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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.