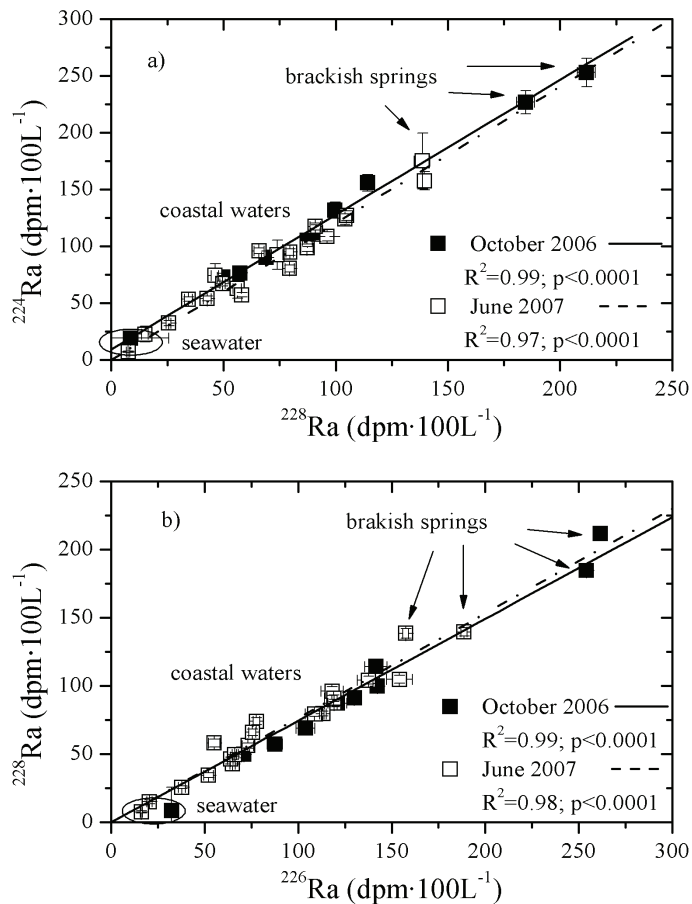
Fig. 4. ^{224}Ra vs. ^{228}Ra **(a)** and ^{228}Ra vs. ^{226}Ra **(b)** plots for surface coastal waters, seawater and coastal springs. The strong positive linear correlations among them suggest surface waters are affected by binary mixing between seawater and spring groundwater.
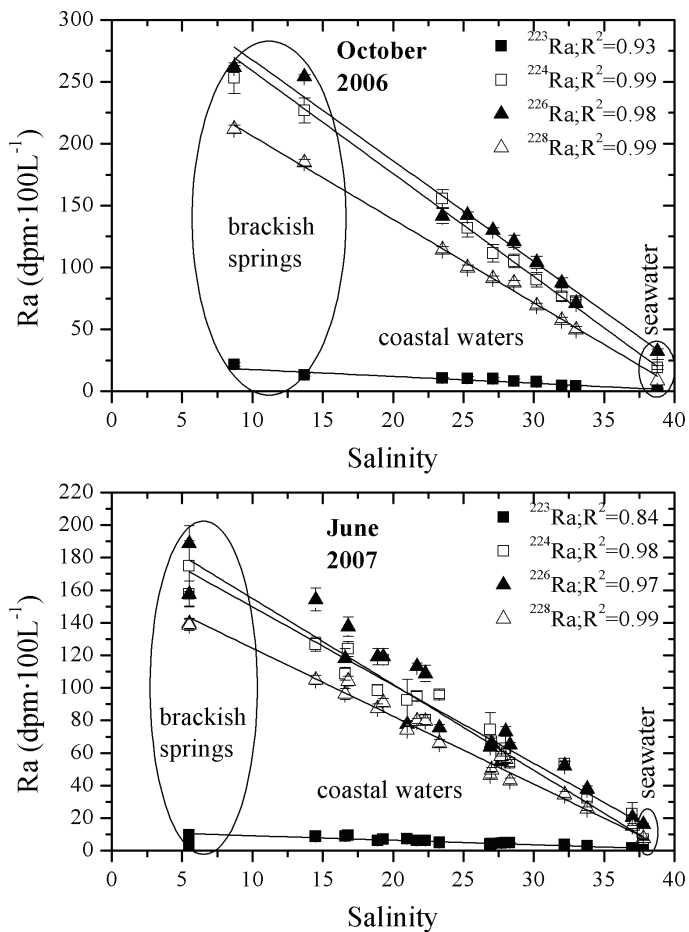
Fig. 5. Ra versus salinity plots for surface coastal waters, seawater and brackish spring ground-water samples indicating a mixing pattern of two end-members: seawater and groundwater.
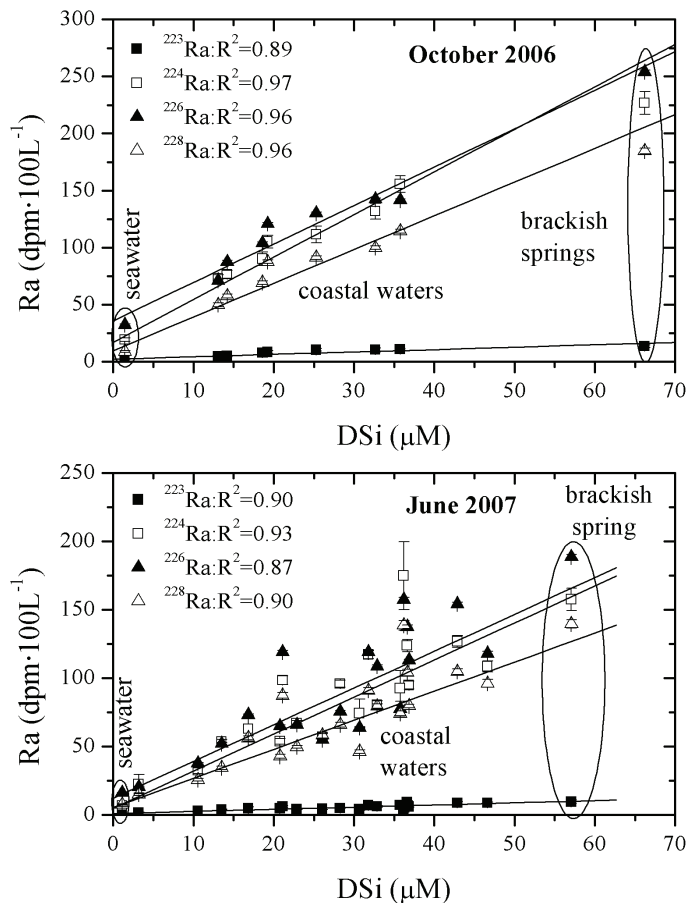
Fig. 6. Radium activities plotted against dissolved inorganic silica (DSi). Positive linear correlations are observed for all isotopes in October 2006 and June 2007, pointing to a conservative behavior of DSi once released from coastal brackish springs.
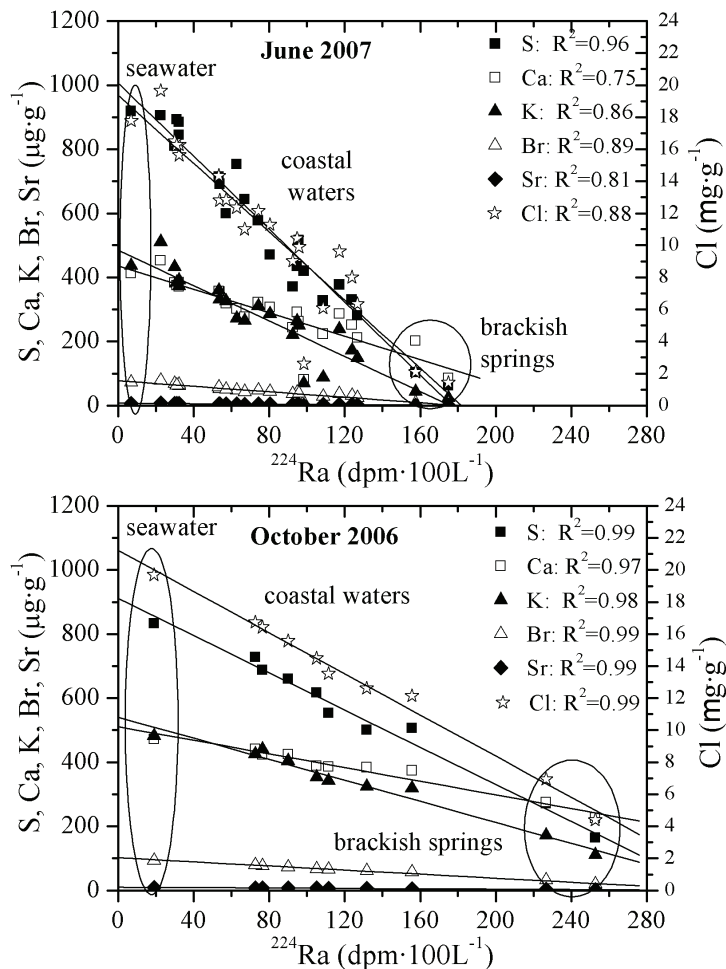
Fig. 7. Major element composition versus ^{224}Ra activities for October 2006 and June 2007.

Fig. 8. Picture of the Badum coastal area showing the rock fissuration of the karstified Maestrat aquifer that allows coastal springs to occur.
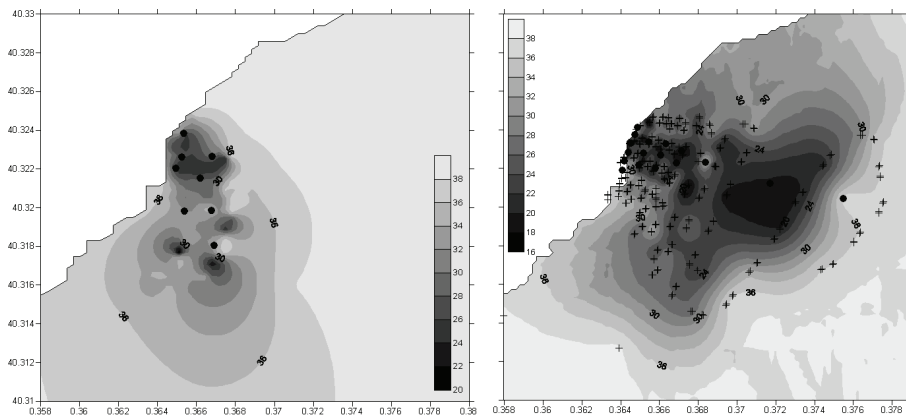
Fig. 9. Salinity contour plots for Badum surface coastal waters in October 2006 (left side) and June 2007 (right side).
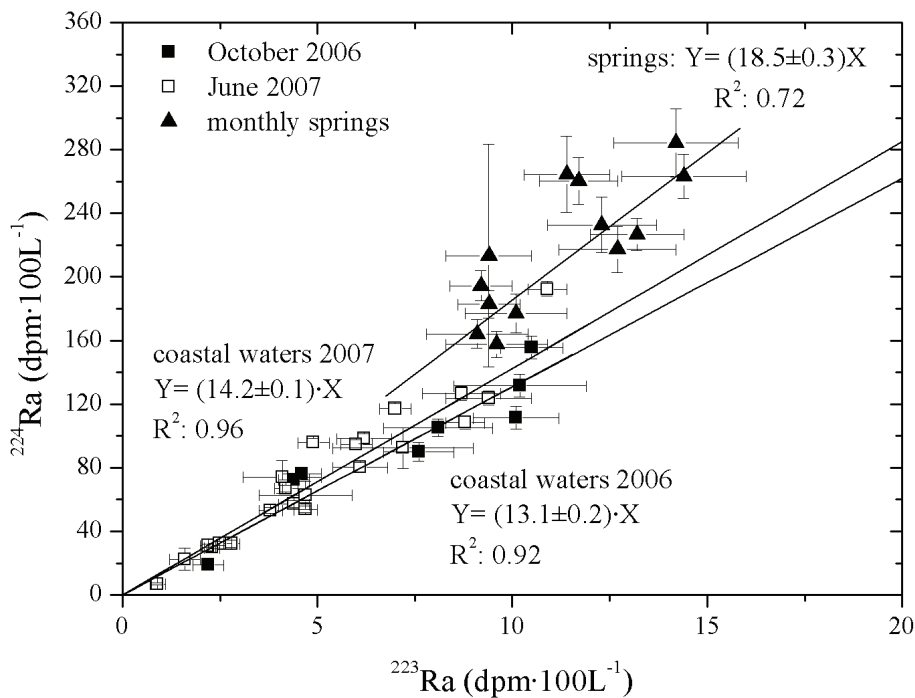
Fig. 10. ^{224}Ra activities plotted versus ^{223}Ra in surface waters from October 2006 and June 2007 and the monthly collected brackish springs. The best-fit lines for the three cases are also specified.
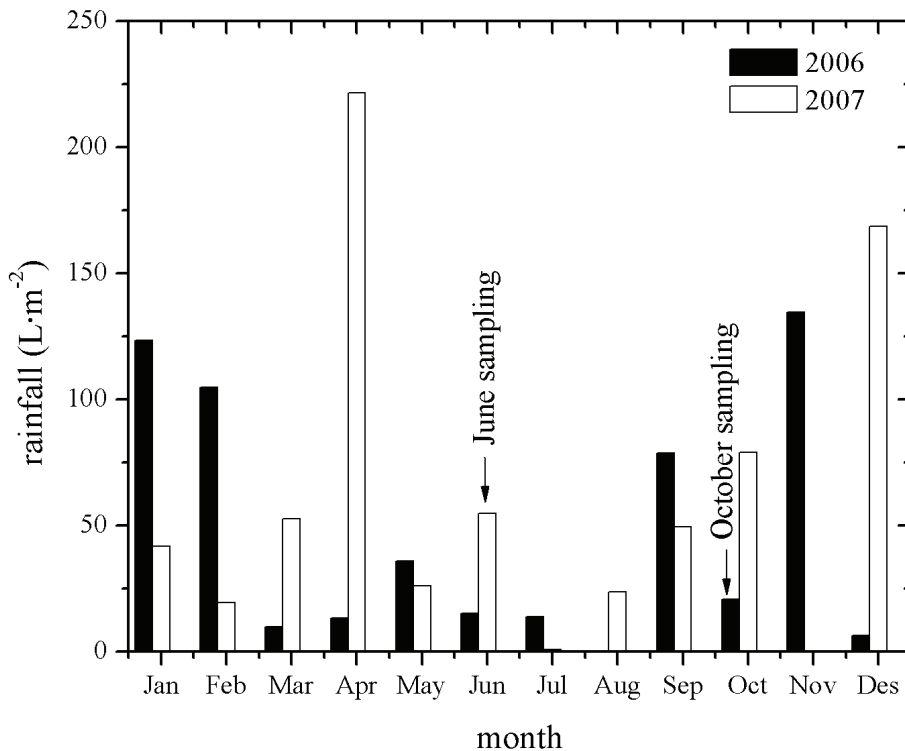
Fig. 11. Monthly precipitation in the Badum area during 2006 and 2007. The dates of the sampling campaigns are indicated. The highest precipitation peak was observed in April 2007, while September 2006 also represented, to a lesser extent, a wet month.

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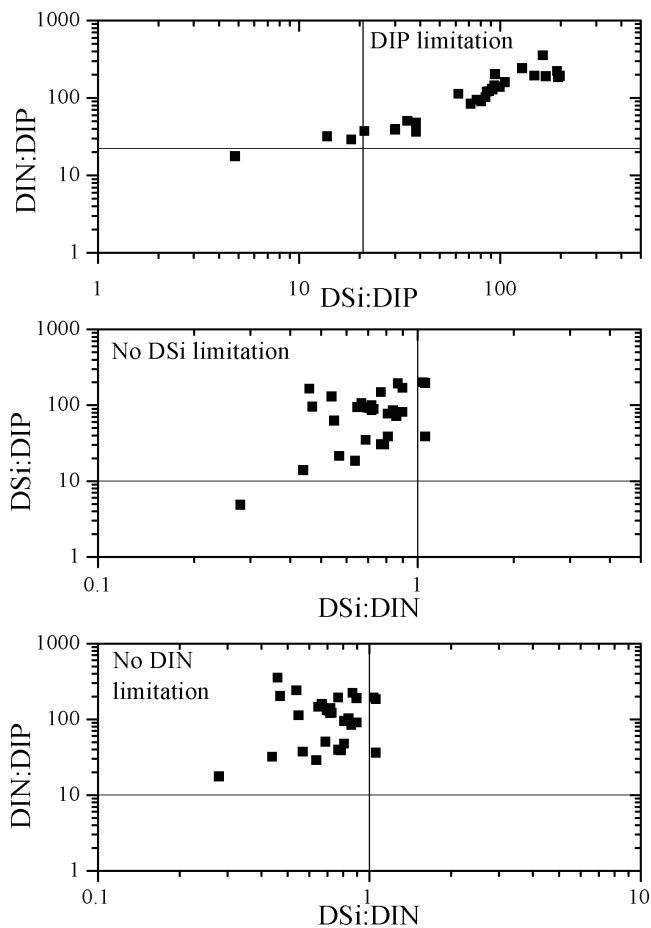
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Fig. 12. Nutrient ratios diagrams for Badum coastal water samples suggesting phosphorus limitation.

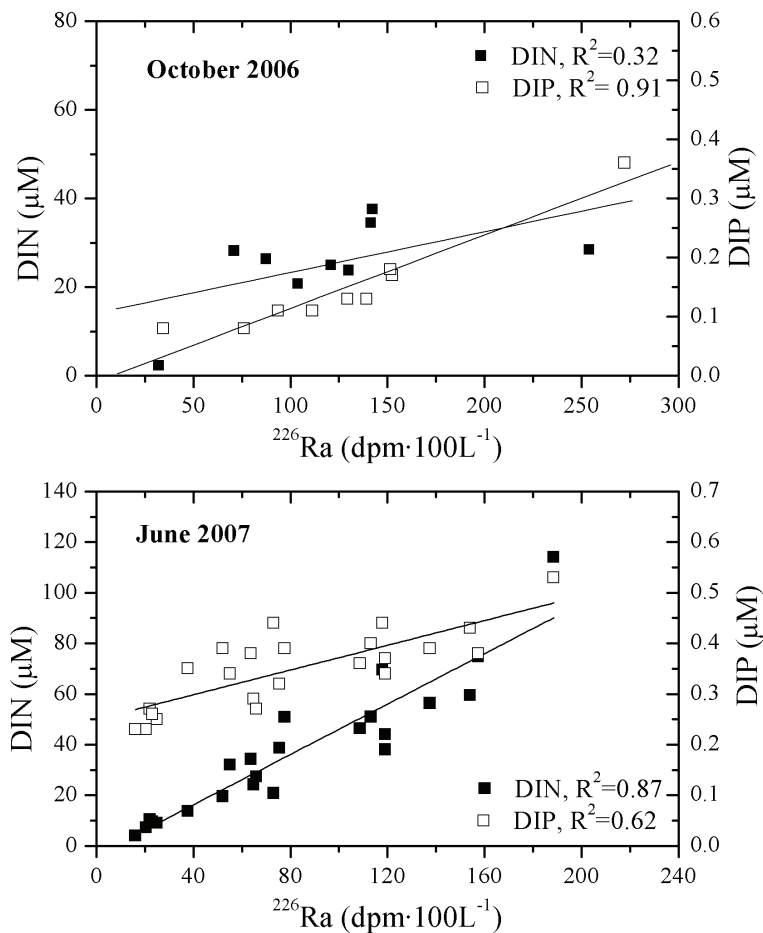**Fig. 13.** DIN (solid squares) and DIP (open squares) versus ^{226}Ra for coastal waters in October 2006 and June 2007 surveys.

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