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Submarine groundwater discharge: A significant source of dissolved trace metals to the North Western Mediterranean Sea

Giada Trezzi [a,*], Jordi Garcia-Orellana [a,b,**], Valentí Rodellas [a,c], Juan Santos-Echeandia [d],
Antonio Tovar-Sánchez [e,f], Ester Garcia-Solsona [g], Pere Masqué [a,b,h,i]

[a] Institut de Ciència i Tecnologia Ambientals, Universitat Autònoma de Barcelona, Spain
[b] Departament de Física, Universitat Autònoma de Barcelona, Spain
[c] CEREGE, Aix-Marseille Université, CNRS, IRD, Coll France, Aix-en-Provence, France
[d] Instituto Español de Oceanografía, Centro Oceanográfico de Murcia, Spain
[e] Instituto de Ciencias Marinas de Andalucía (CSIC), Spain
[f] Instituto Mediterráneo de Estudios Avanzados (CSIC), Spain
[g] Departament de Dinàmica de la Terra i de l'Oceà, Universitat de Barcelona, Spain
[h] School of Natural Sciences and Centre for Marine Ecosystems Research, Edith Cowan University, Australia
[i] Oceans Institute and School of Physics, The University of Western Australia, Australia

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ABSTRACT

Bioactive trace metals play a significant role as micronutrients in the ocean and therefore it is important to evaluate their sources. Submarine groundwater discharge (SGD) has been recognized as an input of trace metals to the coastal sea. Here, we investigated the significance of SGD as a source of dissolved trace metals (dTM) to the coastal sea in a regional area such as the North Western (NW) Mediterranean Sea. We analysed dTM concentrations in SGD end-members and incorporate data on SGD dTM concentrations and water flows reported in previous studies carried out in this area, to estimate the following ranges of SGD-driven dTM fluxes (in 10^6 mol y^{-1}): Cd: 0.0007–0.03, Co: 0.004–0.11, Cu: 0.09–1.9, Fe: 1.8–29, Ni: 0.09–1.9, Pb: 0.002–0.06, Zn: 0.38–12. These fluxes were compared to dTM fluxes from riverine discharge and atmospheric deposition, demonstrating that SGD is a major source of dTM to the NW Mediterranean Sea. Whilst riverine inputs are limited to the surrounding of river mouths and atmospheric fluxes are distributed throughout the whole basin mainly during sporadic depositional events, SGD represents a permanent, albeit seasonally variable, source of metals to most of the coastal areas. SGD-driven dTM inputs may be even more significant, in relative terms, in other coastal regions of the Mediterranean Sea where rivers are scarce, as it is the case of the African coast and many islands. This study highlights the relevance of SGD as a source of dTM to the Mediterranean Sea and the need of its consideration in the calculation of metal budgets in the basin and in the investigation of biogeochemical cycles in coastal areas.

1. Introduction

The availability of bioactive trace metals (e.g. Fe, Mn, Co, Ni, Cu, Zn and Cd) plays an important role in supporting primary productivity in the oceans (Bruland et al., 1991; Morel and Price, 2003; Sunda, 2012). Understanding the biogeochemical cycling of these micronutrients requires a detailed knowledge of their diverse sources and sinks. The main continental sources of trace metals to the ocean are riverine discharge (e.g. Bewers and Yeats, 1989; Jeandel and Oelkers, 2015; Martin and Whitfield, 1983; Oelkers et al., 2011), atmospheric deposition (e.g. Bowie et al., 2002; Duce et al., 1991; Jickells, 1995; Mackey et al., 2012; Mahowald et al., 2005), benthic fluxes from sediments (e.g. Elrod et al., 2004; Jeandel et al., 2011) and submarine groundwater discharge (SGD), although the latter has received attention only recently (e.g. Beck et al., 2007, 2009; Charette and Buesseler, 2004; Windom et al., 2006). SGD includes both fresh meteoric groundwater and recirculated seawater through permeable sediments of the coastal aquifer. Indeed, the mixing interface between fresh and salty water is a chemical reaction zone called the subterranean estuary, where groundwater can become enriched or depleted in chemical compounds before discharging into the sea (Moore, 1999). The chemical composition of SGD is influenced by several factors, such as the geological matrix and the geochemical conditions of the coastal aquifers (Charette et al., 2005; Mcallister et al., 2015; Santos et al., 2012), the potential impact

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[*] Correspondence to: G.Trezzi, Institut de Ciència i Tecnologia Ambientals, Universitat Autònoma de Barcelona, 08193 Bellaterra, Spain.

[**] Corresponding author.

E-mail addresses: Giada.Trezzi@uab.cat, giada.trezzi@gmail.com (G. Trezzi), Jordi.Garcia@uab.cat (J. Garcia-Orellana).

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of human activities (Beck et al., 2009; de Sieyes et al., 2008; Trezzi et al., 2016) and the type of discharge (e.g. karstic or detrital) (Tovar-Sánchez et al., 2014b).

Globally SGD has been estimated to be 3 to 4 times higher than riverine discharge into the oceans (Kwon et al., 2014). In the Mediterranean Sea, a semi-enclosed oligotrophic basin, SGD is comparable or even larger (up to 16 times) than the riverine water flow (Rodellas et al., 2015a). In this basin, the role of SGD in biogeochemical cycles is also prominent since the estimated SGD-driven macronutrient fluxes (DIN, DIP and DSi) are comparable or even higher than the riverine and atmospheric fluxes (Rodellas et al., 2015a). The relevance of SGD in delivering dissolved trace metals (dTM) to the Mediterranean Sea has been highlighted in some local areas, characterized by the absence of riverine discharge (Rodellas et al., 2014; Tovar-Sánchez et al., 2014b; Trezzi et al., 2016).

The aim of this study is to quantify SGD-driven dTM fluxes at regional scale and evaluate their significance. We determine these fluxes in the North Western (NW) Mediterranean Sea and compare them to other external sources (i.e. riverine discharge and atmospheric deposition). This area was considered an appropriate study site for conducting such a comparison for three main reasons: 1) the existence of several studies reporting local estimations of SGD flows that can be used to obtain a reliable regional estimate of SGD-driven dTM fluxes (i.e., Baudron et al., 2015; Garcia-Solsona et al., 2010a, 2010b; Mejías et al., 2012; Ollivier et al., 2008; Rodellas et al., 2015b, 2014, 2012; Stieglitz et al., 2013; Tovar-Sánchez et al., 2014b; Trezzi et al., 2016); 2) the large riverine discharge in this area compared with most zones of the Mediterranean basin (Ludwig et al., 2009); 3) the influence of atmospheric deposition originating from Europe and the Saharan region (Guerzoni et al., 1999; Guieu et al., 1997).

2. Methodology

2.1. The NW Mediterranean Sea

The Mediterranean Sea is a semi-enclosed basin connected to the Atlantic Ocean through the Strait of Gibraltar, characterized by a net export of nutrients to the Atlantic Ocean, that leads to oligotrophic conditions in the whole basin (Béthoux et al., 1998). Climate conditions of the Mediterranean Sea generally consist of dry summers and rainy autumns and winters, with larger mean annual precipitation in the north and western parts of the basin.

The study area comprises the NW Mediterranean zone (Eastern Spanish coast, including the Balearic Islands, and French Mediterranean coast, up to Marseille city), encompassing a coastline of about 3500 km and a surface area of about 180,000 km^2 (Fig. 1). The Rhone and the Ebro are the main rivers in this area, representing more than the 70% of the total riverine discharge to the Western Mediterranean Sea, with mean water flows of $54 \cdot 10^9$ and $13 \cdot 10^9$ m^3 y^{-1}, respectively (Ludwig et al., 2009). Groundwater inputs occur via both detrital and karstified coastal aquifers. Fractured karstified carbonated aquifers constitute a large portion (about the 40%) of the French and Spanish coasts, including the Balearic Islands (Bakalowicz, 2015, 1999; Instituto Geologico Minero de España (IGME), 1986).

2.2. Sampling

Groundwater samples representative of the water discharging into the sea (i.e. SGD end-members) were collected between November 2013 and June 2015 at several locations along the Spanish and French Mediterranean coasts: 10 samples were collected from karstic systems and 8 from detrital systems (Fig. 1; Table 1).

The karstic waters corresponded to 3 different coastal carbonate aquifers and were collected mostly from flowing coastal springs associated with fractures (Garbí, Suís, Badum, Font Centre, Font South, Estramar, La Palme). One of these springs (Garbí, located close to the Ebro delta) was sampled three times (December 2013; July 2014; May 2015) in order to evaluate the variability in metal concentrations of this source. Groundwater flowing through detrital aquifers was sampled at 7 sites along the Spanish coast. Five of these end-members were obtained in beaches presumably characterized by the flow of fresh groundwater to the sea, from a manual piezometer placed down to the depth where groundwater seeping through the sand was found (Empuriabrava, La Fosca North, La Fosca South, Arenys and Sitges); one was collected in the channel connecting a coastal marshland to the sea (Peníscola), which is representative of the groundwater converging into the coastal wetland (Rodellas et al., 2012; Zarroca et al., 2014); the other two samples were collected from a coastal piezometer, sampled twice after a rainy period (Argentona).

For each sample, 125 mL of water were directly collected following trace metal clean techniques (Tovar-Sánchez, 2012). Water was

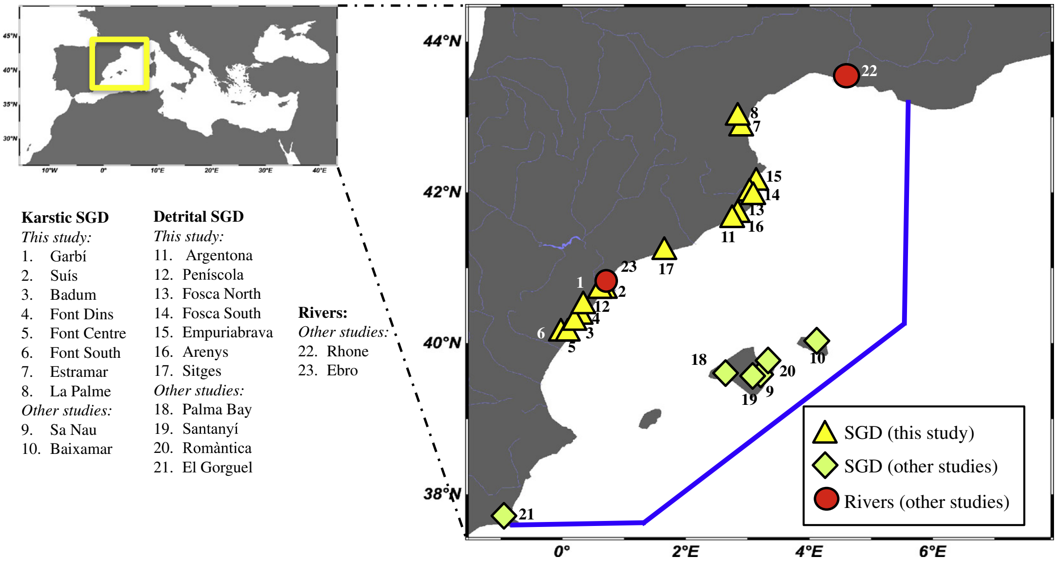

Fig. 1. The study area in the Mediterranean basin (180,000 km^2; delimited in blue) and the localization of SGD end-members, for which dTM concentrations were reported in this study (yellow triangles) or in previous studies (green diamonds). The main rivers of the study area (red circles), analysed in other studies for dTM concentrations, are also plotted on the map. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)