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ORIGINAL RESEARCH ARTICLE

Identifying the main sources of silicate in coastal waters of the Southern Gulf of Valencia (Western Mediterranean Sea)

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Summary Silicon is a major nutrient for siliceous primary producers, which can become a potential limiting nutrient in oligotrophic areas. Most of the silicon inputs to the marine environment come from continental discharges, from both superficial and ground waters. This study analyses the main sources of silicon and their dynamics along the southernmost 43 km of shoreline in the Gulf of Valencia (Western Mediterranean Sea). The salinity and silicate concentration in the different compartments (springs, freshwater wells, beach groundwater, surf zone and coastal waters) in this coastal area were determined. In addition, chlorophyll *a* and phytoplankton community were analyzed in the surf zone and coastal waters. Silicate concentrations in freshwater wells ranged between 130 and 150 μM, whereas concentrations of this nutrient declined to 49 μM in freshwater—seawater mixture transects. At the same time, there was a positive gradient in silicate for both freshwater and coastal waters southward. An amount of 18.7 t of dissolved silicate was estimated in the nearest first kilometre nearest to the coastline, 6 t of this silicate belonged to the background sea level. On the other hand, the sum of the main

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rivers in the area supplies 1.6 t of dissolved silicate per day. This implies that a large amount of the remaining 11.1 t must derive from submarine groundwater discharges, which would thus represent 59% of the coastal dissolved silicate budget. Overall, it is suggested that a subterranean transport pathway must contribute considerably to silicate concentrations throughout this zone, which is characterized as permeable.

1. Introduction

The Mediterranean Sea is an oligotrophic sea as a consequence of general water circulation (Schroeder et al., 2010; Zenetos et al., 2002). High evaporation exceeds freshwater inputs due to surface water warming and to the low humidity of continental winds. A significant surface inflow enters the Mediterranean basin through the Strait of Gibraltar to compensate for evaporation losses, producing a water exchange as a deep layer of water flows from the Mediterranean Sea to the Atlantic Ocean (Bergamasco and Malanotte-Rizzoli, 2010). Consequently, the nutrient balance between the Atlantic Ocean and the Mediterranean Sea generates a deficit in the latter. The surface flow entering the Mediterranean basin is poor in nutrients. Conversely, the Mediterranean Sea is continuously losing a large amount of nutrients through the nutrient-rich deep current that heads into the Atlantic Ocean, since solutes tend to accumulate in deeper layers (Crispi et al., 2001; Hopkins, 1985). For example, in the Strait of Gibraltar, silicate concentrations in the surface (Atlantic) waters and in the deep (Mediterranean) waters are around 2.7 and 7.7 μM respectively (Dafner et al., 2003).

Regarding nutrients, the demand for silicon by primary producers is not as great as it is for phosphorus or nitrogen. Nevertheless, the cycle of this nutrient has acquired significant attention in relation to its role in marine primary production in recent decades (Dugdale and Wilkerson, 2001; Smetacek, 1999). Only diatoms, one of the most abundant taxonomic groups of phytoplankton which play an important role in organic matter export to the deep sea, require silicon as much as nitrogen and phosphorus for their development (Buesseler, 1998; Goldman, 1993; Nelson et al., 1995). Other planktonic groups that present silification are chrysophytes and silicoflagellates, but their quantitative importance in the silicon cycle is secondary. Silicon concentrations in the Mediterranean Sea are generally low, around 1—4 μM due to its oligotrophy (Marty et al., 2002; Ribera d'Alcalà et al., 2009; Schroeder et al., 2010), decreasing to 0.003 μM in the Northeastern Levantine basin (Aktan, 2011).

In the Northwestern sub-basin of the Mediterranean Sea, phosphorus is considered to be the potential limiting nutrient (Gadea et al., 2013; Lucea et al., 2005; Sala et al., 2002). However, when silicon is also taken into consideration as a limiting element, which is the case for siliceous primary producers, silicate limitation may have become a widespread phenomenon in the Mediterranean Sea (Ludwig et al., 2009). For instance, Olivos et al. (2002) concluded that silicate acts as a potential limiting nutrient in over 50% of cases, with percentages as high as 75% for stations sampled near the coast (0.5—2 km), in their study carried out in the Catalan Sea (Northwestern Mediterranean Sea). Gadea et al. (2013) noted that the phytoplankton community in the southern sector of the Gulf of Valencia was dominated by diatoms mainly in autumn, winter and summer. Furthermore, they considered phosphorus as a potential limiting nutrient in the area, although silicon could also act as a limiting nutrient in over 30% of cases during winter campaigns.

Currently, the most important sources of dissolved silicate in the global ocean come from the continental fluvial system and from groundwater discharges, according to Frings et al. (2016). These inputs are mainly: dissolved silicate in rivers (60%), the dissolution of river particulate matter (20%) and groundwater (7%). The remaining silicate reaches seawater from atmospheric depositions, and from seabed alterations, or is washed there.

Rivers are important sources of freshwater and nutrients for the Mediterranean Sea. Many studies have pointed out that Mediterranean rivers have suffered a significant reduction in freshwater discharges between 1960 and 2000 (Ludwig et al., 2009; MED-HYCOS, 2001; Vörösmarty et al., 1998). This is in part due to more severe hydrological droughts, but mainly to the construction of dams, reservoirs and hydroelectric power plants, and flow derivation (García-Ruiz et al., 2011; Nixon, 2003). A similar decrease could also be expected for the fluxes of dissolved silicate, which are highly dependent on water discharges and potentially reduced by river damming as well (Conley et al., 2008; Humborg et al., 1997). Contrariwise, the fluxes of nitrogen and phosphorus in the Mediterranean Sea, have been significantly enhanced by anthropogenic sources (Howarth et al., 1996; Ludwig et al., 2009).

Submarine groundwater discharge (SGD) has been recognized as one of the largest sources of macro- and micronutrients in the coastal environment (Krest et al., 2000; Moore, 1999; Niencheski et al., 2007; Santos et al., 2008; Windom et al., 2006). Generally, nutrient concentrations in SGD are much higher than in rivers, compensating for the lower flow of groundwater in comparison with superficial runoff. Consequently, SGD transports nutrient amounts into the ocean that are comparable to superficial runoff inputs, or even higher, as is the case for the coast of Southern Brazil (Niencheski et al., 2014), the Eastern Florida Bay (Corbett et al., 1999, 2000) and the salt marshes on the South Carolina coast (Krest et al., 2000). In particular, Rodellas et al. (2015) found that along the entire Mediterranean coast silica inputs associated with SGD are comparable, in magnitude, to those from rivers.

Globally, atmospheric inputs represent *ca.* 3% of silicon discharges into oceans (Frings et al., 2016). In the Mediterranean region, a great number of studies about atmospheric depositions and their implications for primary production have been carried out. However, most of these researches have focused on nitrogen, phosphorus and trace metal inputs into the sea (Carbo et al., 2005; Guerzoni et al., 1997, 1999; Koçak et al., 2004; Theodosi et al., 2010). With regard to silicon, Koçak et al. (2010) stipulate that atmospheric inputs of this nutrient can represent up to 10% in the Northeastern Levantine basin of the Eastern Mediterranean Sea. On the other hand, de Fommervault et al. (2015), studying the Northwestern area of the Mediterranean Sea, highlight the insufficient amount of data (post 1990) of atmospheric deposition in order to draw conclusions. A single dust deposition event of short duration could represent up to 30% of the total annual flux for Si (Bergametti et al., 1989) due to the proximity of the Sahara in this Western basin.

The southern sector of the Gulf of Valencia (Western Mediterranean Sea) is characterized by oligotrophic conditions (Gadea et al., 2013; Sebastiá et al., 2013; Sebastiá and Rodilla, 2013) so nutrient inputs from various sources play a key role in marine productivity. However, in the case of silicon, many questions still need to be investigated in our study area: what is its origin? Is the silicate discharged by rivers enough to supply diatom populations? Otherwise, what are the other sources? In order to answer these questions, the present study aims to investigate silicate concentrations along the coastal zone of the southern sector of the Gulf of Valencia, and to identify the main sources. For this purpose, silicate concentrations were analyzed in different compartments throughout the studied area: in groundwater, in the main rivers, and in the coastal marine area. Furthermore, the silica requirement by phytoplanktonic microorganisms in coastal waters was also explored.

2. Study area and methods

2.1. Study area

The study area falls within the southernmost sector of the Gulf of Valencia and covers about 43 km of coastline from Cullera Cape to about 5 km south of the Racons River (Fig. 1). The Gulf of Valencia is in the Balearic Sea, Western Mediterranean Sea, off the eastern coast of Spain. The coastal area of this gulf is characterized by the dominance of sand barriers and coastal lagoons (quaternary origin) in which sand spits have formed on both sides of river mouths (Albarracín et al., 2013). The material deposition carried out by rivers over time has augmented the silting of coastal lagoons in this area, until they have become shallow swamps (Dupré et al., 1988). Representative examples of these habitats in the southern sector of this gulf are (from north to south) Valencia Albufera, the Southern Júcar, Safor, and Pego-Oliva wetlands (represented in dotted shading in Fig. 1).

Sandy beaches along the southern sector of the Gulf of Valencia border with fertile lowlands that are dedicated to rice crops and irrigated agriculture (mainly citrus fruits and vegetables) (Rico-Amorós and Hernández-Hernández, 2008; Sebastiá et al., 2012b). However, much of the territory has suffered from the process of urbanization (this is one of the most densely inhabited and touristic areas in Spain), which has occupied the barrier dunes and some floodable areas (Zornoza-Gallego, 2013).

The rivers that discharge into the sea along these 43 km are (from north to south) the Júcar, Serpis, Vedat and Racons (Fig. 1).

The Júcar and Serpis Rivers, of 508.8 and 74.5 km in length respectively, have a Mediterranean regime characterized by high seasonality, with a dry period during the summer, and a wet period with torrential downpours mainly in autumn (Falco et al., 2007; Sebastiá et al., 2013). In addition to the Mediterranean climate, these rivers undergo artificial regulation and intensive water use, leading to a situation of no permanent flow in their final sections.

The Júcar River is strictly controlled by dams, due to intensive agricultural exploitation upstream. This results in a flow that decreases along the river, until it disappears completely during some periods of the year at the last gauging station (the Cullera irrigation dam) belonging to the Júcar Hydrographic Confederation (CHJ) situated 14 km from the river mouth. Júcar river flow data for the last 10 years (from January 2006 to January 2016) was obtained from the Cullera gauging station (CHJ, 2016). In addition, the volume of water destined to the Cullera Community of Irrigators (CHJ, 2015) has to be subtracted from the flows that come to this dam, resulting in an average flow to the sea of 1.42 $m^3 s^{-1}$, over the last 10 years (2006—2016). This value may still be overestimated due to the presence, downstream, of the Júcar-Vinalopó diversion (currently with operating problems) and two motors which are also able to pump water from the river for irrigation (Cullera Community of Irrigators, personal communication).

The Serpis River and its tributary the Vernissa River are artificially regulated by a complex system of weirs and irrigation channels that provide freshwater for the irrigated crops of the Safor County. The estimated average flow (from the union of these rivers (CHJ, 2016) minus the extraction for irrigation systems, CHJ, 2015) that reached the sea was 1.94 $m^3 s^{-1}$ for the period between 2006 and 2016.

The Racons and Vedat Rivers, unlike the previous waterways, are short rivers of about 7 km that drain water from the Pego-Oliva wetland. Both rivers are mainly fed by springs and pumping drainage. For the period of 2004—2011, mean flows were estimated as 1.62 and 1.93 $m^3 s^{-1}$ in the Vedat and Racons Rivers respectively (IGME and DPA, 2013).

Regarding aquifers, in the study area, the Betic and Iberic structural domains meet (Rey and Fumanal, 1996), creating contact between the south of the Plana Valencia hydrogeological system — which is part of the Iberic domain — and the Prebetic of Valencia-Alicante hydrogeological system — which belongs to the Betic domain (IGME, 1989). These two hydrogeological systems can be observed in Fig. 1. In the northernmost region within the study area, the aquifer of the Southern Júcar wetland (Cullera) belonging to the Plana Valencia hydrogeological system, borders the Mediterranean Sea. Various subsystems can be distinguished in the Prebetic of Valencia-Alicante hydrogeological system, although the Plana Gandia-Dénia is the only one that comes into contact with the Mediterranean Sea in our study area. In the Plana Gandia-Dénia subsystem (250 km^2 extension), two aquifers can be identified: Xeraco-Gandia and Oliva-Pego. All these detritic aquifers in the study area are rich in nitrate, with

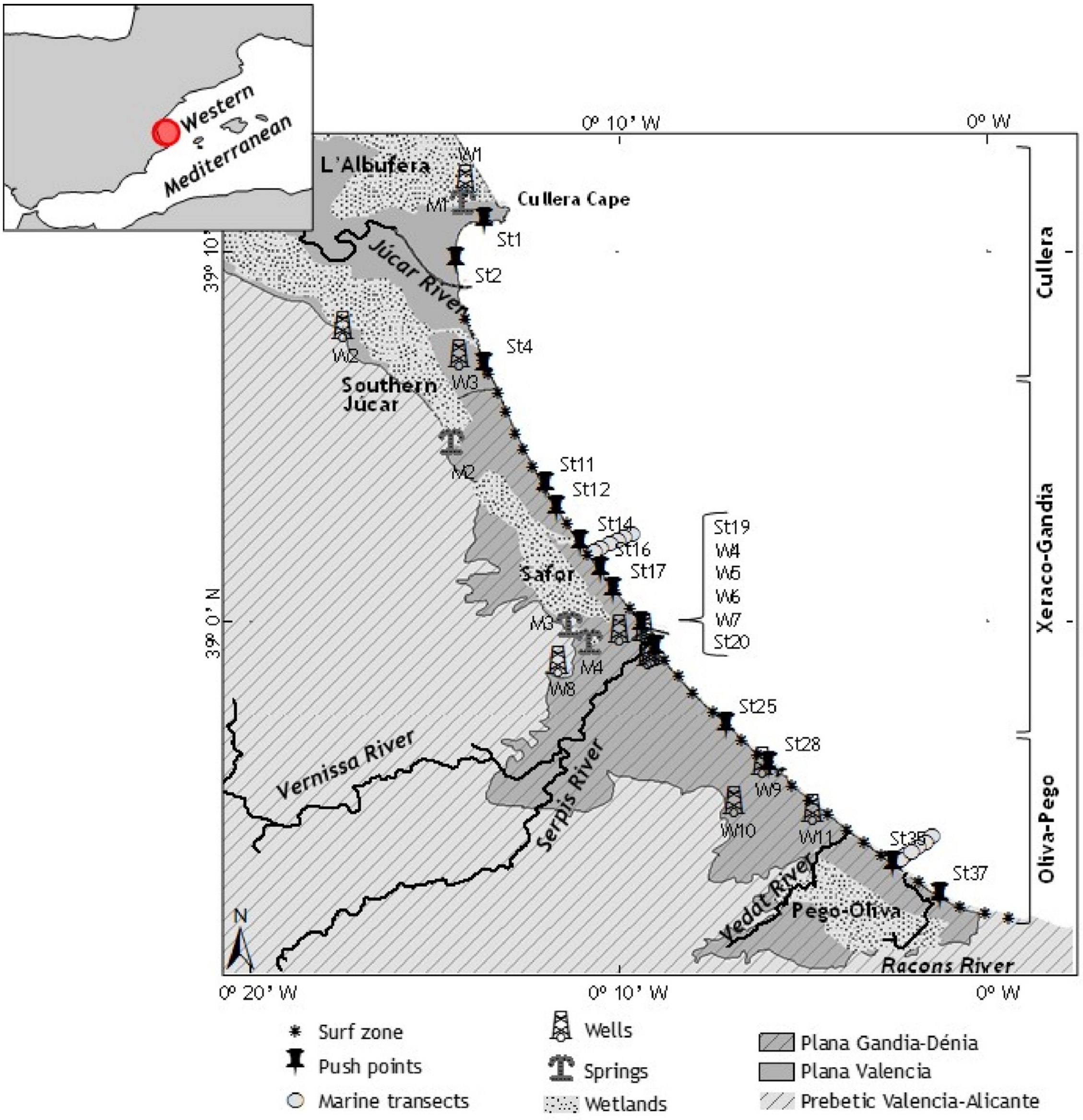

Figure 1 Study zone (asterisks and pins from St2 to St38: 2008 surf zone; pins: 2009 and 2013 push-point transects; circles: 2010 and 2013 sea transect; springs: 2013 springs; wells: 2013 permanent wells). St: sampled stations; W: sampled permanent freshwater wells; M: sampled springs.

values above 50 mg L^{-1} and even 200 mg L^{-1} in some zones (IGME and DPA, 2007; IGME, 1989; Pernía et al., 1996). The recommended nitrogen doses for citrus and horticultural crops have historically been exceeded in this area (MARM, 2010). In consequence, both surface runoff and groundwater flow are characterized by high nitrate concentrations and the areas have been declared as Nitrate Vulnerable Zones (MARM, 2010).

2.2. Field and laboratory methods

Various sampling campaigns were conducted in the study area between 2008 and 2013 (Table A in the online information). Sampling was designed taking into account that the Iberian Mediterranean rivers are characterized by high seasonality because of rainfall-based flow regime with maxima in autumn and spring and a minimum in summer (Sabater et al., 2009). For this reason, our sampling campaigns were carried out in autumn (two sampling campaigns in November 2008 and 2009), spring (June 2010 and March 2013) and the dry season (August 2012 and 2013).

The first sampling campaign was carried out in November 2008 (6th and 7th). Owing to the lack of a balanced spatial distribution of DSi data in the study area, 39 stations in the surf zone were sampled along 43 km of shoreline, approximately one at each kilometre along the entire shoreline, from St2, close to Cullera Cape, to St40, 5 km south of the Racons River (Fig. 1). These samples were analyzed for salinity, dissolved silicate (DSi) and chlorophyll *a* (Chl-*a*).

A new sampling campaign was designed in November 2009 (from 9th to 16th). The aim of this campaign was to cover the entire study zone, with focus on the central area. Water samples were once again collected from the surf zone, in 11 of the previously sampled stations plus one more (St1) that was sampled for the first time at the northern part (pins St1, St2, St4, St11, St12, St14, St16, St17, St20, St25, St28 and St37 in Fig. 1). Perpendicular transects to the shoreline on the beach were also carried out in this campaign for sampling groundwater with a push-point piezometer system. Beach groundwater samples (1 m deep) were collected from the surf zone at 5, 10, 20, 30, 40, 50 and up to 70 m inland. This sampling strategy was aimed to obtain a groundwater salinity gradient, to verify if the biogeochemical processes behaved conservatively or not. Salinity and DSi were analyzed in all samples. Additionally, Chl-*a* and phytoplankton composition were determined in the surf zone samples.

In order to complete our dataset on the distribution of silicate in the coastal marine environment, two perpendicular transects to the coast (circles in St15 and St35, Fig. 1) were carried out in June 2010 (8th and 9th) at approximately 0, 400, 700, 1000, 1350, 1800 and 2100 m. Moreover, samples from the surf zone were collected in seven stations (St3, St8, St15, St22, St29, St35 and St40). Salinity, DSi and Chl-*a* were analyzed in all these samples.

In addition, in August 2012 and 2013, seawater samples were taken along 4 km of the southernmost shoreline, between the stations St32 and St37. In total, 13 points were collected: five at a distance of 200 m from shoreline, two points at 400 m, three at 600 m and three points at 800 m from the shore. Salinity, DSi, Chl-*a* and phytoplankton composition were analyzed in each sample.

The results acquired in the previous campaigns were decisive in the development of a more comprehensive sampling method in March 2013. This sampling campaign included 11 permanent groundwater wells (W1—W11), 4 springs (M1—M4) and 5 push-points (1 m deep) drilled at variable distances (between 20 and 40 m) across the beach to collect beach groundwater at intermediate salinity (between 10 and 15), at the stations St2, St15, St19, St25 and St35. Moreover, a perpendicular transect to the shoreline was sampled (at 0, 50, 100, 150, 200, 250, 300 m) in the sea at St19 (Fig. 1).

The surf zone water was sampled by wading to a depth of about 1 m and using a 2-L polyethylene bottle, and coastal water was sampled using a Niskin Teflon bottle.

A push-point piezometer system was used, similar to that used by Niencheski et al. (2007), to sample groundwater along the beach down to a depth of 1 m during the 2009 and 2013 sampling campaigns. The push-point system consisted of a stainless steel pipe through which a Teflon tube was passed and connected to the stainless steel, screened intake end. Samples were collected using a peristaltic pumping system.

Coastal water samples were collected in 2010, 2012 and 2013 across perpendicular transects to shore using a rubber boat. The first half metre below the sea surface was sampled using a Niskin Teflon bottle.

In the 2013 sampling campaign, groundwater from a permanent well and water from springs were collected using the same peristaltic pumping system described previously.

In the laboratory, salinity was determined by means of a multiparameter probe (Multi 340i/SET WTW). Water samples were filtered through a 0.45 μm pore diameter cellulose acetate filter and frozen in plastic bottles for later analysis. DSi was analyzed using the method described by Aminot and Chaussepied (1983). Chl-*a* was determined using the trichromatic method, based on spectrophotometry, according to APHA et al. (2012). The precision for Chl-*a* was 5%, whereas for DSi it was 3%.

Phytoplankton (Phyto) quantitative samples were placed in 125-mL jars and fixed *in situ* with 20% formaldehyde solution neutralized with hexamethylenetetramine (Throndsen, 1978). Sub-samples (50 mL) were allowed to settle for 24 h in HydroBios chambers and then counted and identified at ×400 magnifications with a Leica DMIL inverted microscope (Utermohl, 1958). Counts were made following the methodology of Andersen and Throndsen (2003). This did not include the small-size fraction of phytoplankton (picoplankton and some portion of the nanoplankton). The phytoplankton community was classified to the lowest taxonomic level possible, according to Tomas (1997).

2.3. Data processing and statistical analysis

In order to calculate the silicate budget in coastal waters, and to balance the data number along the 43 km of coastline, in addition to working with data collected at the surf zone and costal water in this study, we included more coastal water data. The coastal water data of DSi, Chl-*a* and the percentage of diatoms which cover a complete annual cycle (Falco et al., 2007; Gadea et al., 2013) were added to the northern and central sectors. Only data obtained from points located within the first kilometre of coastline were used, and those sites significantly influenced by fresh water (salinity <34.5 according to European Commission, 2013) were discarded from this calculation.

The biogenic silica estimate (biogenic Si) was explored according to Falco et al. (2010). It was based on the available percentage of diatoms within the phytoplankton community and the amount of chlorophyll *a*. An estimate of carbon content was made with reference to the relationship between carbon and chlorophyll (Ciotti et al., 1995). The average amount of silicate in the diatoms was calculated using the Redfield ratio (Redfield et al., 1963).

Non-parametric Kruskal—Wallis tests were conducted to assess statistically significant differences between regions (Cullera, Xeraco-Gandia and Oliva-Pego) for permanent wells, surf zone and coastal water samples. A p-value less than 0.05 was considered to indicate statistical significance. Multiple comparisons between groups were implemented using Bonferroni adjustment of p-values. Spearman—Rank correlation tests were performed in order to detect monotonic relationships between ranked variables in beach groundwater, surf zone and coastal water variables. These non-parametric tests were carried out with R statistical software.

3. Results

The main results presented below follow a chronological order within each subset.

3.1. Surf zone and beach groundwater

Table 1 presents the minimum, maximum and average values of salinity, DSi, Chl-*a* and phytoplankton density in the surf

Table 1 Minimum, maximum and average of salinity, dissolved silicate (DSi), chlorophyll *a* (Chl-*a*) and phytoplankton density and composition in the surf zone during 2008, 2009 and 2010. The name of the station is in parentheses.

Year		2008	2009	2010
Salinity	Min—Max	4.9(St20)—37.5(St3,St6,St23)	29.2(St4)—37.5(St14,St25)	33.4(St3)—36.7(St29)
	Avg.	35.1	35.9	35.9
DSi [μM]	Min—Max	1.8(St8)—47.4(St14)	2.7(St16)—42.5(St20)	3.3(St29)—19.6(St3)
	Avg.	8.9	11.5	7.9
Chl-*a* [$\mu g\ L^{-1}$]	Min—Max	0.41(St20)—12.78(St14)	0.76(St37)—5.60(St17)	—
	Avg.	1.90	1.91	—
Phyto [cells L^{-1}]	Min—Max	—	71,688(St4)—290,165(St20)	—
	Avg.	—	128,299	—
Diatom [%]	Min—Max	—	20(St20)—77(St14)	—
	Avg.	—	43	—

zone samples. In the 2008 campaign, it was observed that sampling stations with lower salinity values, St14 (5.6), St20 (4.9), St27 (34.9) and St36 (33.5), had the highest DSi concentration, 47.4, 32.2, 21.2 and 18.9 μM respectively. These low values of salinity were located, in most cases, in zones subject to the influence of rivers (St20 near to the Serpis River, St36 close to the Racons River) and to the drainage of irrigation channels. These variations were a consequence of the sampling strategy employed in this study. We tried to obtain a detailed study of the coast by collecting samples at every kilometre of shoreline, without taking into account the grouping of sampling stations based on freshwater input influence. Thus, Chl-*a* values ranged between 0.41 and 12.78 $\mu g\ L^{-1}$ in St20 and St14 respectively, without any statistical correlation with salinity or DSi. On the other hand, when looking only at those samples with a salinity above 34.5 (assuming this value as a threshold between marine waters and those waters more influenced by continental discharges, as determined by the European Commission, 2013), a clear decrease in DSi average was observed for the surf waters (from 8.9 to 6.4 μM). The same trend was seen in Chl-*a*, with an average value of 1.6 $\mu g\ L^{-1}$ in these high-salinity samples.

In the 2009 sampling campaign, Chl-*a* ranged between 0.76 and 5.60 $\mu g\ L^{-1}$ (Table 1). As in the 2008 campaign, once again, no pattern was detected between salinity and Chl-*a*. In this campaign, the study of phytoplankton composition was added. On average, 43% of phytoplankton community was composed of diatoms. The two stations with the lowest salinity, St4 (29.2) and St20 (30.5), exhibited high DSi concentrations, 41.0 and 42.5 μM respectively. In the remaining 10 stations, salinity was greater than 34.5, and average DSi concentration decreased to 5.4 μM. This was remarkable, as DSi increased by one order of magnitude in those samples influenced by freshwater.

Thereby, we speculated that groundwater advection together with river contribution could be responsible for the high DSi concentrations. It should be emphasized that the rivers in this area exhibit a strong seasonal flow regime, producing a highly irregular contribution, whereas groundwater is discharged continuously. For this reason, beach piezometers were deployed along transects on the beach to collect groundwater at 1 m depth in the 12 stations sampled in 2009. Fig. 2A depicts salinity in beach groundwater at 1 m depth along the perpendicular transects from the coastline up to 70 m inland. This figure shows the existence of a subterranean estuary is clearly perceived, where permeable sediments provide a reaction zone in which freshwater and seawater are mixed in a similar way as occurs at the surface estuarine zone (Charette and Sholkovitz, 2006). Fig. 2B represents the DSi distribution along the saline gradient in the beach aquifer from the samples collected in these beach piezometers. It can be observed that there are greater DSi concentrations in freshwater samples than in marine waters, even more than one order of magnitude.

In 2010, the seven stations selected, among the 39 initially sampled stations, presented salinity and DSi concentrations within the intervals observed in preceding campaigns for surf zone samples (Table 1). In the same way as the 2008 and

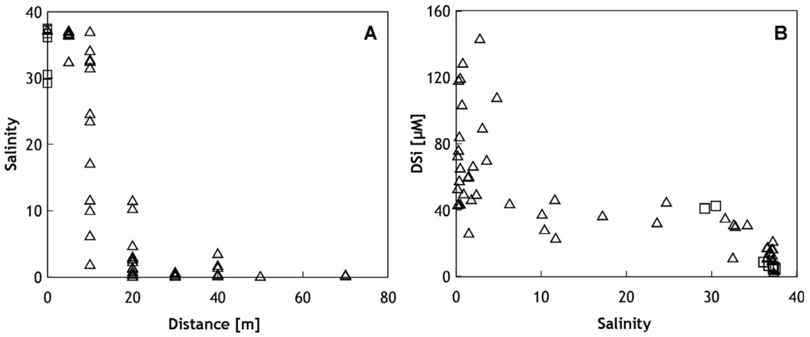

Figure 2 (A) Cross-beach profile in salinity from the surf zone (squares) and beach groundwater samples (triangles) collected in the 12 stations carried out in 2009. (B) Concentrations of dissolved silicate (DSi) in the surf zone (squares) and beach groundwater (triangles) in the 12 sampling stations, in samples from 2009.

2009 campaigns, there were samples with low salinity and high DSi (St03 with 33.4 and 9.6 μM). However, those samples with salinity above 34.5 — between 35.7 and 36.7 — showed an average DSi value of 5.9 μM, coinciding with the values previously observed, indicating a similar process.

3.2. Coastal waters

In the coastal marine environment, the two perpendicular transects to the coast carried out in Xeraco-Gandia (St15) and Oliva-Pego (St35) in 2010, showed negative gradients in DSi concentrations from the shoreline towards offshore. This is the pattern commonly found in other regions around the Mediterranean Sea (Aktan, 2011; Olivos et al., 2002), the continental influence on coastal waters being clearly visible.

Both sampling campaigns performed in coastal waters in Oliva-Pego during 2012 and 2013 were useful for increasing knowledge about DSi in the southern sector of the Gulf of Valencia. This nutrient showed an average value of 3.9 and 4.7 μM in 2012 and 2013 respectively. No sampling station presented salinity values influenced by freshwater surface inputs in these campaigns. Chl-*a* concentration was higher in 2012, with an average of 0.61 μg L^{-1}, while they were around 0.20 μg L^{-1} in 2013. In all stations sampled in these two campaigns, diatoms accounted for *ca*. 81% of the phytoplankton community.

In addition, another transect was made at St19 in 2013, where DSi values ranged from 0.7 to 11.2 μM, while there was not a clear DSi concentration gradient in coastal water, as was the case in 2010.

3.3. Groundwater in permanent wells and springs

The study area was divided into three regions, taking into account the different hydrogeological characteristics. From north to south, the first region, Cullera, is included within the hydrogeological system of Plana Valencia (from St1 to St5), while the other two regions, Xeraco-Gandia (from St6 to St26) and Oliva-Pego (from St27 to St40), belong to the Plana Gandia-Dénia hydrogeological subsystem (Fig. 1).

Table 2 depicts the average values of salinity and DSi in the sampled permanent wells. It is shown that groundwater DSi concentration was lower — but with higher salinity — in those permanent wells placed further north (130.2 μM), in Cullera. On the other hand, the highest DSi concentrations were determined towards the south, in the Oliva-Pego region (181.0 μM). Nonetheless, these differences were not statistically significant.

Regarding springs, it was not possible to detect any gradient among these data. The sample collected within the Cullera region presented a value of 180.3 μM and 3.0 for DSi and salinity respectively. The remaining three samples, collected in spring water bodies from Xeraco-Gandia, ranged between 98.7 and 149.8 μM of DSi and 0.1—0.2 for salinity.

4. Discussion

Fig. 3 shows all the water samples (surf zone, coastal area, push-points, permanent wells and springs) collected during the 2009, 2010, 2012 and 2013 campaigns. This figure depicts that DSi concentrations in aquifer groundwater — represented by permanent well samples (160.4 ± 51.6 μM) — are up to two orders of magnitude higher than in coastal waters, both in the surf zone (5.6 ± 1.9 μM) and in the coastal area (3.6 ± 1.9 μM). It is assumed that aquifer groundwater is able to supply high silicate amounts (a mean concentration in beach groundwater of 48.7 ± 32.5 μM) to the marine region by transporting submarine groundwater (SGD). This SGD can vary considerably due to rainfall and the hydrogeological features of aquifers (Tovar-Sánchez et al., 2014). For example, Tovar-Sánchez et al. (2014) observed that SGD from karstic aquifers is higher than SGD from detrital aquifers, being responsible for 75% of silicon fluxes in the Island of Majorca (Spain). In addition, aquifers in the study area supply springs with enriched silicate water (143.2 ± 33.7 μM) that may also reach the coastal environment through surface runoff.

Evident proof of water moving *via* a subterranean estuary is the distribution of DSi concentrations along the salinity gradient, supported by the superficial push-point piezometer transects on the sandy beach region (Fig. 2B). This pattern could also be observed beyond the beach zone from data collected in the central and southern coastal waters of the study area. Due to the lack of data in the northernmost region within the study area, it was necessary to resort to data obtained by Falco et al. (2007) to complete the knowledge of DSi distribution in the coastal marine environment.

With regard to the DSi sources in the coastal zone, rivers are an important source to take into consideration. In fact, rivers are responsible for 80% of dissolved silicate inputs to the ocean on a global scale. These sources include the dissolved silicate in river waters — which account for 60% of total inputs — and the subsequent dissolution of river particulate matter (20%) (Frings et al., 2016). Nonetheless, the river discharges into the sea are very low in the study area, amounting to zero throughout most of the year, due to the strict control of the main rivers by dams. Atmospheric inputs could be another source, although the lack of data concerning

Table 2 Salinity and dissolved silicate (DSi) in the permanent wells (*M*: mean and SD: standard deviation) sampled in 2013.

Region	Hydrogeological system/subsystem	Conductivity [μS cm^{-1}]		Salinity		DSi [μM]		Number of wells
		M	SD	*M*	SD	*M*	SD	
Cullera	Plana Valencia	1373	560	0.5	0.3	130.2	51.1	3
Xeraco-Gandia	Plana Gandia-Dénia	838	385	0.2	0.2	166.2	63.2	5
Oliva-Pego	Plana Gandia-Dénia	1142	797	0.4	0.5	181.0	24.9	3

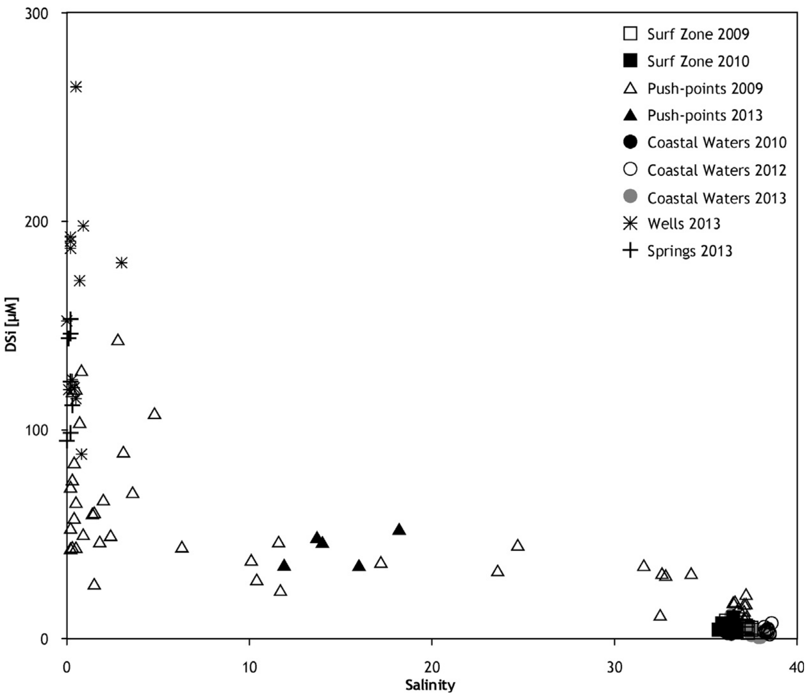

Figure 3 Scatter plot of dissolved silicate (DSi) concentrations in function of salinity from samples collected in the 2009, 2010, 2012 and 2013 campaigns (square: surf zone; triangle: push-point piezometer system; circle: coastal water; asterisk: permanent wells; cross: springs).

atmospheric fluxes of silicon in the Mediterranean do not allow for a proper assessment (Bartoli et al., 2005; de Fommervault et al., 2015). However, Koçak et al. (2010) calculated that silicon atmospheric fluxes could possibly account for as much as 10%, when comparing river inputs in the Northeastern Levantine basin. Marine bottoms could represent another source of silicate by means of benthic metabolism. The study area consists of permeable sands where Sospedra et al. (2015) determined that benthic silicate fluxes were not sufficient to supply the theoretical Si demand of microphytobenthos in a sampling station at 9 m depth. Thus, this nutrient must come from other sources. Therefore, it is assumed that there are other sources that could supply silicate to the coastal environment.

4.1. Submarine groundwater discharge

The conceptual model presented in Fig. 4 (modified from Niencheski et al., 2007) shows the silicate flux associated with the various water fluxes. These fluxes include: (1) fresh groundwater moving towards the ocean (F1), (2) SGD entering the ocean (F2), (3) seawater recirculating through permeable sediments (F3), and (4) the flux to the inner shelf (F4).

The groundwater flux pathway (F1) with a salinity end-member of 0.3, has an average DSi concentration of 160.4 µM (average in permanent wells). This groundwater is mixed with the coastal waters (F3) which have 36.8 of salinity and 5.6 µM of DSi (mean values in the 2009 and 2010 surf zone) as they advance towards the sea. It results in a conservative

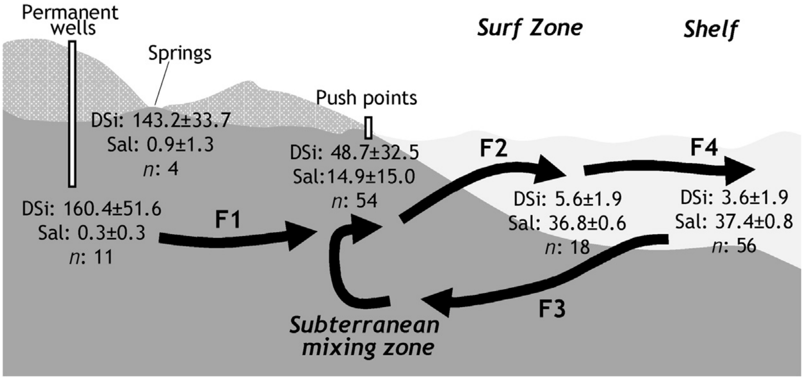

Figure 4 Conceptual model (not to scale) of silicate flux in the coastal surface water-groundwater system, based on Niencheski et al. (2007). The average and standard deviation of dissolved silicate (in µM), salinity and number of samples are shown for each compartment.

mixing process, therefore, the coastal region is supplied by continental groundwater enriched in silicate (F2) with an average concentration of 49 μM for an average salinity of 15 (values in 2009 and 2013 beach groundwater). Finally, the silicate-enriched water originating from this groundwater mixing zone is transported to the continental shelf (F4) with a mean of 37.4 and 3.6 μM of salinity and silicate respectively (values in the coastal waters of 2010, 2012 and 2013).

This conceptual model of how the submarine groundwater discharges Si flux is maintained as follows: there is a continual supply of silicate in fresh groundwater moving towards the coastline driven by local and/or regional hydraulic gradients. The Plana Valencia system and Plana Gandia-Dénia subsystem certainly provide local hydraulic gradients resulting in groundwater flow towards the Mediterranean Sea along a *ca.* 43 km length of coastline (IGME, 1989). The beach surface is dominated by sands — permeable sediments — where SGD is evident. It is suggested, however, that the dynamic circulation of seawater through the permeable beach sand allows a significant amount of silicate to escape into the surf zone with the SGD.

4.2. Silicate budget in coastal waters

As groundwater fluxes in this coastal area are unknown, it was investigated whether river contributions could be enough to support seawater silicate including silicate contained within phytoplankton. For this purpose, silicate fluxes (Si_DSi) for each river in the study area were calculated by multiplying mean river flows with the mean DSi concentrations and assuming that DSi concentrations were representative of conditions in these rivers. This method of flux calculation was selected because of the limited available data (GESAMP, 1987). Afterwards, silicate fluxes were multiplied by a conversion factor to express them in t d^{-1}. From these calculations, it was observed that silicate flux in the Júcar River was 0.3 t d^{-1}, whereas in the Serpis, Vedat and Racons Rivers these mass fluxes were *ca.* 0.4 t d^{-1} for each of them. In the case of the Júcar River, this value may still be overestimated due to the presence, downstream, of the Júcar-Vinalopó diversion (currently with operating problems) and two motors which are also able to pump water from the river for irrigation (Cullera Community of Irrigators, personal communication). The sum of these fluxes represents a total input towards the sea of 1.56 t d^{-1} in the whole study area (Table 3). In the Mediterranean Sea, other rivers with similar flows discharge similar amounts of Si to the sea. For example, the Pamisos River (Greece), the Rižana River (Slovenia) and the Lamas River (Turkey), with an average flow about 3 $m^3 s^{-1}$, deliver 0.9 t d^{-1} (Pavlidou et al., 2014), 0.5 t d^{-1} (from Cozzi and Giani, 2011) and 0.8 t d^{-1} (from Koçak et al., 2010), respectively.

Mean salinity, DSi, Chl-*a* concentrations and percentage of diatoms were estimated in each of the three regions for the first kilometre nearest to the coast and along the 43 km of coastline (Table 4) based on the work of Sebastiá et al. (2012a), which determined that the highest concentrations of chlorophyll *a* are observed in the 1000 m nearest to the coast. For this purpose, coastal water data from Cullera (Falco et al., 2007) and Gandia (Gadea et al., 2013) were also used. Those points significantly influenced by freshwater (salinity <34.5) were discarded. Regarding DSi, higher concentrations were clearly observed in Oliva-Pego, followed by Xeraco-Gandia and Cullera, showing statistically significant differences ($p < 0.01$) between the three regions. The increasing trend from north to south along the coastline might have matched with river DSi inputs, as higher discharges were displayed in the Oliva-Pego region (Table 3). Furthermore, this gradient could also correspond to the observed pattern for permanent wells (Table 2). This would suggest a connection between SGD and coastal waters where SGD could represent a significant percentage of Si contribution to the marine ecosystem.

The DSi content (t) for each region, could be estimated (Table 5) from the water volume (calculated from the shoreline length in each area (Table 4) and assuming that depth increases progressively up to 10 m at 1 km from the shoreline) and the DSi mean in each region (Table 4). Moreover, biogenic Si content was also calculated from the diatom percentage within the phytoplankton community (Table 4) and its corresponding Chl-*a* amount, assuming that all groups have similar levels of Chl-*a*. Diatom chlorophyll *a* was converted into carbon units using C:Chl-*a* 50: 1 ratio (Ciotti et al., 1995) and converted to Si moles according to the Redfield ratio (C:Si, 106:16) (Redfield et al., 1963) in order to estimate the biogenic Si belonging to diatoms in each of the three regions (Table 5). Finally, the total Si content for each region was obtained from the sum of dissolved Si and biogenic Si content. A total silicon amount of 21.3 t was estimated for the

Table 3 Mean discharges (*Q*) their corresponding period (*Q* period), mean dissolved silicate concentrations (DSi) and silicate fluxes (Si_DSi flux). The study region corresponding to each river is shown in parentheses.

Rivers (region)	*Q* period	*Q* [$m^3 s^{-1}$]	DSi [μM]	Si_DSi flux [t d^{-1}]
Júcar (Cullera)	2006—2016	1.42	87.8[a]	0.30
Serpis (Xeraco-Gandia)	2006—2016	1.94	93.3[b]	0.44
Vedat (Oliva-Pego)	2004—2011	1.62	96.0[c]	0.38
Racons (Oliva-Pego)	2004—2011	1.93	96.0[c]	0.45
Total				1.56

Sources:

[a] Falco et al. (2007).

[b] Sebastiá and Rodilla (2013).

[c] Values measured in 2010.

Table 4 Mean salinity, dissolved silicate (DSi) and chlorophyll *a* (Chl-*a*) concentrations and percentage of diatoms in the nearest kilometre to the coast in each region within the southern sector of the Gulf of Valencia.

	Cullera (*n* = 70)	Xeraco-Gandia (*n* = 101)	Oliva-Pego (*n* = 45)	Gulf of Valencia (southern sector)
Coastline [km]	10.0	21.3	11.9	43.2
Salinity	37.1	37.3	36.9	37.1
DSi [μM]	1.7	2.8	4.9	3.1
Chl-*a* [$\mu g\ L^{-1}$]	1.87	0.96	1.28	1.26
% Diatoms [%]	46.7	62.0	52.4	55.8

Values for the southern sector of the Gulf of Valencia were calculated as a weighted average from the three regions sampled, depending on their coastline length. These results are provided from data collected at the surf zone and coastal waters during 2008, 2009, 2010, 2012 and 2013 and Falco et al. (2007) and Gadea et al. (2013). The number of samples in each region are shown in brackets.

Table 5 Dissolved and biogenic Si content in the nearest kilometre to the coast in each study region and in the whole southern sector of the Gulf of Valencia.

	Cullera	Xeraco-Gandia	Oliva	Gulf of Valencia (southern sector)
Dissolved Si content [t]	2.4	8.2	8.1	18.7
Biogenic Si content [t]	0.8	1.1	0.7	2.6
Total Si content [t]	3.2	9.3	8.8	21.3

waterbody along the study area. Only 2.6 t were related with biogenic Si, which represent 13% of the total budget in the water column. This point implies that there is a sufficient amount of DSi to maintain diatom population in the study area, so the diatom community should have not been heavily dependent on continental inputs of this nutrient.

To study dissolved silicate sources within the nearest 1000 m to the coast in the study zone, the background level of this nutrient in seawater should be subtracted from the 18.7 t (Table 5). According to the data obtained by Sebastiá et al. (2013), which analyzed seawater quality in a sampling station placed in the central zone of the study area — approximately 9 km from the coastline — with low terrestrial input influence, a background level of 1 μM was assumed. Following this approach, there is a background level of 6 t within the study area (by multiplying the sea background concentration and the water volume in the first kilometre along the 43 km of shoreline), so it would be only necessary to justify an additional amount of 12.7 t of the 18.7 t dissolved. The local rivers in the study area — Júcar, Serpis, Vedat and Racons — discharge a total flux of 1.56 t d^{-1} into the sea (Table 3), requiring *ca.* 8 days to supply all this additional amount of Si through river inputs. The remaining 11.1 t (59% of dissolved silicate) could be related to SGD.

The amount discharged by local rivers — 1.56 t d^{-1} — must be increased by a groundwater flow enriched in silicate (F2, Fig. 4). This groundwater discharge, with mean values of 15 and 49 μM for salinity and DSi respectively, contributes to the increased Si concentration in the coastal region. Based on groundwater DSi content, it is speculated that the Plana Gandia-Dénia subsystem produces higher groundwater fluxes than the Plana Valencia system due to the higher Si concentrations found in southern sampling stations.

5. Conclusions

The coastal aquifers placed within the hydrogeological system of Plana Valencia and the subsystem of Plana Gandia-Dénia presented DSi values between 130 and 180 μM, displaying a positive gradient from north to south. The aquifers discharged into the coastal zone with an average salinity of 15 and a DSi concentration of 49 μM. Coastal waters have a mean DSi concentration of 3.1 μM, meaning that a continental influence is present when compared to concentrations obtained in Mediterranean Sea offshore waters. This continental influence could be more evident in those points located further south, where the highest DSi values were detected. The positive gradient observed corresponded with the DSi trend in coastal aquifers, so that SGD may represent an important percentage of Si inputs to the marine ecosystem. The silica requirement of diatoms in coastal waters was *ca.* 2.6 t, clearly lower than the amount dissolved (18.7 t). From this dissolved pool, nearly 6 t came from marine waters, 1.6 t from rivers and the rest must be provided by the SGD (59% of dissolved silicate in the first kilometre of the coast). There is obviously great uncertainty in these estimates because of the inherent heterogeneity of this system in time and space. This includes both temporal and spatial variability in silicon concentrations and advective transport. Constraining our estimates will require a considerable amount of additional work, including the use of isotopes of radium to assess SGD flux and cross-shelf transport.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.oceano.2017.07.004.

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