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

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Keywords: submarine groundwater discharge (SGD); trace metals; micronutrients; Mediterranean Sea

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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 analyzed 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  $10^6 \text{ mol y}^{-1}$ ): 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.

Barcelona, July 29<sup>th</sup>, 2016

Dear Prof -Hein de Baar,

Please, find enclosed the revised version of the manuscript written by G. Trezzi, J. Garcia-Orellana, V. Rodellas, J. Santos-Echeandia, A. Tovar-Sánchez, E. Garcia-Solsona, and P. Masqué, entitled “Submarine groundwater discharge: a significant source of dissolved trace metals to the North Western Mediterranean Sea” (Ref. # MARCHE-D-16-00006R1).

We think that this new version of the manuscript has been improved by addressing the reviewers’ comments and we would like to thank the reviewers for their suggestions.

As recommended by the reviewers, we have expanded the discussion about differences in dissolved metal concentrations between karstic and detrital SGD and we have added details in the manuscript about the uncertainty in the selection of SGD end-members and the calculation of SGD trace metal fluxes using these end-members.

We have also paid attention to the minor comments done by the reviewers, introducing the appropriate corrections in the manuscript.

The responses to the reviewers’ comments and the revised manuscript have been uploaded. Two versions of the manuscript have been sent: i) the revised manuscript with all the changes marked; ii) the revised manuscript where all the changes have been accepted for facilitating the reading.

Yours faithfully,

Giada Trezzi

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Prof -Hein de Baar,  
Associated Editor of Marine Chemistry  
Barcelona, July 29<sup>th</sup>, 2016

**Re: Revision of manuscript Ref. # MARCHE-D-16-00006R1 by Trezzi et al.**

Please find below the responses to the comments made by the reviewers. We have carefully read the corrections and suggestions provided and improved the manuscript accordingly. Concerning the main comment made by Reviewer 1, we have tried to examine in depth the differences in dissolved metal concentrations in karstic and detrital SGD. Because of the paucity of data and studies on this matter, we can provide only the possible interpretations explained now in the manuscript. Nevertheless, we believe that this is not the central point of the manuscript and that the information provided on the comparison of the different continental fluxes of dissolved trace metals to the NW Mediterranean Sea are not affected by these interpretations.

#### **COMMENTS MADE BY REVIEWER 1**

##### ***General comments:***

*Following the first round of reviews, the authors made an effort to answer both reviewers comments, included the suggested references and provide a better explanation on the determination of fluxes.*

*However, I am still not convinced by the discussion regarding differences in trace metal concentrations between karstic and detrital systems (lines 291-307). Compared to the first version, the authors yet provide more details about the ranges of concentrations but do not really improve the discussion. Same sentences are repeated (e.g. l.298-299: "In karstic systems, groundwater flows rapidly through fractures and conduits ...". The*

*authors argue that higher concentrations of Cu, Ni and Co in detrital systems are due to the fact that these elements are crustal derived, and were longer in interaction with the sediment in comparison to the karstic systems. However, Fe, which is also a well-known crustal-derived element, shows 1.5 times less concentrations in detrital , and I would like to see a real discussion.*

**Answer:** We have now improved the discussion about differences in trace metal concentrations between karstic and detrital systems, providing possible interpretations for the higher concentrations of Co, Cu and Ni in detrital SGD and the lack of this enrichment for the other trace metals (Cd, Fe, Pb and Zn). The paragraph about this discussion (lines 274 - 310) reads as: “There are two possible main explanations for these differences in dTM concentrations between karstic and detrital SGD. The different geological matrix of the karstic and detrital aquifers can contribute differently to the chemical composition of the interacting groundwater; while karstic systems are composed predominantly by carbonate minerals, detrital systems can be characterized by different lithologies and a consequent larger variability of minerals. Secondly, the geochemical reactions that occur in the subterranean estuary, before groundwater discharges into the coastal sea, largely affect solute concentrations in SGD. In karstic systems, infiltrated groundwater can be rapidly transferred to the coastal sea due to the presence of underground fractures and preferential pathways (Garcia-Solsona et al., 2010b; Gonnee et al., 2014; Tovar-Sánchez et al., 2014b). Thus, the SGD discharging into the coastal sea through coastal springs is generally oxygenated and characterized by a limited interaction with the geological matrix of the aquifer. Contrary, detrital SGD flows across the permeable sediments of the coastal aquifers, where it mixes with recirculated seawater before discharging into the sea. Detrital SGD is thus subjected to several geochemical transformations such as redox-controlled solubility, adsorption on organic matter and/or on Fe and Mn oxides, release from these oxides and desorption

from sediments (Charette and Sholkovitz, 2006). Co and Ni are redox-sensitive elements controlled by Mn geochemistry in porewater of coastal and shelf sediments (Beck et al., 2007, 2010; Santos-Echeandia et al., 2009). The higher concentrations of Co and Ni in detrital SGD samples with respect to the karstic ones may be related to their release from Mn oxides during the diagenetic remobilization of Mn (Beck et al., 2010; Santos-Echeandia et al., 2009). On the other hand, Cu is strongly associated to the organic matter (Du Laing et al., 2009; Santos-Echeandia et al., 2009; Shaw et al., 1990), which is commonly more abundant in detrital systems than in the karstic ones. This may explain the higher concentration of Cu in detrital SGD. The comparable concentrations of dissolved Fe between karstic and detrital SGD may be due to the oxygenated conditions of karstic SGD and to the precipitation of Fe, with the formation of Fe oxides, when recirculated seawater mixes with groundwater in detrital systems (Charette and Sholkovitz, 2006, 2002; Windom et al., 2006). Finally, for Cd, Pb and Zn, the generally comparable ranges of concentrations in karstic and detrital SGD may be ascribed to their lower redox-sensitivity (for Pb and Zn) (Santos-Echeandia et al., 2009), to their lower association with the organic matter (for Cd, Pb and Zn) (Roux et al., 1998; Santos-Echeandia et al., 2009) or to their removal from the solution due to the presence of the so-called Fe-curtain (for Cd and Zn) (Charette and Sholkovitz, 2006, 2002; Trezzi et al., 2016). These properties may prevent the detrital SGD to get distinctly more enriched in Cd, Fe, Pb and Zn with respect to karstic SGD.”

***Specific comments:***

***Rev. 1: Highlights: given the fact that median riverine metal fluxes are 2 to 7 times higher than estimated SGD fluxes, and that atmospheric fluxes are also much higher than SGD fluxes, I think the third statement "SGD is a major source of dissolved metals to the coastal NW mediterranean" should be removed***

**Answer 1:** In our opinion, this highlight should remain because SGD is comparable to atmospheric fluxes when normalizing SGD and atmospheric dissolved trace metal fluxes to the NW Mediterranean Sea for the relative areas of influence, as it is explained in lines 429 - 451 (See Figure 6). This work demonstrated that SGD is, together with atmospheric deposition, the most important source of dissolved trace metals to the coastal sea out of the areas of influence of rivers (river plumes). Thus, SGD is a major source of dissolved trace metals to the coastal sea in the NW Mediterranean Sea. This fact does not mean that SGD fluxes are higher than riverine and atmospheric fluxes in Figure 4.

**Rev. 2:** l. 208: *say which samples are lower than the limit of detection. "Some samples" is not precise enough.*

**Answer 2:** Done

**Rev. 3:** l. 451. *I think the authors could calculate the same inputs considering a distance of 2km since their statement in line 445. This would provide a range of fluxes rather than an upper limit for Cu, Fe, Ni and Zn.*

**Answer 3:**

We thank the reviewer for the comment. However, we think that the approach chosen in the previous version of the manuscript is the most appropriate one. Indeed, as it is stated in lines 433 - 440, several studies (Gonneea et al., 2014; Mejías et al., 2012; Moore, 2003; Rodellas et al., 2014; Trezzi et al., 2016; Windom et al., 2006) showed that the maximum distance of coastal seawater where it is generally recognizable SGD by using Ra isotopes or salinity as tracers is 2-3 km offshore. However, Cu, Fe, Ni and Zn can be removed from the water column within this distance, because of the biological uptake or the adsorption onto inorganic particles. It is difficult to establish the distance offshore affected by SGD-driven dissolved metal fluxes, in particular because of the lack in published studies of complementary investigations on processes affecting the distribution of trace metals in the water column of coastal sites characterized by SGD. Thus, we prefer to consider just the upper limit of 3 km, supplied by salinity and Ra isotopes, for the calculation of area-normalized SGD metal fluxes, rather than a range of

distances. In this way we are considering a conservative estimation of the significance of SGD for Cu, Ni, Zn and Fe. If a shorter distance offshore had been used for the calculation, the relative significance of SGD as source of dissolved trace metals to the coastal sea with respect to the atmospheric deposition would have been higher than what highlighted in the manuscript.

## COMMENTS MADE BY REVIEWER 2

### ***General comments:***

*Second review of „Submarine groundwater discharge: a significant source of dissolved trace metals to the North Western Mediterranean Sea" by Trezzi et al. (Marine Chemistry)*

*I carefully read the authors' response to my comments and inspected the revised manuscript. Thanks to the authors' explanations and modifications I am now ready to believe that submarine groundwater discharge (SGD) may represent a significant source of trace metals to the north-western Mediterranean Sea (and even more so to the southern and eastern Mediterranean Sea).*

*I have a number of remaining points of criticism which should be addressed prior to publication.*

*In my first review I noted that the term end member is somewhat misleading for samples with salinities between 0.2 and 36 since dissolved-particulate interaction likely modify these concentrations upon mixing of seawater and groundwater. I understand that this complication is inherent to all SGD studies. However, given the authors' far-reaching interpretation and comparison with river- and dust-related fluxes, I feel that a more thorough treatment/discussion of this uncertainty in the paper (rather than in the response letter alone) would be in order.*

**Answer:** We have now improved this part of the manuscript including a more detailed discussion of this point. Thus, this discussion reads as (lines 366 – 378 and 387 - 393):  
“Trace metal inputs through SGD are conditioned by the multiple and complex processes occurring during the transport through the sediments and/or aquifer, which

can affect the dTM concentrations of SGD. Indeed, the selection of appropriate SGD end-members is one of the most challenging points in the assessment of SGD-driven metal fluxes to the ocean. The SGD end-members collected in this work were certainly representative of the water effectively discharging into the sea in the case of the coastal karstic springs. For detrital systems, the most real SGD end-member was determined by collecting several SGD samples of different salinities (fresh and brackish groundwater and recirculated seawater) and by including literature data of dTM already considered as representative of the SGD end-members by the respective authors. This approach permits to obtain a first approximation of SGD-driven dTM fluxes, whose magnitude can be compared to riverine discharge and atmospheric deposition, with the aim of evaluating the relevance that SGD can have in the NW Mediterranean Sea.” and “Notice that the repeated sampling of two SGD end-members, collected twice and three times (Argentona and Garbí, respectively), showed a minimum variability of the dTM concentrations compared to the range of concentrations reported for groundwater samples. Thus, even considering temporal variability of SGD, the magnitude of the calculated SGD-driven dTM fluxes can be still compared to continental inputs of dTM via riverine discharge and atmospheric deposition.”

***Specific comments:***

***Rev.1:*** Line 48: '*off*' the African coast.

**Answer 1:** We think that “of” is the correct preposition for the meaning of the sentence.

***Rev. 2:*** Line 142: *Why not adding the explanation regarding the origin of the water in the channel that was given in the response letter?*

**Answer 2:** Done.



**Rev. 3** Line 182: *I guess you are referring to 'diffuse' rather than 'diffusive' flows.*

**Answer 3:** Corrected.

**Rev. 4:** Line 185: *Based on what method (228Ra mass balance). Please mention.*

**Answer 4:** Done: We have added “by using Ra isotopes and <sup>222</sup>Rn as tracers of the process” (lines 177 – 178).

**Rev. 5:** Line 301-307: *Please provide citations or a more detailed reasoning for these interpretations. Note that not only Cd and Fe have been described to undergo flocculation in the salinity gradient but also Cu, Ni and Co (Sholkowitz 1987, The flocculation of dissolved Fe, Mn, Al, Cu, Ni, Co and Cd during estuarine mixing, EPSL 1, 77-86).*

**Answer 5:** On the base of this comment and the comments provided by Reviewer 1, we have now provided more detailed reasons for our interpretations (lines 274 - 310): “There are two possible main explanations for these differences in dTM concentrations between karstic and detrital SGD. The different geological matrix of the karstic and detrital aquifers can contribute differently to the chemical composition of the interacting groundwater; while karstic systems are composed predominantly by carbonate minerals, detrital systems can be characterized by different lithologies and a consequent larger variability of minerals. Secondly, the geochemical reactions that occur in the subterranean estuary, before groundwater discharges into the coastal sea, largely affect solute concentrations in SGD. In karstic systems, infiltrated groundwater can be rapidly transferred to the coastal sea due to the presence of underground fractures and preferential pathways (Garcia-Solsona et al., 2010b; Gonnee et al., 2014; Tovar-Sánchez et al., 2014b). Thus, the SGD discharging into the coastal sea through coastal springs is generally oxygenated and characterized by a limited interaction with the

geological matrix of the aquifer. Contrary, detrital SGD flows across the permeable sediments of the coastal aquifers, where it mixes with recirculated seawater before discharging into the sea. Detrital SGD is thus subjected to several geochemical transformations such as redox-controlled solubility, adsorption on organic matter and/or on Fe and Mn oxides, release from these oxides and desorption from sediments (Charette and Sholkovitz, 2006). Co and Ni are redox-sensitive elements controlled by Mn geochemistry in porewater of coastal and shelf sediments (Beck et al., 2007, 2010; Santos-Echeandia et al., 2009). The higher concentrations of Co and Ni in detrital SGD samples with respect to the karstic ones may be related to their release from Mn oxides during the diagenetic remobilization of Mn (Beck et al., 2010; Santos-Echeandia et al., 2009). On the other hand, Cu is strongly associated to the organic matter (Du Laing et al., 2009; Santos-Echeandia et al., 2009; Shaw et al., 1990), which is commonly more abundant in detrital systems than in the karstic ones. This may explain the higher concentration of Cu in detrital SGD. The comparable concentrations of dissolved Fe between karstic and detrital SGD may be due to the oxygenated conditions of karstic SGD and to the precipitation of Fe, with the formation of Fe oxides, when recirculated seawater mixes with groundwater in detrital systems (Charette and Sholkovitz, 2006, 2002; Windom et al., 2006). Finally, for Cd, Pb and Zn, the generally comparable ranges of concentrations in karstic and detrital SGD may be ascribed to their lower redox-sensitivity (for Pb and Zn) (Santos-Echeandia et al., 2009), to their lower association with the organic matter (for Cd, Pb and Zn) (Roux et al., 1998; Santos-Echeandia et al., 2009) or to their removal from the solution due to the presence of the so-called Fe-curtain (for Cd and Zn) (Charette and Sholkovitz, 2006, 2002; Trezzi et al., 2016). These properties may prevent the detrital SGD to get distinctly more enriched in Cd, Fe, Pb and Zn with respect to karstic SGD.”

**Rev. 6:** *Line 357-359: It would make sense to assign a mechanism, reasoning or citation to this general statement (regarding pH/redox/etc.).*

**Answer 6:** Done. We have now modified the sentence in this way: “These differences may be related to the distinctive environments of coastal aquifers and rivers, with steep redox gradients in subterranean estuaries and the presence of microbes that can affect the speciation and mobility of trace metals (Knee and Paytan, 2011; O’Connor et al., 2015).”

**Rev. 7:** *Generally speaking, the added discussion regarding differential trace metal behaviour in the context of SGD (as rightly requested by the other reviewer) does not seem very motivated or convincing to me.*

**Answer 7:** We have now improved this discussion (see Answer 5)

**Rev. 8:** *Line 332: Exchange 'included in' by 'within'*

**Answer 8:** Done.

**Rev. 9:** *Line 482: 'variability', not 'variable'*

**Answer 9:** Done.

**Rev. 10:** *Line 505: Add 'of' after paucity*

**Answer 10:** Done. We have now rewritten the sentence, so that it results clearer: “the paucity of data on dTM concentrations of SGD end-members of the South Western and Eastern Mediterranean basins and the difficulty to obtain these data” (lines 494 – 496).

**Rev. 11:** *Line 564: 'on' islands.*

**Answer 11:** We think that the preposition “in” is more correct for the meaning of the sentence.

1 **Submarine groundwater discharge: a significant source of dissolved**  
2 **trace metals to the North Western Mediterranean Sea**

3  
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5 <sup>4</sup>, *Antonio Tovar-Sánchez*<sup>5,6</sup>, *Ester Garcia-Solsona*<sup>7</sup>, *Pere Masqué*<sup>1,2,8,9</sup>.

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33 Key words: submarine groundwater discharge (SGD), trace metals, micronutrients,

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36 Mediterranean Sea, rivers, atmospheric deposition  
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28 Abstract

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30 Bioactive trace metals play a significant role as micronutrients in the ocean and  
31 therefore it is important to evaluate their sources. Submarine Groundwater Discharge  
32 (SGD) has been recognized as an input of trace metals to the coastal sea. Here, we  
33 investigated the significance of SGD as a source of dissolved trace metals (dTM) to the  
34 coastal sea in a regional area such as the North Western (NW) Mediterranean Sea. We  
35 analyzed dTM concentrations in SGD end-members and incorporate data on SGD dTM  
36 concentrations and water flows reported in previous studies carried out in this area, to  
37 estimate the following ranges of SGD-driven dTM fluxes (in  $10^6 \text{ mol y}^{-1}$ ): Cd: 0.0007 -  
38 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:  
39 0.38 - 12. These fluxes were compared to dTM fluxes from riverine discharge and  
40 atmospheric deposition, demonstrating that SGD is a major source of dTM to the NW  
41 Mediterranean Sea. Whilst riverine inputs are limited to the surrounding of river mouths  
42 and atmospheric fluxes are distributed throughout the whole basin mainly during  
43 sporadic depositional events, SGD represents a permanent, albeit seasonally variable,  
44 source of metals to most of the coastal areas. SGD-driven dTM inputs may be even  
45 more significant, in relative terms, in other coastal regions of the Mediterranean Sea  
46 where rivers are scarce, as it is the case of the African coast and many islands. This  
47 study highlights the relevance of SGD as a source of dTM to the Mediterranean Sea and  
48 the need of its consideration in the calculation of metal budgets in the basin and in the  
49 investigation of biogeochemical cycles in coastal areas.

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52 **1 Introduction**

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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. Bowers 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 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

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79 prominent since the estimated SGD-driven macronutrient fluxes (DIN, DIP and DSi)  
80 are comparable or even higher than the riverine and atmospheric fluxes (Rodellas et al.,  
81 2015a). The relevance of SGD in delivering dissolved trace metals (dTM) to the  
82 Mediterranean Sea has been highlighted in some local areas, characterized by the  
83 absence of riverine discharge (Rodellas et al., 2014; Tovar-Sánchez et al., 2014b; Trezzi  
84 et al., 2016).  
85 The aim of this study is to quantify SGD-driven dTM fluxes at regional scale and  
86 evaluate their significance. We determine these fluxes in the North Western (NW)  
87 Mediterranean Sea and compare them to other external sources (i.e. riverine discharge  
88 and atmospheric deposition). This area was considered an appropriate study site for  
89 conducting such a comparison for three main reasons: 1) the existence of several studies  
90 reporting local estimations of SGD flows that can be used to obtain a reliable regional  
91 estimate of SGD-driven dTM fluxes (i.e., Baudron et al., 2015; Garcia-Solsona et al.,  
92 2010a, 2010b; Mejías et al., 2012; Ollivier et al., 2008; Rodellas et al., 2015b, 2014,  
93 2012; Stieglitz et al., 2013; Tovar-Sánchez et al., 2014b; Trezzi et al., 2016); 2) the  
94 large riverine discharge in this area compared with most zones of the Mediterranean  
95 basin (Ludwig et al., 2009); 3) the influence of atmospheric deposition originating from  
96 Europe and the Saharan region (Guerzoni et al., 1999; Guieu et al., 1997).

## 97 98 **2 Methodology**

### 99 100 2.1 The NW Mediterranean Sea

101  
102 The Mediterranean Sea is a semi-enclosed basin connected to the Atlantic Ocean  
103 through the Strait of Gibraltar, characterized by a net export of nutrients to the Atlantic

104 Ocean, that leads to oligotrophic conditions in the whole basin (Béthoux et al., 1998).

105 Climate conditions of the Mediterranean Sea generally consist of dry summers and

106 rainy autumns and winters, with larger mean annual precipitation in the north and

107 western parts of the basin.

108 The study area comprises the NW Mediterranean zone (Eastern Spanish coast, including

109 the Balearic Islands, and French Mediterranean coast, up to Marseille city),

110 encompassing a coastline of about 3,500 km and a surface area of about 180,000 km<sup>2</sup>

111 (Figure 1). The Rhone and the Ebro are the main rivers in this area, representing more

112 than the 70% of the total riverine discharge to the Western Mediterranean Sea, with

113 mean water flows of  $54 \cdot 10^9$  and  $13 \cdot 10^9$  m<sup>3</sup> y<sup>-1</sup>, respectively (Ludwig et al., 2009).

114 Groundwater inputs occur via both detrital and karstified coastal aquifers. Fractured

115 karstified carbonated aquifers constitute a large portion (about the 40%) of the French

116 and Spanish coasts, including the Balearic Islands (Bakalowicz, 2015, 1999; Instituto

117 Geologico Minero de España (IGME), 1986).

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## 119 2.2 Sampling

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121 Groundwater samples [representative of the water discharging into the sea \(i.e. SGD](#)

122 [end-members](#)) were collected between November 2013 and June 2015 at several

123 locations along the Spanish and French Mediterranean coasts: 10 samples were

124 collected from karstic systems and 8 from detrital systems (Figure 1; Table 1).

125 The karstic waters corresponded to 3 different coastal carbonate aquifers and were

126 collected mostly from flowing coastal springs associated with fractures (Garbí, Suís,

127 Badum, Font Centre, Font South, Estramar, La Palme). One of these springs (Garbí,

128 located close to the Ebro delta) was sampled three times (December 2013; July 2014;



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129 May 2015) in order to evaluate the variability in metal concentrations of this source.  
130 Groundwater flowing through detrital aquifers was sampled at 7 sites along the Spanish  
131 coast. Five of these end-members were obtained in beaches presumably characterized  
132 by the flow of fresh groundwater to the sea, from a manual piezometer placed down to  
133 the depth where groundwater seeping through the sand was found (Empuriabrava, La  
134 Fosca North, La Fosca South, Arenys and Sitges); one was collected in the channel  
135 connecting a coastal marshland to the sea (Peníscola), [which is representative of the](#)  
136 [groundwater converging into the coastal wetland \(Rodellas et al., 2012; Zarroca et al.,](#)  
137 [2014\)](#); the other two samples were collected from a coastal piezometer, sampled twice  
138 after a rainy period (Argentona).

139  
140 For each sample, 125 mL of water were directly collected following trace metal clean  
141 techniques (Tovar-Sánchez, 2012). Water was pumped through an acid-clean Teflon  
142 tube using a peristaltic pump, filtered with a 0.2 µm SuporCap filter and stored in acid-  
143 cleaned plastic bottles. Samples were then acidified to pH < 2 with trace metal grade  
144 HCl acid. At each sampling point, salinity was measured with an YSI 556 handheld  
145 probe.

### 146 147 2.3 Analysis

148  
149 Concentrations of dTM (Cd, Co, Cu, Fe, Ni, Pb, Zn) in groundwater samples were  
150 determined by stripping voltammetry using a Metrohm VA-797 Computrace and a  
151 Metrohm 663 VA. These instruments were equipped with a hanging mercury drop  
152 electrode as the working electrode, Ag/AgCl as the reference electrode and a Pt wire as  
153 the counter electrode. Before the determination, water samples were UV-digested for 3

154 h in a UV digester equipped with a high-pressure mercury lamp at 200 W (Achterberg  
155 and Van den Berg, 1994). Two different analytical methods were employed depending  
156 on the metal to be determined. Anodic stripping voltammetry was used for the  
157 determination of Zn, Pb and Cd (Gardiner and Stiff, 1974). Adsorptive cathodic  
158 stripping voltammetry with mixed ligands was utilized for Fe (Obata and Van den Berg,  
159 2001) and Cu, Ni and Co (Santos-Echeandía, 2011). Each sample was analyzed at least  
160 two times to check the precision of the measurement. The relative standard deviation  
161 was below 11%. The accuracy of the analytical procedure was assessed by the analyses  
162 of CASS 4 (NRC-CNRC), a nearshore seawater certified reference material (CRM).  
163 Results for CASS 4 differed within 10% of the certified values for Zn, Cu, Fe, Ni and  
164 Cd and within 17% for Pb. The detection limits were 0.04 nmol L<sup>-1</sup> for Cd, 0.06 nmol L<sup>-1</sup>  
165 <sup>1</sup> for Co, 0.31 nmol L<sup>-1</sup> for Cu, 3.9 nmol L<sup>-1</sup> for Fe, 0.12 nmol L<sup>-1</sup> for Ni, 0.04 nmol L<sup>-1</sup>  
166 for Pb and 0.85 nmol L<sup>-1</sup> for Zn. Results were corrected for blank analyses.

167

## 168 2.4 Calculations of continental trace metal fluxes

169

170 Metal concentrations in SGD end-members and magnitudes of SGD water flows to the  
171 NW Mediterranean Sea are required in order to quantify the SGD-driven dTM fluxes to  
172 the study area. We differentiated karstic from detrital SGD systems, because the  
173 hydrogeological setting of the aquifer and the discharge type (i.e. rapid discharges  
174 through fractures in karstified carbonates and slow [diffuse diffusive](#) flows through  
175 permeable sediments in detrital aquifers) can affect the chemical composition of SGD  
176 (Tovar-Sánchez et al., 2014b).  
177 SGD water flows into the NW Mediterranean Sea have been quantified [by using Ra](#)  
178 [isotopes and <sup>222</sup>Rn as tracers of the process](#) in several locations of the Spanish and

179 French coasts in the last decade, both in detrital contexts (Baudron et al., 2015; Ollivier  
180 et al., 2008; Rodellas et al., 2014, 2012; Tovar-Sánchez et al., 2014b; Trezzi et al.,  
181 2016) and in karstified carbonate formations (Garcia-Solsona et al., 2010a, 2010b;  
182 Mejías et al., 2012; Rodellas et al., 2015b; Stieglitz et al., 2013; Tovar-Sánchez et al.,  
183 2014b) (Supporting Information, Appendix A). We used SGD estimations normalized  
184 to the shoreline length of the different sites to estimate SGD-driven dTM fluxes. When  
185 the studies focused on specific sites did not report shore-normalized SGD flows, we  
186 used the values reported in Rodellas et al. (2015a), where the SGD flows were divided  
187 by the approximate shore length or the bay mouth width of the study area. We also  
188 applied this methodology to obtain shore-normalized SGD flows for those locations not  
189 included in Rodellas et al. (2015a). We considered the median values and the ranges  
190 between the 1<sup>st</sup> and the 3<sup>rd</sup> quartiles of the data set as the best representation of shore-  
191 normalized water flows in karstic and detrital SGD systems (Supporting Information,  
192 Appendix A).

193 Trace metal concentrations in SGD end-members have been reported in the literature  
194 only for few sites in the NW Mediterranean Sea (Rodellas et al., 2014; Tovar-Sánchez  
195 et al., 2014b; Trezzi et al., 2016). Therefore, we integrated these data with additional  
196 SGD end-members of different salinities collected along the Spanish and French  
197 Mediterranean coasts (Table 1). As for the water flow estimations, the median values  
198 and the ranges between the 1<sup>st</sup> and the 3<sup>rd</sup> quartiles were considered as the best  
199 representation of metal concentrations in karstic and detrital SGD systems. When dTM  
200 concentrations measured in water samples were lower than the limits of detection  
201 (which was the case for Cd (samples Garbí, Suís, badum, peníscola and Arenys), for Co  
202 (samples Garbí) and for Pb (samples Garbí and Font Centre) ~~in some samples~~), the limit  
203 of detection itself was used in the calculations, leading to an upper limit in the

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204 estimation of the flux.

205 Dissolved metal concentrations in karstic and detrital SGD end-members were

206 multiplied by the respective SGD water flows. Karstic and detrital SGD-driven dTM

207 fluxes to the NW Mediterranean Sea were calculated separately, classifying 40% of the

208 coastline as karstic systems and the remaining 60% as detrital. The sum of these metal

209 fluxes was considered as the total contribution of SGD to the study area. Coastline-

210 normalized karstic and detrital SGD dTM fluxes were multiplied by the corresponding

211 shore length (3,500 km) in order to obtain values in mol y<sup>-1</sup>.

212

213 Dissolved trace metal concentrations for the main rivers of the NW Mediterranean Sea

214 (Rhone and Ebro) reported in the literature (Elbaz-Poulichet et al., 1996, 1989; Guieu et

215 al., 1997, 1993; Ollivier et al., 2011; UNEP/MAP/MED POL, 2003) were used for the

216 calculation of fluxes of dTM associated to riverine discharge (Supporting Information,

217 Appendix B). These rivers were considered the most representative rivers of the area, as

218 they account for a large portion of the total riverine discharge (Guieu et al., 1997). The

219 median metal concentrations and the ranges between the 1<sup>st</sup> and the 3<sup>rd</sup> quartiles of the

220 data set were considered as the best representation of dissolved concentrations of Cd,

221 Cu, Ni, Pb and Zn in the river end-member. For Co and Fe, dissolved concentrations in

222 the Rhone and the Ebro Rivers are reported only in a limited number of works (Elbaz-

223 Poulichet et al., 1989; Guieu et al., 1997, 1993), so that we calculated the mean of the

224 concentrations of these metals and the relative standard deviations. Dissolved metal

225 concentrations were multiplied by the sum of the water flows from rivers in the study

226 area ( $71 \cdot 10^9 \text{ m}^3 \text{ y}^{-1}$ ) (UNEP/MAP/MED POL, 2003) in order to obtain the fluxes of

227 dTM through rivers into the NW Mediterranean Sea.

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229 Dissolved trace metal fluxes from the atmospheric deposition were estimated from  
230 literature data for the combination of wet and dry deposition metal fluxes to the  
231 Mediterranean Sea (Bonnet and Guieu, 2006; Chester et al., 1999; Guerzoni et al., 1999;  
232 Guieu et al., 2010, 1997, 1993; Migon et al., 1997, 1991; Ridame et al., 1999; Sandroni  
233 and Migon, 2002) (Supplementary Information, Appendix C). When values of dTM  
234 fluxes were not directly reported, we calculated them from data on the total fraction of  
235 metals (dissolved + particulate), by using the percentages of partitioning between the  
236 different fractions provided by Guieu et al. (1997). Mean values of atmospheric dTM  
237 fluxes (in mol km<sup>-2</sup> y<sup>-1</sup>) for each literature work are reported in the Supplementary  
238 Information, Appendix C. The median values and the ranges between the 1<sup>st</sup> and the 3<sup>rd</sup>  
239 quartiles of the data set were considered as the best representation of atmospheric  
240 dissolved fluxes of Cd, Cu, Fe, Ni, Pb and Zn to the NW Mediterranean Sea. For Co,  
241 data of atmospheric fluxes are reported only in a limited number of works (Chester et  
242 al., 1999; Guieu et al., 1997, 1993), so that we used the mean dissolved atmospheric  
243 fluxes and the relative standard deviations. The obtained metal atmospheric fluxes were  
244 multiplied by the surface of the study area (180,000 km<sup>2</sup>) to obtain atmospheric metal  
245 fluxes in mol y<sup>-1</sup>. For trace metals of anthropogenic origin such as Cd, Pb and Zn, the  
246 calculated atmospheric fluxes represent an upper limit, due to the decrease of their  
247 emission in the atmosphere since the second half of the 1980s (Heimbürger et al., 2010).

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### 249 **3 Results and Discussion**

250

#### 251 **3.1 Metal characterization of SGD**

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253 SGD end-members spanned a wide range of salinities: karstic SGD had salinities  
254 ranging between 0.3 and 9.7, whereas detrital SGD samples were in the range of 0.2–36  
255 (Table 1). The higher variability in salinity for detrital SGD with respect to karstic SGD  
256 is related to the intrusion of recirculated seawater through permeable beach sediments  
257 (Moore, 1999).

258 The variability of trace metal concentrations in SGD systems depends on the geological  
259 composition of the coastal aquifers, the possible groundwater contamination through  
260 anthropogenic activities (Beck et al., 2009; Trezzi et al., 2016), the residence time of  
261 groundwater in the aquifers and the mixing of freshwater and seawater in the  
262 subterranean estuary (Beck et al., 2007; Moore, 1999). In karstic SGD, the ranges of  
263 dTM concentrations (in  $\text{nmol L}^{-1}$ ) were <0.04 – 3.1 for Cd, <0.06 – 4.0 for Co, 0.68 –  
264 24 for Cu, 18 - 840 for Fe, 1.6 – 43 for Ni, <0.04 – 2.1 for Pb and 7.2 – 300 for Zn. In  
265 detrital SGD, the ranges of dTM concentrations (in  $\text{nmol L}^{-1}$ ) were <0.04 – 14 for Cd,  
266 0.10 – 6.9 for Co, 1.7 – 160 for Cu, 44 – 460 for Fe, 4.5 – 83 for Ni, 0.19 – 7.4 for Pb,  
267 and 13 – 2100 for Zn.

268 Figure 2 shows the comparison between metal concentrations in karstic and detrital  
269 SGD end-members, for which ranges between the 1<sup>st</sup> and the 3<sup>rd</sup> quartiles were reported.  
270 Detrital SGD was distinctively more enriched in Co, Cu and Ni than karstic SGD. For  
271 the other trace metals (Cd, Fe, Pb and Zn), the ranges of concentrations in karstic and  
272 detrital SGD were comparable, although the median values of Fe were higher in karstic  
273 SGD (up to 1.5 times) and the median values of Pb were higher in detrital SGD (up to  
274 2.5 times). **There are two possible main explanations for these differences in dTM**  
275 **concentrations between karstic and detrital SGD. The different geological matrix of the**  
276 **karstic and detrital aquifers can contribute differently to the chemical composition of**  
277 **the interacting groundwater; while karstic systems are composed predominantly by**

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278 carbonate minerals, detrital systems can be characterized by different lithologies and a  
279 consequent larger variability of minerals. Secondly, the geochemical reactions that  
280 occur in the subterranean estuary, before groundwater discharges into the coastal sea,  
281 largely affect solute concentrations in SGD. In karstic systems, infiltrated groundwater  
282 can be rapidly transferred to the coastal sea due to the presence of underground  
283 fractures and preferential pathways (Garcia-Solsona et al., 2010b; Gonnee et al., 2014;  
284 Tovar-Sánchez et al., 2014b). Thus, the SGD discharging into the coastal sea through  
285 coastal springs is generally oxygenated and characterized by a limited interaction with  
286 the geological matrix of the aquifer. Contrary, detrital SGD flows across the permeable  
287 sediments of the coastal aquifers, where it mixes with recirculated seawater before  
288 discharging into the sea. Detrital SGD is thus subjected to several geochemical  
289 transformations such as redox-controlled solubility, adsorption on organic matter and/or  
290 on Fe and Mn oxides, release from these oxides and desorption from sediments  
291 (Charette and Sholkovitz, 2006). Co and Ni are redox-sensitive elements controlled by  
292 Mn geochemistry in porewater of coastal and shelf sediments (Beck et al., 2007, 2010;  
293 Santos-Echeandia et al., 2009). The higher concentrations of Co and Ni in detrital SGD  
294 samples with respect to the karstic ones may be related to their release from Mn oxides  
295 during the diagenetic remobilization of Mn (Beck et al., 2010; Santos-Echeandia et al.,  
296 2009). On the other hand, Cu is strongly associated to the organic matter (Du Laing et  
297 al., 2009; Santos-Echeandia et al., 2009; Shaw et al., 1990), which is commonly more  
298 abundant in detrital systems than in the karstic ones. This may explain the higher  
299 concentration of Cu in detrital SGD. The comparable concentrations of dissolved Fe  
300 between karstic and detrital SGD may be due to the oxygenated conditions of karstic  
301 SGD and to the precipitation of Fe, with the formation of Fe oxides, when recirculated  
302 seawater mixes with groundwater in detrital systems (Charette and Sholkovitz, 2006,

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303 2002; Windom et al., 2006). Finally, for Cd, Pb and Zn, the generally comparable  
304 ranges of concentrations in karstic and detrital SGD may be ascribed to their lower  
305 redox-sensitivity (for Pb and Zn) (Santos-Echeandia et al., 2009), to their lower  
306 association with the organic matter (for Cd, Pb and Zn) (Roux et al., 1998; Santos-  
307 Echeandia et al., 2009) or to their removal from the solution due to the presence of the  
308 so-called Fe-curtain (for Cd and Zn) (Charette and Sholkovitz, 2006, 2002; Trezzi et al.,  
309 2016). These properties may prevent the detrital SGD to get distinctly more enriched in  
310 Cd, Fe, Pb and Zn with respect to karstic SGD.

~~311 Differences in metal concentrations between karstic and detrital SGD can be in part  
312 related to the type of water discharge itself. In karstic systems, groundwater flows  
313 rapidly through fractures and conduits and therefore the time for the interaction of  
314 groundwater with the aquifer matrix is lower in comparison with detrital systems  
315 (Tovar-Sánchez et al., 2014b). Thus, the higher concentrations of Cu, Ni and Co in  
316 detrital SGD samples with respect to the karstic ones could be related to the fact that  
317 they are crustal-derived elements and become enriched in groundwater mainly due to  
318 the interaction with the sediments of the aquifer. The generally comparable ranges of  
319 concentrations of Cd, Fe, Pb and Zn in karstic and detrital aquifers can indicate that  
320 these components may be removed from the solution when groundwater mixes with  
321 recirculated seawater, in particular in detrital subterranean estuaries.~~

322  
323 The karstic SGD end-member analysed in three different seasons (Garbí) displayed  
324 variability in dTM concentrations, in particular for Cd ( $< 0.04 - 0.49 \text{ nmol L}^{-1}$ ) and Fe  
325 ( $35 - 840 \text{ nmol L}^{-1}$ ). The detrital SGD system sampled twice in 10 days after a rain  
326 event (Argentona) also showed some variability in metal concentrations for Cd, Cu, Ni  
327 and Zn, in addition to a variation in salinity (Table 1). This temporal variability of Garbí



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328 and Argenton samples illustrated the difficulty on establishing appropriate SGD end-  
329 members, which is traditionally one of the most significant uncertainties in the  
330 investigation of SGD processes. The different dTM concentrations showed by Garbí  
331 and Argenton samples were generally ~~within included in~~ the ranges between minimum  
332 and maximum values measured in the other SGD end-members. Therefore, we assume  
333 that the temporal variability of the other SGD end-members was also included in the  
334 ranges of dTM concentrations used as the best representation of the SGD end-member  
335 in the study area (see Section 2.4).

336  
337 Dissolved metals concentrations in SGD end-members were higher than those of  
338 seawater of the open Western Mediterranean Sea (2.6 - 4.5 nmol L<sup>-1</sup> for Zn, 1.1 - 2.3  
339 nmol L<sup>-1</sup> for Cu, 3.2 - 3.6 nmol L<sup>-1</sup> for Ni, 1.4 - 8.0 nmol L<sup>-1</sup> for Fe, 0.13 - 0.28 nmol L<sup>-1</sup>  
340 for Pb, 0.05 - 0.17 nmol L<sup>-1</sup> for Co and 0.06 - 0.08 nmol L<sup>-1</sup> for Cd) (Tovar-Sánchez et  
341 al., 2014a; Yoon et al., 1999) for most of the metals, as shown in Figure 3. This was  
342 particularly evident for Zn and Fe (up to two orders of magnitude). Concentrations of  
343 Pb in SGD were comparable to the ones of open seawater for most of the samples,  
344 indicating that SGD probably is not a relevant source of dissolved Pb to the NW  
345 Mediterranean Sea.

346  
347 The concentrations of dTM in SGD end-members (obtained unifying the data set on  
348 karstic and detrital systems) were compared to those reported in the literature for the  
349 Rhone and the Ebro Rivers (Figure 3). For the data set presented in this work, the  
350 clearest differences were the higher concentrations of dissolved Zn in SGD and  
351 dissolved Cu in the rivers. For the other trace metals, the ranges of concentrations were  
352 comparable in SGD and in rivers, although the median concentrations of Cd, Co, Ni and

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353 Pb in rivers were higher than in SGD. These differences may be related to the  
354 distinctive environments of coastal aquifers and rivers, with steep redox gradients in  
355 subterranean estuaries and the presence of microbes that can affect the speciation and  
356 mobility of trace metals (Knee and Paytan, 2011; O'Connor et al., 2015). ~~different~~  
357 ~~pH/redox conditions in subterranean estuaries with respect to surface estuaries.~~ The  
358 comparison of dTM concentrations in SGD and rivers confirmed that SGD must be  
359 evaluated as a potential source of metals to the coastal ocean, given that dTM  
360 concentrations of SGD end-members are at least similar to those of rivers for most of  
361 the metals. Thus, the volume of riverine and SGD water discharges will determine the  
362 relative significance of these two inputs of dTM to the coastal sea.

363

### 364 3.2 Comparison of trace metal fluxes into the NW Mediterranean Sea

365

366 Trace metal inputs through SGD are ~~also~~ conditioned by the multiple and complex  
367 processes occurring during the transport through the sediments and/or aquifer, ~~which~~  
368 ~~can affect the dTM concentrations of SGD.~~ Indeed, the selection of appropriate SGD  
369 ~~end-members is one of the most challenging points in the assessment of SGD-driven~~  
370 ~~metal fluxes to the ocean.~~ The SGD end-members collected in this work were certainly  
371 ~~representative of the water effectively discharging into the sea in the case of the coastal~~  
372 ~~karstic springs.~~ For detrital systems, the most real SGD end-member was determined by  
373 ~~collecting several SGD samples of different salinities (fresh and brackish groundwater~~  
374 ~~and recirculated seawater) and by including literature data of dTM already considered~~  
375 ~~as representative of the SGD end-members by the respective authors.~~ This approach  
376 ~~permits to obtain a first approximation of SGD-driven dTM fluxes, whose magnitude~~

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377 can be compared to riverine discharge and atmospheric deposition, with the aim of  
378 evaluating the relevance that SGD can have in the NW Mediterranean Sea.

379

380 A summary of the calculated SGD-driven, riverine and atmospheric dTM fluxes to the  
381 NW Mediterranean Sea is shown in Figure 4 and in Table 2.

382 SGD-driven dTM fluxes (in  $10^6 \text{ mol y}^{-1}$ ) to the NW Mediterranean Sea are (0.0007 –  
383 0.03) for Cd, (0.004 – 0.11) for Co, (0.09 – 1.9) for Cu, (1.8 - 29) for Fe, (0.09 – 1.9)  
384 for Ni, (0.002 – 0.06) for Pb and (0.38 - 12) for Zn. Trace metals inputs through SGD  
385 can be subjected to seasonal variability. Unfortunately, detailed information about  
386 temporal characterization of SGD (metal concentrations and/or water flow) in each  
387 coastal aquifer considered in the work is not available. Notice that the repeated  
388 sampling of two SGD end-members, collected twice and three times (Argentona and  
389 Garbí, respectively), showed a minimum variability of the dTM concentrations  
390 compared to the range of concentrations reported for groundwater samples. Thus, even  
391 considering temporal variability of SGD, the magnitude of the calculated SGD-driven  
392 dTM fluxes can be still compared to continental inputs of dTM via riverine discharge  
393 and atmospheric deposition.

394 ~~Nevertheless, the magnitude of the calculated SGD-driven dTM fluxes can be still~~  
395 ~~compared to continental inputs of dTM via riverine discharge and atmospheric~~  
396 ~~deposition, with the aim of evaluating the relevance that SGD can have in the NW~~  
397 ~~Mediterranean Sea.~~

398 Dissolved trace metal fluxes from rivers to the NW Mediterranean Sea (in  $10^6 \text{ mol y}^{-1}$ ),  
399 calculated using data from the literature as explained in Section 2.4, are (0.02 – 0.03)  
400 for Cd, (0.08 – 0.09) for Co, (1.9 – 2.4) for Cu, (13 – 17) for Fe, (1.5 – 1.7) for Ni, (0.01  
401 – 0.03) for Pb and (1.1 – 1.4) for Zn.

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402 Dissolved trace metal fluxes from atmospheric deposition to the NW Mediterranean Sea  
403 (in  $10^6 \text{ mol y}^{-1}$ ), calculated with literature data as explained in Section 2.4, are (0.07 -  
404 0.44) for Cd, (0.04 - 0.52) for Co, (2.2 - 3.5) for Cu, (91 - 280) for Fe, (1.1 - 2.5) for Ni,  
405 (1.1 - 1.6) for Pb and (15 - 110) for Zn.

406  
407 Our estimates of the continental inputs of dTM into the NW Mediterranean Sea show  
408 that riverine metal fluxes of dissolved Cd, Co, Fe, Ni, Pb and Zn fall within the ranges  
409 of the SGD-driven fluxes. However, the median SGD-driven fluxes of these dTM are  
410 distinctively lower than riverine fluxes (from 2 to 7 times, depending on the metal),  
411 with the exception of Zn, which is comparable (Figure 4; Table 2). The SGD-driven  
412 flux of dissolved Cu is distinctly lower than the riverine one. This comparison between  
413 SGD and rivers does not consider riverine fluxes of particulate material, which are  
414 thought to be important for dissolved elements in seawater in relation to the potential  
415 dissolution of the transported particles (Jeandel and Oelkers, 2015; Oelkers et al., 2011).  
416 Compared to atmospheric dTM fluxes, the ranges of SGD-driven fluxes of dissolved  
417 Cd, Cu, Fe, Pb and Zn are distinctively lower (Figure 4; Table 2). The SGD-driven  
418 fluxes of dissolved Co and Ni are also generally lower than the atmospheric ones,  
419 showing a difference of one order of magnitude for the median values.

### 420 421 3.3 Spatial and temporal influence of the continental trace metal fluxes

422  
423 The presented comparison between continental inputs of dTM to the NW Mediterranean  
424 Sea did not consider the spatial and temporal distribution of SGD, rivers and  
425 atmospheric deposition. These distributions are different (Figure 5) and should be taken  
426 into account for an appropriate evaluation of the effects of the sources of dTM on

1 427 coastal geochemical cycles. Conversely to SGD and riverine discharge, which are short-  
2 428 scale coastal processes, atmospheric deposition occurs over the whole NW  
3  
4 429 Mediterranean basin. Consequently, even if the atmospheric dTM fluxes calculated in  
5  
6 430 Section 3.2 are clearly higher than those through SGD, the real contribution of these  
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8 431 two inputs to the coastal sea should be evaluated dividing the calculated dTM fluxes by  
9  
10 432 the respective areas of influence. For the atmospheric deposition, the area of influence is  
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12 433 the total study area (180,000 km<sup>2</sup>). In the case of SGD, several local studies have  
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14 434 highlighted that this process usually does not reach a distance offshore higher than 2-3  
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16 435 km (on the base of Ra isotopes and/or salinity differences in coastal seawater) and that  
17  
18 436 inputs of macronutrients and metals through SGD decrease towards the open seawater,  
19  
20 437 being concentrated in the first hundreds of meters (Gonneea et al., 2014; Mejías et al.,  
21  
22 438 2012; Moore, 2003; Rodellas et al., 2014; Trezzi et al., 2016; Windom et al., 2006).  
23  
24 439 Dissolved trace metals supplied to this coastal seawater can also be removed from the  
25  
26 440 water column by means of biogeochemical processes (Bruland and Lohan, 2003).  
27  
28 441 Therefore, if we consider a distance of 3 km offshore as an upper limit affected by SGD  
29  
30 442 and multiply it by the 3,500 km of coastline of the study area, a maximum area of  
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32 443 influence for SGD of about 10,500 km<sup>2</sup> is obtained. Thus, we calculate the area-  
33  
34 444 weighted SGD-driven dTM fluxes, which are a lower limit (at least for Cu, Fe, Ni and  
35  
36 445 Zn) of the possible SGD contribution to the coastal area. In the case of Cd, Co and Pb,  
37  
38 446 the obtained SGD values are not necessarily a lower limit, since for the samples  
39  
40 447 characterized by no detectable metal concentrations, the limit of detection itself was  
41  
42 448 considered in the calculations (see Section 2.4). The comparison of these SGD-driven  
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44 449 fluxes with the atmospheric dTM fluxes (in mol y<sup>-1</sup> km<sup>-2</sup>) highlights that SGD inputs to  
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46 450 the coastal sea are comparable or higher than atmospheric deposition for all the metals  
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48 451 studied here, with the exception of Pb (Figure 6).  
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452 SGD and river inputs have also a significant difference in their spatial distribution.  
453 Trace metal inputs driven by SGD are ubiquitous all along the coast, since fresh  
454 groundwater discharges anywhere an aquifer with a positive head relative to sea level is  
455 hydraulically connected with the sea (Johannes, 1980) and the recirculation of seawater  
456 through the coastal aquifer is also expected to occur in most of the coastal systems  
457 (Knee and Paytan, 2011). On the contrary, riverine discharge is limited to the  
458 surroundings of river mouths. River plumes are the maximum boundaries where dTM  
459 provided by rivers could be detected, if they are not removed before through biological  
460 uptake, scavenging by particles or precipitation (Bruland and Lohan, 2003). River  
461 plumes are influenced by winds and marine currents: for example, the plume of the  
462 Ebro River is usually deviated southwards and reach a maximum distance of 80 km  
463 from the river mouth (Palanques and Drake, 1990). Consequently, no direct influence of  
464 this river would be expected in the northern area and beyond 80 km in the southern  
465 zone. For smaller rivers or ephemeral streams, the river influence would be restricted to  
466 a shorter distance from the river mouth. Thus, in areas characterized by the absence of  
467 rivers or river plumes, SGD, together with atmospheric deposition, is the major source  
468 of dTM to the coastal sea.

469  
470 [A](#) Temporal ~~variability variable~~ should also be considered when comparing the different  
471 continental inputs of dTM to the NW Mediterranean Sea. Thus, whilst SGD and rivers  
472 can be considered a permanent source of dTM to the coastal areas (even if they are  
473 affected by water flow fluctuations on annual scale), atmospheric deposition in the  
474 Mediterranean Sea has a very high intra-annual and inter-annual variability, with most  
475 of the flux concentrated in few strong events during the year (Avila et al., 1998; Guieu  
476 et al., 2010). This is particularly true for crustal-derived trace metals (Fe, Co and part of

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477 Ni and Cu), whose atmospheric deposition is related principally to Saharan dust events  
478 (Heimbürger et al., 2010). Therefore, the relative significance of SGD-driven dTM  
479 fluxes to the NW Mediterranean Sea can be actually higher in absence of dust events  
480 and lower during the dust events.

481

### 482 3.4 Relevance of SGD for the global Mediterranean Sea

483

484 The Mediterranean Sea is one of the most oligotrophic and exploited seas in the world,  
485 where the sources of nutrients are limited (Macias et al., 2014). Atmospheric deposition  
486 (Guerzoni et al., 1999; Guieu et al., 2010, 1997) and riverine runoff (Ludwig et al.,  
487 2009; Macias et al., 2014) have been traditionally considered the main continental  
488 sources of nutrients, while other sources such as SGD are not commonly considered or  
489 documented. However, the relevance of SGD as a source of macronutrients to the whole  
490 Mediterranean basin was recently demonstrated (Rodellas et al., 2015a) and the present  
491 study represents the first evidence of the potential relevance of SGD as a source of dTM  
492 (e.g. Cd, Co, Cu, Fe, Ni, Pb and Zn) at regional scale. While this study is particularly  
493 focused on the NW Mediterranean Sea, the paucity of data on dTM concentrations of  
494 SGD end-members of the South Western and Eastern Mediterranean basins and the  
495 difficulty to obtain these data currently prevent the extension of these calculations to the  
496 whole Mediterranean Sea. However, some general considerations about the key role of  
497 SGD in contributing dTM to the whole Mediterranean Sea can be made.

498

499 Although median SGD-driven dTM fluxes seem to be lower (for Cd, Co, Cu, Fe, Ni and  
500 Pb) or comparable (for Zn) with respect to riverine fluxes in the NW Mediterranean  
501 zone, it should be noticed that this area is characterized by the presence of the second

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502 (Rhone) and the forth (Ebro) major rivers of the Mediterranean Sea (Ludwig et al.,  
503 2009). If we consider other areas of the Mediterranean basin, the riverine discharge is  
504 distinctively lower, with the exception of the Adriatic Sea (Po river) and the area of the  
505 Nile delta (Ludwig et al., 2009). This is particularly true for the arid and semi-arid  
506 regions of the Mediterranean Sea, such as the Eastern coast, the African coast and many  
507 islands. For instance, the riverine discharge along 4,400 km of coastline from Morocco  
508 to Libya is less than  $10^9 \text{ m}^3 \text{ y}^{-1}$  (Ludwig et al., 2009), whereas the riverine discharge in  
509 the NW Mediterranean Sea, with a slightly shorter coastline (3,500 km), is more than 70  
510 times higher.

511 A first-order estimation of SGD-driven dTM fluxes for the African coast could be  
512 obtained with the same procedure described for the NW basin, using the shore-  
513 normalized SGD water flow of the whole Mediterranean Sea (Rodellas et al., 2015a)  
514 and assuming the same dTM concentrations of SGD end-members from the NW  
515 Mediterranean area. Thereby, SGD-driven dTM fluxes from the African coast would be  
516 distinctively higher than riverine metal fluxes (up to 3 orders of magnitude), assuming  
517 similar concentrations in rivers of North Africa and the NW Mediterranean Sea (notice  
518 that recent data on the African Moulouya River showed dTM concentrations  
519 comparable or lower than those of the Ebro and Rhone Rivers (Tovar-Sánchez et al.,  
520 2016) ). SGD would thus be a much more significant source of dTM than rivers for  
521 coastal seawater in the arid and semi-arid regions of the Mediterranean Sea.

522

### 523 3.5 Biogeochemical implications of SGD

524

525 Most of the trace metals analysed in this work (i.e. Cd, Co, Cu, Fe, Ni and Zn) are  
526 essential micronutrients for the planktonic community, as their deficiency can limit



1 527 oceanic plankton production, whereas they can be toxic at high levels (Jordi et al., 2012;  
2 528 Lafabrie et al., 2013; Morel and Price, 2003; Twining and Baines, 2013). Considering  
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4 529 that SGD is a significant source of dTM to the coastal sea, in particular in those areas  
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7 530 where the presence of rivers is limited, SGD may potentially have a strong impact on  
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10 531 the coastal productivity of the Mediterranean Sea. The involvement of SGD on  
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12 532 biogeochemical cycles of the Mediterranean Sea was already emphasized at regional  
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14 533 scale for macronutrient inputs (DIN, DIP and DSi) (Rodellas et al., 2015a). Therefore,  
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17 534 taking into account the results of this study, we hypothesize that the significance of  
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19 535 SGD for coastal biological communities in the oligotrophic Mediterranean Sea is related  
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22 536 not only to inputs of macronutrients but also of bioactive trace metals. However, the  
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24 537 link between SGD-driven dTM fluxes to the coastal sea and coastal productivity is a  
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26 538 complex topic that should be further investigated, as dTM can be removed from the  
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29 539 coastal seawater by several biogeochemical processes (Bruland and Lohan, 2003).  
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32 540 Nevertheless, SGD should be certainly considered in studies on the biogeochemistry of  
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34 541 coastal areas and in the assessment of trace metal budgets.

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#### 37 38 39 543 4 Conclusions

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43 545 This study is a first effort to estimate regional inputs of dTM (Cd, Co, Cu, Fe, Ni, Pb  
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45  
46 546 and Zn) through SGD to the oligotrophic Mediterranean Sea. SGD-driven dTM fluxes,  
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49 547 calculated for the NW basin and compared to riverine discharge and atmospheric  
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51 548 deposition, reveal that SGD is a significant source of dTM to the coastal Mediterranean  
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54 549 Sea. The relevance of SGD may be even higher in coastal areas of the Southern and  
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56 550 Eastern Mediterranean Sea or in many islands, which are characterized by scarce  
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58 551 riverine discharge. Therefore SGD should be taken into account for the assessment of  
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552 trace metal budgets and for biogeochemical studies in coastal areas, as some of the  
553 metals delivered by this process are crucial micronutrients for primary productivity in  
554 the ocean.

555 Further investigations on trace metal inputs through SGD in the Mediterranean Sea are  
556 required in order to improve the estimation of SGD fluxes presented in this study.

557 Indeed, spatial and temporal variability of trace metal concentrations in SGD end-

558 members, as well as relations between concentrations and magnitude of water flows,

559 need to be investigated in a large number of subterranean estuaries. At the same time,

560 the present data set should be expanded with the characterization of metal inputs

561 through SGD in areas that are not well studied at the moment, such the African Coast.

562

## 563 SUPPORTING INFORMATION

564 Karstic and detrital SGD-driven flows reported in the literature for local studies in the

565 NW Mediterranean Sea (Appendix A); dissolved trace metal concentrations of the

566 Rhone and the Ebro Rivers reported in the literature (Appendix B); atmospheric

567 dissolved trace metal fluxes to the Mediterranean Sea reported in the literature

568 (Appendix C).

569

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1           **Submarine groundwater discharge: a significant source of dissolved**  
2           **trace metals to the North Western Mediterranean Sea**

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26           Key words: submarine groundwater discharge (SGD), trace metals, micronutrients,

27           Mediterranean Sea, rivers, atmospheric deposition

28 Abstract

29

30 Bioactive trace metals play a significant role as micronutrients in the ocean and  
31 therefore it is important to evaluate their sources. Submarine Groundwater Discharge  
32 (SGD) has been recognized as an input of trace metals to the coastal sea. Here, we  
33 investigated the significance of SGD as a source of dissolved trace metals (dTM) to the  
34 coastal sea in a regional area such as the North Western (NW) Mediterranean Sea. We  
35 analyzed dTM concentrations in SGD end-members and incorporate data on SGD dTM  
36 concentrations and water flows reported in previous studies carried out in this area, to  
37 estimate the following ranges of SGD-driven dTM fluxes (in  $10^6 \text{ mol y}^{-1}$ ): Cd: 0.0007 -  
38 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:  
39 0.38 - 12. These fluxes were compared to dTM fluxes from riverine discharge and  
40 atmospheric deposition, demonstrating that SGD is a major source of dTM to the NW  
41 Mediterranean Sea. Whilst riverine inputs are limited to the surrounding of river mouths  
42 and atmospheric fluxes are distributed throughout the whole basin mainly during  
43 sporadic depositional events, SGD represents a permanent, albeit seasonally variable,  
44 source of metals to most of the coastal areas. SGD-driven dTM inputs may be even  
45 more significant, in relative terms, in other coastal regions of the Mediterranean Sea  
46 where rivers are scarce, as it is the case of the African coast and many islands. This  
47 study highlights the relevance of SGD as a source of dTM to the Mediterranean Sea and  
48 the need of its consideration in the calculation of metal budgets in the basin and in the  
49 investigation of biogeochemical cycles in coastal areas.

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52 **1 Introduction**

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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. Bowers 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 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

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79 prominent since the estimated SGD-driven macronutrient fluxes (DIN, DIP and DSi)  
80 are comparable or even higher than the riverine and atmospheric fluxes (Rodellas et al.,  
81 2015a). The relevance of SGD in delivering dissolved trace metals (dTM) to the  
82 Mediterranean Sea has been highlighted in some local areas, characterized by the  
83 absence of riverine discharge (Rodellas et al., 2014; Tovar-Sánchez et al., 2014b; Trezzi  
84 et al., 2016).  
85 The aim of this study is to quantify SGD-driven dTM fluxes at regional scale and  
86 evaluate their significance. We determine these fluxes in the North Western (NW)  
87 Mediterranean Sea and compare them to other external sources (i.e. riverine discharge  
88 and atmospheric deposition). This area was considered an appropriate study site for  
89 conducting such a comparison for three main reasons: 1) the existence of several studies  
90 reporting local estimations of SGD flows that can be used to obtain a reliable regional  
91 estimate of SGD-driven dTM fluxes (i.e., Baudron et al., 2015; Garcia-Solsona et al.,  
92 2010a, 2010b; Mejías et al., 2012; Ollivier et al., 2008; Rodellas et al., 2015b, 2014,  
93 2012; Stieglitz et al., 2013; Tovar-Sánchez et al., 2014b; Trezzi et al., 2016); 2) the  
94 large riverine discharge in this area compared with most zones of the Mediterranean  
95 basin (Ludwig et al., 2009); 3) the influence of atmospheric deposition originating from  
96 Europe and the Saharan region (Guerzoni et al., 1999; Guieu et al., 1997).

## 97 98 **2 Methodology**

### 99 100 2.1 The NW Mediterranean Sea

101  
102 The Mediterranean Sea is a semi-enclosed basin connected to the Atlantic Ocean  
103 through the Strait of Gibraltar, characterized by a net export of nutrients to the Atlantic

104 Ocean, that leads to oligotrophic conditions in the whole basin (Béthoux et al., 1998).

105 Climate conditions of the Mediterranean Sea generally consist of dry summers and

106 rainy autumns and winters, with larger mean annual precipitation in the north and

107 western parts of the basin.

108 The study area comprises the NW Mediterranean zone (Eastern Spanish coast, including

109 the Balearic Islands, and French Mediterranean coast, up to Marseille city),

110 encompassing a coastline of about 3,500 km and a surface area of about 180,000 km<sup>2</sup>

111 (Figure 1). The Rhone and the Ebro are the main rivers in this area, representing more

112 than the 70% of the total riverine discharge to the Western Mediterranean Sea, with

113 mean water flows of  $54 \cdot 10^9$  and  $13 \cdot 10^9$  m<sup>3</sup> y<sup>-1</sup>, respectively (Ludwig et al., 2009).

114 Groundwater inputs occur via both detrital and karstified coastal aquifers. Fractured

115 karstified carbonated aquifers constitute a large portion (about the 40%) of the French

116 and Spanish coasts, including the Balearic Islands (Bakalowicz, 2015, 1999; Instituto

117 Geologico Minero de España (IGME), 1986).

118

## 119 2.2 Sampling

120

121 Groundwater samples representative of the water discharging into the sea (i.e. SGD

122 end-members) were collected between November 2013 and June 2015 at several

123 locations along the Spanish and French Mediterranean coasts: 10 samples were

124 collected from karstic systems and 8 from detrital systems (Figure 1; Table 1).

125 The karstic waters corresponded to 3 different coastal carbonate aquifers and were

126 collected mostly from flowing coastal springs associated with fractures (Garbí, Suís,

127 Badum, Font Centre, Font South, Estramar, La Palme). One of these springs (Garbí,

128 located close to the Ebro delta) was sampled three times (December 2013; July 2014;



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129 May 2015) in order to evaluate the variability in metal concentrations of this source.  
130 Groundwater flowing through detrital aquifers was sampled at 7 sites along the Spanish  
131 coast. Five of these end-members were obtained in beaches presumably characterized  
132 by the flow of fresh groundwater to the sea, from a manual piezometer placed down to  
133 the depth where groundwater seeping through the sand was found (Empuriabrava, La  
134 Fosca North, La Fosca South, Arenys and Sitges); one was collected in the channel  
135 connecting a coastal marshland to the sea (Peníscola), which is representative of the  
136 groundwater converging into the coastal wetland (Rodellas et al., 2012; Zarroca et al.,  
137 2014); the other two samples were collected from a coastal piezometer, sampled twice  
138 after a rainy period (Argentona).

139  
140 For each sample, 125 mL of water were directly collected following trace metal clean  
141 techniques (Tovar-Sánchez, 2012). Water was pumped through an acid-clean Teflon  
142 tube using a peristaltic pump, filtered with a 0.2 µm SuporCap filter and stored in acid-  
143 cleaned plastic bottles. Samples were then acidified to pH < 2 with trace metal grade  
144 HCl acid. At each sampling point, salinity was measured with an YSI 556 handheld  
145 probe.

### 146 147 2.3 Analysis

148  
149 Concentrations of dTM (Cd, Co, Cu, Fe, Ni, Pb, Zn) in groundwater samples were  
150 determined by stripping voltammetry using a Metrohm VA-797 Computrace and a  
151 Metrohm 663 VA. These instruments were equipped with a hanging mercury drop  
152 electrode as the working electrode, Ag/AgCl as the reference electrode and a Pt wire as  
153 the counter electrode. Before the determination, water samples were UV-digested for 3

154 h in a UV digester equipped with a high-pressure mercury lamp at 200 W (Achterberg  
155 and Van den Berg, 1994). Two different analytical methods were employed depending  
156 on the metal to be determined. Anodic stripping voltammetry was used for the  
157 determination of Zn, Pb and Cd (Gardiner and Stiff, 1974). Adsorptive cathodic  
158 stripping voltammetry with mixed ligands was utilized for Fe (Obata and Van den Berg,  
159 2001) and Cu, Ni and Co (Santos-Echeandía, 2011). Each sample was analyzed at least  
160 two times to check the precision of the measurement. The relative standard deviation  
161 was below 11%. The accuracy of the analytical procedure was assessed by the analyses  
162 of CASS 4 (NRC-CNRC), a nearshore seawater certified reference material (CRM).  
163 Results for CASS 4 differed within 10% of the certified values for Zn, Cu, Fe, Ni and  
164 Cd and within 17% for Pb. The detection limits were 0.04 nmol L<sup>-1</sup> for Cd, 0.06 nmol L<sup>-1</sup>  
165 <sup>1</sup> for Co, 0.31 nmol L<sup>-1</sup> for Cu, 3.9 nmol L<sup>-1</sup> for Fe, 0.12 nmol L<sup>-1</sup> for Ni, 0.04 nmol L<sup>-1</sup>  
166 for Pb and 0.85 nmol L<sup>-1</sup> for Zn. Results were corrected for blank analyses.

## 168 2.4 Calculations of continental trace metal fluxes

169  
170 Metal concentrations in SGD end-members and magnitudes of SGD water flows to the  
171 NW Mediterranean Sea are required in order to quantify the SGD-driven dTM fluxes to  
172 the study area. We differentiated karstic from detrital SGD systems, because the  
173 hydrogeological setting of the aquifer and the discharge type (i.e. rapid discharges  
174 through fractures in karstified carbonates and slow diffuse flows through permeable  
175 sediments in detrital aquifers) can affect the chemical composition of SGD (Tovar-  
176 Sánchez et al., 2014b).  
177 SGD water flows into the NW Mediterranean Sea have been quantified by using Ra  
178 isotopes and <sup>222</sup>Rn as tracers of the process in several locations of the Spanish and

179 French coasts in the last decade, both in detrital contexts (Baudron et al., 2015; Ollivier  
180 et al., 2008; Rodellas et al., 2014, 2012; Tovar-Sánchez et al., 2014b; Trezzi et al.,  
181 2016) and in karstified carbonate formations (Garcia-Solsona et al., 2010a, 2010b;  
182 Mejías et al., 2012; Rodellas et al., 2015b; Stieglitz et al., 2013; Tovar-Sánchez et al.,  
183 2014b) (Supporting Information, Appendix A). We used SGD estimations normalized  
184 to the shoreline length of the different sites to estimate SGD-driven dTM fluxes. When  
185 the studies focused on specific sites did not report shore-normalized SGD flows, we  
186 used the values reported in Rodellas et al. (2015a), where the SGD flows were divided  
187 by the approximate shore length or the bay mouth width of the study area. We also  
188 applied this methodology to obtain shore-normalized SGD flows for those locations not  
189 included in Rodellas et al. (2015a). We considered the median values and the ranges  
190 between the 1<sup>st</sup> and the 3<sup>rd</sup> quartiles of the data set as the best representation of shore-  
191 normalized water flows in karstic and detrital SGD systems (Supporting Information,  
192 Appendix A).

193 Trace metal concentrations in SGD end-members have been reported in the literature  
194 only for few sites in the NW Mediterranean Sea (Rodellas et al., 2014; Tovar-Sánchez  
195 et al., 2014b; Trezzi et al., 2016). Therefore, we integrated these data with additional  
196 SGD end-members of different salinities collected along the Spanish and French  
197 Mediterranean coasts (Table 1). As for the water flow estimations, the median values  
198 and the ranges between the 1<sup>st</sup> and the 3<sup>rd</sup> quartiles were considered as the best  
199 representation of metal concentrations in karstic and detrital SGD systems. When dTM  
200 concentrations measured in water samples were lower than the limits of detection  
201 (which was the case for Cd (samples Garbí, Suís, badum, peníscola and Arenys), for Co  
202 (samples Garbí) and for Pb (samples Garbí and Font Centre)), the limit of detection  
203 itself was used in the calculations, leading to an upper limit in the estimation of the flux.

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204 Dissolved metal concentrations in karstic and detrital SGD end-members were  
205 multiplied by the respective SGD water flows. Karstic and detrital SGD-driven dTM  
206 fluxes to the NW Mediterranean Sea were calculated separately, classifying 40% of the  
207 coastline as karstic systems and the remaining 60% as detrital. The sum of these metal  
208 fluxes was considered as the total contribution of SGD to the study area. Coastline-  
209 normalized karstic and detrital SGD dTM fluxes were multiplied by the corresponding  
210 shore length (3,500 km) in order to obtain values in mol y<sup>-1</sup>.

211  
212 Dissolved trace metal concentrations for the main rivers of the NW Mediterranean Sea  
213 (Rhone and Ebro) reported in the literature (Elbaz-Poulichet et al., 1996, 1989; Guieu et  
214 al., 1997, 1993; Ollivier et al., 2011; UNEP/MAP/MED POL, 2003) were used for the  
215 calculation of fluxes of dTM associated to riverine discharge (Supporting Information,  
216 Appendix B). These rivers were considered the most representative rivers of the area, as  
217 they account for a large portion of the total riverine discharge (Guieu et al., 1997). The  
218 median metal concentrations and the ranges between the 1<sup>st</sup> and the 3<sup>rd</sup> quartiles of the  
219 data set were considered as the best representation of dissolved concentrations of Cd,  
220 Cu, Ni, Pb and Zn in the river end-member. For Co and Fe, dissolved concentrations in  
221 the Rhone and the Ebro Rivers are reported only in a limited number of works (Elbaz-  
222 Poulichet et al., 1989; Guieu et al., 1997, 1993), so that we calculated the mean of the  
223 concentrations of these metals and the relative standard deviations. Dissolved metal  
224 concentrations were multiplied by the sum of the water flows from rivers in the study  
225 area ( $71 \cdot 10^9 \text{ m}^3 \text{ y}^{-1}$ ) (UNEP/MAP/MED POL, 2003) in order to obtain the fluxes of  
226 dTM through rivers into the NW Mediterranean Sea.

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228 Dissolved trace metal fluxes from the atmospheric deposition were estimated from  
229 literature data for the combination of wet and dry deposition metal fluxes to the  
230 Mediterranean Sea (Bonnet and Guieu, 2006; Chester et al., 1999; Guerzoni et al., 1999;  
231 Guieu et al., 2010, 1997, 1993; Migon et al., 1997, 1991; Ridame et al., 1999; Sandroni  
232 and Migon, 2002) (Supplementary Information, Appendix C). When values of dTM  
233 fluxes were not directly reported, we calculated them from data on the total fraction of  
234 metals (dissolved + particulate), by using the percentages of partitioning between the  
235 different fractions provided by Guieu et al. (1997). Mean values of atmospheric dTM  
236 fluxes (in mol km<sup>-2</sup> y<sup>-1</sup>) for each literature work are reported in the Supplementary  
237 Information, Appendix C. The median values and the ranges between the 1<sup>st</sup> and the 3<sup>rd</sup>  
238 quartiles of the data set were considered as the best representation of atmospheric  
239 dissolved fluxes of Cd, Cu, Fe, Ni, Pb and Zn to the NW Mediterranean Sea. For Co,  
240 data of atmospheric fluxes are reported only in a limited number of works (Chester et  
241 al., 1999; Guieu et al., 1997, 1993), so that we used the mean dissolved atmospheric  
242 fluxes and the relative standard deviations. The obtained metal atmospheric fluxes were  
243 multiplied by the surface of the study area (180,000 km<sup>2</sup>) to obtain atmospheric metal  
244 fluxes in mol y<sup>-1</sup>. For trace metals of anthropogenic origin such as Cd, Pb and Zn, the  
245 calculated atmospheric fluxes represent an upper limit, due to the decrease of their  
246 emission in the atmosphere since the second half of the 1980s (Heimbürger et al., 2010).

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### 248 **3 Results and Discussion**

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#### 250 **3.1 Metal characterization of SGD**

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252 SGD end-members spanned a wide range of salinities: karstic SGD had salinities  
253 ranging between 0.3 and 9.7, whereas detrital SGD samples were in the range of 0.2–36  
254 (Table 1). The higher variability in salinity for detrital SGD with respect to karstic SGD  
255 is related to the intrusion of recirculated seawater through permeable beach sediments  
256 (Moore, 1999).

257 The variability of trace metal concentrations in SGD systems depends on the geological  
258 composition of the coastal aquifers, the possible groundwater contamination through  
259 anthropogenic activities (Beck et al., 2009; Trezzi et al., 2016), the residence time of  
260 groundwater in the aquifers and the mixing of freshwater and seawater in the  
261 subterranean estuary (Beck et al., 2007; Moore, 1999). In karstic SGD, the ranges of  
262 dTM concentrations (in  $\text{nmol L}^{-1}$ ) were  $<0.04 - 3.1$  for Cd,  $<0.06 - 4.0$  for Co,  $0.68 -$   
263  $24$  for Cu,  $18 - 840$  for Fe,  $1.6 - 43$  for Ni,  $<0.04 - 2.1$  for Pb and  $7.2 - 300$  for Zn. In  
264 detrital SGD, the ranges of dTM concentrations (in  $\text{nmol L}^{-1}$ ) were  $<0.04 - 14$  for Cd,  
265  $0.10 - 6.9$  for Co,  $1.7 - 160$  for Cu,  $44 - 460$  for Fe,  $4.5 - 83$  for Ni,  $0.19 - 7.4$  for Pb,  
266 and  $13 - 2100$  for Zn.

267 Figure 2 shows the comparison between metal concentrations in karstic and detrital  
268 SGD end-members, for which ranges between the 1<sup>st</sup> and the 3<sup>rd</sup> quartiles were reported.  
269 Detrital SGD was distinctively more enriched in Co, Cu and Ni than karstic SGD. For  
270 the other trace metals (Cd, Fe, Pb and Zn), the ranges of concentrations in karstic and  
271 detrital SGD were comparable, although the median values of Fe were higher in karstic  
272 SGD (up to 1.5 times) and the median values of Pb were higher in detrital SGD (up to  
273 2.5 times). There are two possible main explanations for these differences in dTM  
274 concentrations between karstic and detrital SGD. The different geological matrix of the  
275 karstic and detrital aquifers can contribute differently to the chemical composition of  
276 the interacting groundwater; while karstic systems are composed predominantly by

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277 carbonate minerals, detrital systems can be characterized by different lithologies and a  
278 consequent larger variability of minerals. Secondly, the geochemical reactions that  
279 occur in the subterranean estuary, before groundwater discharges into the coastal sea,  
280 largely affect solute concentrations in SGD. In karstic systems, infiltrated groundwater  
281 can be rapidly transferred to the coastal sea due to the presence of underground  
282 fractures and preferential pathways (Garcia-Solsona et al., 2010b; Gonnee et al., 2014;  
283 Tovar-Sánchez et al., 2014b). Thus, the SGD discharging into the coastal sea through  
284 coastal springs is generally oxygenated and characterized by a limited interaction with  
285 the geological matrix of the aquifer. Contrary, detrital SGD flows across the permeable  
286 sediments of the coastal aquifers, where it mixes with recirculated seawater before  
287 discharging into the sea. Detrital SGD is thus subjected to several geochemical  
288 transformations such as redox-controlled solubility, adsorption on organic matter and/or  
289 on Fe and Mn oxides, release from these oxides and desorption from sediments  
290 (Charette and Sholkovitz, 2006). Co and Ni are redox-sensitive elements controlled by  
291 Mn geochemistry in porewater of coastal and shelf sediments (Beck et al., 2007, 2010;  
292 Santos-Echeandia et al., 2009). The higher concentrations of Co and Ni in detrital SGD  
293 samples with respect to the karstic ones may be related to their release from Mn oxides  
294 during the diagenetic remobilization of Mn (Beck et al., 2010; Santos-Echeandia et al.,  
295 2009). On the other hand, Cu is strongly associated to the organic matter (Du Laing et  
296 al., 2009; Santos-Echeandia et al., 2009; Shaw et al., 1990), which is commonly more  
297 abundant in detrital systems than in the karstic ones. This may explain the higher  
298 concentration of Cu in detrital SGD. The comparable concentrations of dissolved Fe  
299 between karstic and detrital SGD may be due to the oxygenated conditions of karstic  
300 SGD and to the precipitation of Fe, with the formation of Fe oxides, when recirculated  
301 seawater mixes with groundwater in detrital systems (Charette and Sholkovitz, 2006,

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302 2002; Windom et al., 2006). Finally, for Cd, Pb and Zn, the generally comparable  
303 ranges of concentrations in karstic and detrital SGD may be ascribed to their lower  
304 redox-sensitivity (for Pb and Zn) (Santos-Echeandia et al., 2009), to their lower  
305 association with the organic matter (for Cd, Pb and Zn) (Roux et al., 1998; Santos-  
306 Echeandia et al., 2009) or to their removal from the solution due to the presence of the  
307 so-called Fe-curtain (for Cd and Zn) (Charette and Sholkovitz, 2006, 2002; Trezzi et al.,  
308 2016). These properties may prevent the detrital SGD to get distinctly more enriched in  
309 Cd, Fe, Pb and Zn with respect to karstic SGD.

310

311 The karstic SGD end-member analysed in three different seasons (Garbí) displayed  
312 variability in dTM concentrations, in particular for Cd ( $< 0.04 - 0.49 \text{ nmol L}^{-1}$ ) and Fe  
313 ( $35 - 840 \text{ nmol L}^{-1}$ ). The detrital SGD system sampled twice in 10 days after a rain  
314 event (Argentona) also showed some variability in metal concentrations for Cd, Cu, Ni  
315 and Zn, in addition to a variation in salinity (Table 1). This temporal variability of Garbí  
316 and Argentona samples illustrated the difficulty on establishing appropriate SGD end-  
317 members, which is traditionally one of the most significant uncertainties in the  
318 investigation of SGD processes. The different dTM concentrations showed by Garbí  
319 and Argentona samples were generally within the ranges between minimum and  
320 maximum values measured in the other SGD end-members. Therefore, we assume that  
321 the temporal variability of the other SGD end-members was also included in the ranges  
322 of dTM concentrations used as the best representation of the SGD end-member in the  
323 study area (see Section 2.4).

324

325 Dissolved metals concentrations in SGD end-members were higher than those of  
326 seawater of the open Western Mediterranean Sea ( $2.6 - 4.5 \text{ nmol L}^{-1}$  for Zn,  $1.1 - 2.3$



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327 nmol L<sup>-1</sup> for Cu, 3.2 - 3.6 nmol L<sup>-1</sup> for Ni, 1.4 - 8.0 nmol L<sup>-1</sup> for Fe, 0.13 - 0.28 nmol L<sup>-1</sup>  
328 for Pb, 0.05 - 0.17 nmol L<sup>-1</sup> for Co and 0.06 - 0.08 nmol L<sup>-1</sup> for Cd) (Tovar-Sánchez et  
329 al., 2014a; Yoon et al., 1999) for most of the metals, as shown in Figure 3. This was  
330 particularly evident for Zn and Fe (up to two orders of magnitude). Concentrations of  
331 Pb in SGD were comparable to the ones of open seawater for most of the samples,  
332 indicating that SGD probably is not a relevant source of dissolved Pb to the NW  
333 Mediterranean Sea.

334  
335 The concentrations of dTM in SGD end-members (obtained unifying the data set on  
336 karstic and detrital systems) were compared to those reported in the literature for the  
337 Rhone and the Ebro Rivers (Figure 3). For the data set presented in this work, the  
338 clearest differences were the higher concentrations of dissolved Zn in SGD and  
339 dissolved Cu in the rivers. For the other trace metals, the ranges of concentrations were  
340 comparable in SGD and in rivers, although the median concentrations of Cd, Co, Ni and  
341 Pb in rivers were higher than in SGD. These differences may be related to the  
342 distinctive environments of coastal aquifers and rivers, with steep redox gradients in  
343 subterranean estuaries and the presence of microbes that can affect the speciation and  
344 mobility of trace metals (Knee and Paytan, 2011; O'Connor et al., 2015). The  
345 comparison of dTM concentrations in SGD and rivers confirmed that SGD must be  
346 evaluated as a potential source of metals to the coastal ocean, given that dTM  
347 concentrations of SGD end-members are at least similar to those of rivers for most of  
348 the metals. Thus, the volume of riverine and SGD water discharges will determine the  
349 relative significance of these two inputs of dTM to the coastal sea.

350

351 3.2 Comparison of trace metal fluxes into the NW Mediterranean Sea

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2 353 Trace metal inputs through SGD are conditioned by the multiple and complex processes  
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4 354 occurring during the transport through the sediments and/or aquifer, which can affect  
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6 355 the dTM concentrations of SGD. Indeed, the selection of appropriate SGD end-  
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9 356 members is one of the most challenging points in the assessment of SGD-driven metal  
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11 357 fluxes to the ocean. The SGD end-members collected in this work were certainly  
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13 358 representative of the water effectively discharging into the sea in the case of the coastal  
14  
15 359 karstic springs. For detrital systems, the most real SGD end-member was determined by  
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17 360 collecting several SGD samples of different salinities (fresh and brackish groundwater  
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19 361 and recirculated seawater) and by including literature data of dTM already considered  
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21 362 as representative of the SGD end-members by the respective authors. This approach  
22  
23 363 permits to obtain a first approximation of SGD-driven dTM fluxes, whose magnitude  
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25 364 can be compared to riverine discharge and atmospheric deposition, with the aim of  
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27 365 evaluating the relevance that SGD can have in the NW Mediterranean Sea.  
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36 367 A summary of the calculated SGD-driven, riverine and atmospheric dTM fluxes to the  
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38 368 NW Mediterranean Sea is shown in Figure 4 and in Table 2.

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40  
41 369 SGD-driven dTM fluxes (in  $10^6 \text{ mol y}^{-1}$ ) to the NW Mediterranean Sea are (0.0007 –  
42  
43 370 0.03) for Cd, (0.004 – 0.11) for Co, (0.09 – 1.9) for Cu, (1.8 - 29) for Fe, (0.09 – 1.9)  
44  
45 371 for Ni, (0.002 – 0.06) for Pb and (0.38 - 12) for Zn. Trace metals inputs through SGD  
46  
47 372 can be subjected to seasonal variability. Unfortunately, detailed information about  
48  
49 373 temporal characterization of SGD (metal concentrations and/or water flow) in each  
50  
51 374 coastal aquifer considered in the work is not available. Notice that the repeated  
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53 375 sampling of two SGD end-members, collected twice and three times (Argentona and  
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55 376 Garbí, respectively), showed a minimum variability of the dTM concentrations  
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377 compared to the range of concentrations reported for groundwater samples. Thus, even  
378 considering temporal variability of SGD, the magnitude of the calculated SGD-driven  
379 dTM fluxes can be still compared to continental inputs of dTM via riverine discharge  
380 and atmospheric deposition.

381 Dissolved trace metal fluxes from rivers to the NW Mediterranean Sea (in  $10^6$  mol  $y^{-1}$ ),  
382 calculated using data from the literature as explained in Section 2.4, are (0.02 – 0.03)  
383 for Cd, (0.08 – 0.09) for Co, (1.9 – 2.4) for Cu, (13 – 17) for Fe, (1.5 – 1.7) for Ni, (0.01  
384 – 0.03) for Pb and (1.1 – 1.4) for Zn.

385 Dissolved trace metal fluxes from atmospheric deposition to the NW Mediterranean Sea  
386 (in  $10^6$  mol  $y^{-1}$ ), calculated with literature data as explained in Section 2.4, are (0.07 -  
387 0.44) for Cd, (0.04 - 0.52) for Co, (2.2 - 3.5) for Cu, (91 - 280) for Fe, (1.1 - 2.5) for Ni,  
388 (1.1 - 1.6) for Pb and (15 - 110) for Zn.

389

390 Our estimates of the continental inputs of dTM into the NW Mediterranean Sea show  
391 that riverine metal fluxes of dissolved Cd, Co, Fe, Ni, Pb and Zn fall within the ranges  
392 of the SGD-driven fluxes. However, the median SGD-driven fluxes of these dTM are  
393 distinctively lower than riverine fluxes (from 2 to 7 times, depending on the metal),  
394 with the exception of Zn, which is comparable (Figure 4; Table 2). The SGD-driven  
395 flux of dissolved Cu is distinctly lower than the riverine one. This comparison between  
396 SGD and rivers does not consider riverine fluxes of particulate material, which are  
397 thought to be important for dissolved elements in seawater in relation to the potential  
398 dissolution of the transported particles (Jeandel and Oelkers, 2015; Oelkers et al., 2011).  
399 Compared to atmospheric dTM fluxes, the ranges of SGD-driven fluxes of dissolved  
400 Cd, Cu, Fe, Pb and Zn are distinctively lower (Figure 4; Table 2). The SGD-driven

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401 fluxes of dissolved Co and Ni are also generally lower than the atmospheric ones,  
402 showing a difference of one order of magnitude for the median values.

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### 404 3.3 Spatial and temporal influence of the continental trace metal fluxes

405

406 The presented comparison between continental inputs of dTM to the NW Mediterranean

407 Sea did not consider the spatial and temporal distribution of SGD, rivers and

408 atmospheric deposition. These distributions are different (Figure 5) and should be taken

409 into account for an appropriate evaluation of the effects of the sources of dTM on

410 coastal geochemical cycles. Conversely to SGD and riverine discharge, which are short-

411 scale coastal processes, atmospheric deposition occurs over the whole NW

412 Mediterranean basin. Consequently, even if the atmospheric dTM fluxes calculated in

413 Section 3.2 are clearly higher than those through SGD, the real contribution of these

414 two inputs to the coastal sea should be evaluated dividing the calculated dTM fluxes by

415 the respective areas of influence. For the atmospheric deposition, the area of influence is

416 the total study area (180,000 km<sup>2</sup>). In the case of SGD, several local studies have

417 highlighted that this process usually does not reach a distance offshore higher than 2-3

418 km (on the base of Ra isotopes and/or salinity differences in coastal seawater) and that

419 inputs of macronutrients and metals through SGD decrease towards the open seawater,

420 being concentrated in the first hundreds of meters (Gonneea et al., 2014; Mejías et al.,

421 2012; Moore, 2003; Rodellas et al., 2014; Trezzi et al., 2016; Windom et al., 2006).

422 Dissolved trace metals supplied to this coastal seawater can also be removed from the

423 water column by means of biogeochemical processes (Bruland and Lohan, 2003).

424 Therefore, if we consider a distance of 3 km offshore as an upper limit affected by SGD

425 and multiply it by the 3,500 km of coastline of the study area, a maximum area of

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426 influence for SGD of about 10,500 km<sup>2</sup> is obtained. Thus, we calculate the area-  
427 weighted SGD-driven dTM fluxes, which are a lower limit (at least for Cu, Fe, Ni and  
428 Zn) of the possible SGD contribution to the coastal area. In the case of Cd, Co and Pb,  
429 the obtained SGD values are not necessarily a lower limit, since for the samples  
430 characterized by no detectable metal concentrations, the limit of detection itself was  
431 considered in the calculations (see Section 2.4). The comparison of these SGD-driven  
432 fluxes with the atmospheric dTM fluxes (in mol y<sup>-1</sup> km<sup>-2</sup>) highlights that SGD inputs to  
433 the coastal sea are comparable or higher than atmospheric deposition for all the metals  
434 studied here, with the exception of Pb (Figure 6).

435 SGD and river inputs have also a significant difference in their spatial distribution.  
436 Trace metal inputs driven by SGD are ubiquitous all along the coast, since fresh  
437 groundwater discharges anywhere an aquifer with a positive head relative to sea level is  
438 hydraulically connected with the sea (Johannes, 1980) and the recirculation of seawater  
439 through the coastal aquifer is also expected to occur in most of the coastal systems  
440 (Knee and Paytan, 2011). On the contrary, riverine discharge is limited to the  
441 surroundings of river mouths. River plumes are the maximum boundaries where dTM  
442 provided by rivers could be detected, if they are not removed before through biological  
443 uptake, scavenging by particles or precipitation (Bruland and Lohan, 2003). River  
444 plumes are influenced by winds and marine currents: for example, the plume of the  
445 Ebro River is usually deviated southwards and reach a maximum distance of 80 km  
446 from the river mouth (Palanques and Drake, 1990). Consequently, no direct influence of  
447 this river would be expected in the northern area and beyond 80 km in the southern  
448 zone. For smaller rivers or ephemeral streams, the river influence would be restricted to  
449 a shorter distance from the river mouth. Thus, in areas characterized by the absence of

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2 450 rivers or river plumes, SGD, together with atmospheric deposition, is the major source  
3 451 of dTM to the coastal sea.

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7 453 Temporal variability should also be considered when comparing the different  
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9 454 continental inputs of dTM to the NW Mediterranean Sea. Thus, whilst SGD and rivers  
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11 455 can be considered a permanent source of dTM to the coastal areas (even if they are  
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13 456 affected by water flow fluctuations on annual scale), atmospheric deposition in the  
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15 457 Mediterranean Sea has a very high intra-annual and inter-annual variability, with most  
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17 458 of the flux concentrated in few strong events during the year (Avila et al., 1998; Guieu  
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19 459 et al., 2010). This is particularly true for crustal-derived trace metals (Fe, Co and part of  
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21 460 Ni and Cu), whose atmospheric deposition is related principally to Saharan dust events  
22  
23 461 (Heimbürger et al., 2010). Therefore, the relative significance of SGD-driven dTM  
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25 462 fluxes to the NW Mediterranean Sea can be actually higher in absence of dust events  
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27 463 and lower during the dust events.  
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### 35 36 465 3.4 Relevance of SGD for the global Mediterranean Sea

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41 467 The Mediterranean Sea is one of the most oligotrophic and exploited seas in the world,  
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43 468 where the sources of nutrients are limited (Macias et al., 2014). Atmospheric deposition  
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45 469 (Guerzoni et al., 1999; Guieu et al., 2010, 1997) and riverine runoff (Ludwig et al.,  
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47 470 2009; Macias et al., 2014) have been traditionally considered the main continental  
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49 471 sources of nutrients, while other sources such as SGD are not commonly considered or  
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51 472 documented. However, the relevance of SGD as a source of macronutrients to the whole  
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53 473 Mediterranean basin was recently demonstrated (Rodellas et al., 2015a) and the present  
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55 474 study represents the first evidence of the potential relevance of SGD as a source of dTM  
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475 (e.g. Cd, Co, Cu, Fe, Ni, Pb and Zn) at regional scale. While this study is particularly  
476 focused on the NW Mediterranean Sea, the paucity of data on dTM concentrations of  
477 SGD end-members of the South Western and Eastern Mediterranean basins and the  
478 difficulty to obtain these data currently prevent the extension of these calculations to the  
479 whole Mediterranean Sea. However, some general considerations about the key role of  
480 SGD in contributing dTM to the whole Mediterranean Sea can be made.

481  
482 Although median SGD-driven dTM fluxes seem to be lower (for Cd, Co, Cu, Fe, Ni and  
483 Pb) or comparable (for Zn) with respect to riverine fluxes in the NW Mediterranean  
484 zone, it should be noticed that this area is characterized by the presence of the second  
485 (Rhone) and the forth (Ebro) major rivers of the Mediterranean Sea (Ludwig et al.,  
486 2009). If we consider other areas of the Mediterranean basin, the riverine discharge is  
487 distinctively lower, with the exception of the Adriatic Sea (Po river) and the area of the  
488 Nile delta (Ludwig et al., 2009). This is particularly true for the arid and semi-arid  
489 regions of the Mediterranean Sea, such as the Eastern coast, the African coast and many  
490 islands. For instance, the riverine discharge along 4,400 km of coastline from Morocco  
491 to Libya is less than  $10^9 \text{ m}^3 \text{ y}^{-1}$  (Ludwig et al., 2009), whereas the riverine discharge in  
492 the NW Mediterranean Sea, with a slightly shorter coastline (3,500 km), is more than 70  
493 times higher.

494 A first-order estimation of SGD-driven dTM fluxes for the African coast could be  
495 obtained with the same procedure described for the NW basin, using the shore-  
496 normalized SGD water flow of the whole Mediterranean Sea (Rodellas et al., 2015a)  
497 and assuming the same dTM concentrations of SGD end-members from the NW  
498 Mediterranean area. Thereby, SGD-driven dTM fluxes from the African coast would be  
499 distinctively higher than riverine metal fluxes (up to 3 orders of magnitude), assuming

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500 similar concentrations in rivers of North Africa and the NW Mediterranean Sea (notice  
501 that recent data on the African Moulouya River showed dTM concentrations  
502 comparable or lower than those of the Ebro and Rhone Rivers (Tovar-Sánchez et al.,  
503 2016) ). SGD would thus be a much more significant source of dTM than rivers for  
504 coastal seawater in the arid and semi-arid regions of the Mediterranean Sea.

505

### 506 3.5 Biogeochemical implications of SGD

507

508 Most of the trace metals analysed in this work (i.e. Cd, Co, Cu, Fe, Ni and Zn) are  
509 essential micronutrients for the planktonic community, as their deficiency can limit  
510 oceanic plankton production, whereas they can be toxic at high levels (Jordi et al., 2012;  
511 Lafabrie et al., 2013; Morel and Price, 2003; Twining and Baines, 2013). Considering  
512 that SGD is a significant source of dTM to the coastal sea, in particular in those areas  
513 where the presence of rivers is limited, SGD may potentially have a strong impact on  
514 the coastal productivity of the Mediterranean Sea. The involvement of SGD on  
515 biogeochemical cycles of the Mediterranean Sea was already emphasized at regional  
516 scale for macronutrient inputs (DIN, DIP and DSi) (Rodellas et al., 2015a). Therefore,  
517 taking into account the results of this study, we hypothesize that the significance of  
518 SGD for coastal biological communities in the oligotrophic Mediterranean Sea is related  
519 not only to inputs of macronutrients but also of bioactive trace metals. However, the  
520 link between SGD-driven dTM fluxes to the coastal sea and coastal productivity is a  
521 complex topic that should be further investigated, as dTM can be removed from the  
522 coastal seawater by several biogeochemical processes (Bruland and Lohan, 2003).  
523 Nevertheless, SGD should be certainly considered in studies on the biogeochemistry of  
524 coastal areas and in the assessment of trace metal budgets.



525

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2 526 4 Conclusions  
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7 528 This study is a first effort to estimate regional inputs of dTM (Cd, Co, Cu, Fe, Ni, Pb  
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9 529 and Zn) through SGD to the oligotrophic Mediterranean Sea. SGD-driven dTM fluxes,  
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11 530 calculated for the NW basin and compared to riverine discharge and atmospheric  
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13 531 deposition, reveal that SGD is a significant source of dTM to the coastal Mediterranean  
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15 532 Sea. The relevance of SGD may be even higher in coastal areas of the Southern and  
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17 533 Eastern Mediterranean Sea or in many islands, which are characterized by scarce  
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19 534 riverine discharge. Therefore SGD should be taken into account for the assessment of  
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21 535 trace metal budgets and for biogeochemical studies in coastal areas, as some of the  
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23 536 metals delivered by this process are crucial micronutrients for primary productivity in  
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25 537 the ocean.  
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31 538 Further investigations on trace metal inputs through SGD in the Mediterranean Sea are  
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33 539 required in order to improve the estimation of SGD fluxes presented in this study.  
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36 540 Indeed, spatial and temporal variability of trace metal concentrations in SGD end-  
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38 541 members, as well as relations between concentrations and magnitude of water flows,  
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40 542 need to be investigated in a large number of subterranean estuaries. At the same time,  
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42 543 the present data set should be expanded with the characterization of metal inputs  
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44 544 through SGD in areas that are not well studied at the moment, such the African Coast.  
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51 546 SUPPORTING INFORMATION  
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53 547 Karstic and detrital SGD-driven flows reported in the literature for local studies in the  
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55 548 NW Mediterranean Sea (Appendix A); dissolved trace metal concentrations of the  
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57 549 Rhone and the Ebro Rivers reported in the literature (Appendix B); atmospheric  
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550 dissolved trace metal fluxes to the Mediterranean Sea reported in the literature

551 (Appendix C).

552

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HIGHLIGHTS:

- Regional SGD-driven dissolved metal fluxes are estimated for the NW Mediterranean;
- SGD, riverine and atmospheric inputs of dissolved metals are compared
- SGD is a major source of dissolved metals to the coastal NW Mediterranean
- SGD is particularly significant where rivers are scarce (African coast and islands)

**Table 1:** Dissolved trace metal concentrations in karstic and detrital SGD end-members used in this study.

Samples	Sampling time	Salinity	Dissolved metal concentrations (nmol L <sup>-1</sup> )						
			Cd	Co	Cu	Fe	Ni	Pb	Zn
<b>Karstic SGD</b>									
Garbí	Dec 2013	5.4	< 0.04	< 0.06	2.0	840	5.3	< 0.04	26
Garbí	Jul 2014	4.6	0.49	< 0.06	n.a.	410	6.5	< 0.04	7.2
Garbí	May 2015	5.0	0.04	< 0.06	0.68	35	7.2	0.13	21
Suíś	Nov 2013	4.1	< 0.04	0.52	3.1	260	6.2	0.42	48
Badum	Nov 2013	9.7	< 0.04	0.34	1.5	520	2.7	0.22	42
Font Dins	Nov 2013	0.3	0.21	0.54	4.2	550	1.8	0.13	72
Font Centre	Nov 2013	5.3	0.29	0.45	2.5	100	1.6	< 0.04	35
Font South	Nov 2013	4.1	0.15	0.55	2.2	360	2.5	1.1	99
Estramar	Jun 2015	4.6	0.15	0.16	3.0	18	5.9	1.2	45
La Palme	Jun 2015	6.8	0.13	0.17	4.9	130	10	2.0	70
Sa Nau (Tovar-Sanchez et al. 2014) <sup>+</sup>	Nov 2010	3.2	3.1	4.0	7.2	730	32	0.16	300
Baixamar (Tovar-Sánchez, personal communication) <sup>+</sup>	Jun 2010/Jun2011	n.a.	n.a.	3.9	24	570	43	2.1	38
Karstic SGD Median			0.15	0.40	3.0	390	6.1	0.19	44
Karstic SGD (1 <sup>st</sup> -3 <sup>rd</sup> quartiles)			0.04 - 0.25	0.14 - 0.54	2.1 - 4.6	130 - 550	2.7 - 7.9	0.11 - 1.1	33 - 71
<b>Detrital SGD</b>									
Argentona	Dec 2013	5.6	0.16	2.0	7.5	160	5.5	0.65	130
Argentona	Dec 2013	8.0	1.0	2.6	26	260	16	n.a.	350
Peníscola	Nov 2013	5.7	< 0.04	0.51	1.7	240	4.5	0.50	21
Fosca North	May 2015	35.4	0.08	0.10	13	240	11	0.15	13
Fosca South	May 2015	34.7	0.12	0.54	11	120	14	0.19	18

Empuriabrava	May 2015	36.0	0.08	0.32	16	190	11	0.19	24
Arenys	May 2015	0.2	< 0.04	1.9	120	430	8.8	0.25	27
Sitges	Jun 2015	7.5	0.06	1.0	160	110	83	0.96	34
Palma Bay (Rodellas et al. 2014) <sup>+</sup>	May 2010	2.1-31.0*	n.a.	n.a.	30	320	38	0.69	73
Santanyí (Tovar-Sanchez et al. 2014) <sup>+</sup>	Nov 2010	10.9-33.7*	0.73	1.64	59	44	32	0.62	1900
Romàntica (Tovar-Sanchez et al. 2014) <sup>+</sup>	Nov 2010	17.8-32.4*	0.44	6.9	23	420	50	0.19	170
El Gorguel (Trezzi et al., 2016) <sup>+</sup>	Jul 2013	10.8-30.7*	14	n.a.	29	460	35	7.4	2100
Detrital SGD Median			0.12	1.5	25	240	15	0.50	54
Detrital SGD (1 <sup>st</sup> -3 <sup>rd</sup> quartiles)			0.07 - 0.59	0.52 - 2.0	13 - 37	150 - 350	10 - 36	0.19 - 0.67	23 - 220
<b>Total SGD</b>									
SGD Median			0.14	0.53	7.5	260	9.4	0.25	85
SGD (1 <sup>st</sup> -3 <sup>rd</sup> quartiles)			0.05 - 0.40	0.21 - 1.8	2.8 - 25	130 - 440	5.5 - 32	0.16 - 0.82	16 - 120

<sup>+</sup> Metal concentrations reported are average concentrations of several groundwater samples or concentrations of SGD end-members selected in the respective studies for the calculation of the local SGD fluxes

\* Range of salinities of groundwater samples considered in each local study to obtain the SGD end-members

n.a.= not available

**Table 2:** SGD-driven, riverine and atmospheric dTM fluxes to the NW Mediterranean Sea.

		<b>Dissolved metal fluxes (<math>10^6 \text{ mol y}^{-1}</math>)</b>						
		<b>Cd</b>	<b>Co</b>	<b>Cu</b>	<b>Fe</b>	<b>Ni</b>	<b>Pb</b>	<b>Zn</b>
<b>SGD</b>	Median	0.003	0.02	0.36	7.7	0.27	0.009	1.2
	1 <sup>st</sup> - 3 <sup>rd</sup> quartiles	0.0007 -0 .03	0.004 - 0.11	0.09 – 1.9	1.8 - 29	0.09 - 1.9	0.002 - 0.06	0.38 – 1.2
<b>Rivers</b>	Median	0.02		2.2		1.7	0.03	1.4
	1 <sup>st</sup> - 3 <sup>rd</sup> quartiles	0.02 – 0.03		1.9 – 2.4		1.5 – 1.7	0.01 – 0.03	1.1 – 1.4
	Mean		0.08		15			
	$\sigma$		0.005		2.4			
<b>Atmosphere</b>	Median	0.14		2.7	250	1.9	1.2	82
	1 <sup>st</sup> - 3 <sup>rd</sup> quartiles	0.07 – 0.44		2.2 – 3.5	91 - 280	1.1 – 2.5	1.1 – 1.6	15 - 110
	Mean		0.28					
	$\sigma$		0.24					
<b>Total</b>		0.09 – 0.51	0.12 – 0.71	4.2 – 7.7	110 - 330	2.7 – 6.1	1.1 – 1.6	16 - 120

1 **Figure 1**

2 The study area in the Mediterranean basin (180,000 km<sup>2</sup>; delimited in blue) and the  
3 localization of SGD end-members, for which dTM concentrations were reported in this  
4 study (yellow triangles) or in previous studies (green diamonds). The main rivers of the  
5 study area (red circles), analysed in other studies for dTM concentrations, are also  
6 plotted on the map

7

8 **Figure 2**

9 Comparison of dTM concentrations in SGD from karstic (orange) and detrital (grey)  
10 systems. Ranges between the 1<sup>st</sup> and the 3<sup>rd</sup> quartiles and median values of the available  
11 dataset are plotted.

12

13 **Figure 3**

14 Comparison of dTM concentrations in SGD (light blue) and in rivers (white) of the NW  
15 Mediterranean Sea. Ranges between the 1<sup>st</sup> and the 3<sup>rd</sup> quartiles and median values of  
16 the available dataset are plotted for SGD. For the rivers, data are taken from other  
17 studies (Elbaz-Poulichet et al., 1996, 1989; Guieu et al., 1997, 1993; Ollivier et al.,  
18 2011; UNEP/MAP/MED POL, 2003); median values and ranges between the 1<sup>st</sup> and the  
19 3<sup>rd</sup> quartiles are plotted for Zn, Cu, Ni, Pb and Cd, while for Fe and Co mean values and  
20 relative standard deviations are plotted. Dashed lines represent dTM concentrations of  
21 the open Western Mediterranean Sea reported in the literature (Tovar-Sanchez et al.,  
22 2014; Yoon et al., 1999).

23

24 **Figure 4**

25 Comparison of SGD-driven (light blue), riverine (white) and atmospheric (red) dTM  
26 fluxes to the NW Mediterranean Sea. Dissolved metal fluxes through SGD, rivers and  
27 atmospheric deposition were calculated as explained in Section 2.4. Median values and  
28 ranges between the 1<sup>st</sup> and the 3<sup>rd</sup> quartiles are reported for all the dTM fluxes, with the  
29 exception of riverine fluxes of Fe and Co and atmospheric fluxes of Co, for which mean  
30 values and relative standard deviations are plotted.

31

32 **Figure 5**

33 Model of the spatial influence of the main continental sources of dTM to the NW  
34 Mediterranean Sea. Note that SGD (light blue) and rivers (dark blue) influence areas are  
35 not drawn to scale.

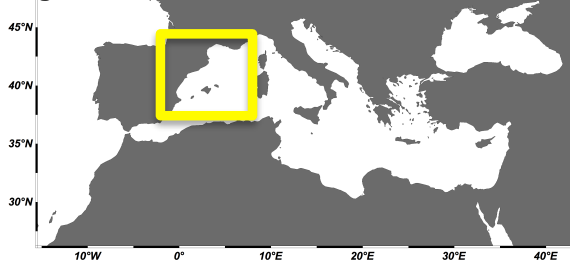
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37 **Figure 6**

38 Comparison of the area-weighted SGD-driven (light blue) and the atmospheric (red)  
39 dTM fluxes to the NW Mediterranean Sea. Area-weighted SGD-driven dTM fluxes  
40 were calculated considering a distance offshore of 3 km as upper limit affected by SGD  
41 (see Section 3.3).

42



**Figure 1****Karstic SGD***This study:*

1. Garbí
2. Suís
3. Badum
4. Font Dins
5. Font Centre
6. Font South
7. Estramar
8. La Palme

*Other studies:*

9. Sa Nau
10. Baixamar

**Detrital SGD***This study:*

11. Argentona
12. Peníscola
13. Fosca North
14. Fosca South
15. Empuriabrava
16. Arenys
17. Sitges

*Other studies:*

18. Palma Bay
19. Santanyí
20. Romàntica
21. El Gorguel

**Rivers:***Other studies:*

22. Rhone
23. Ebro

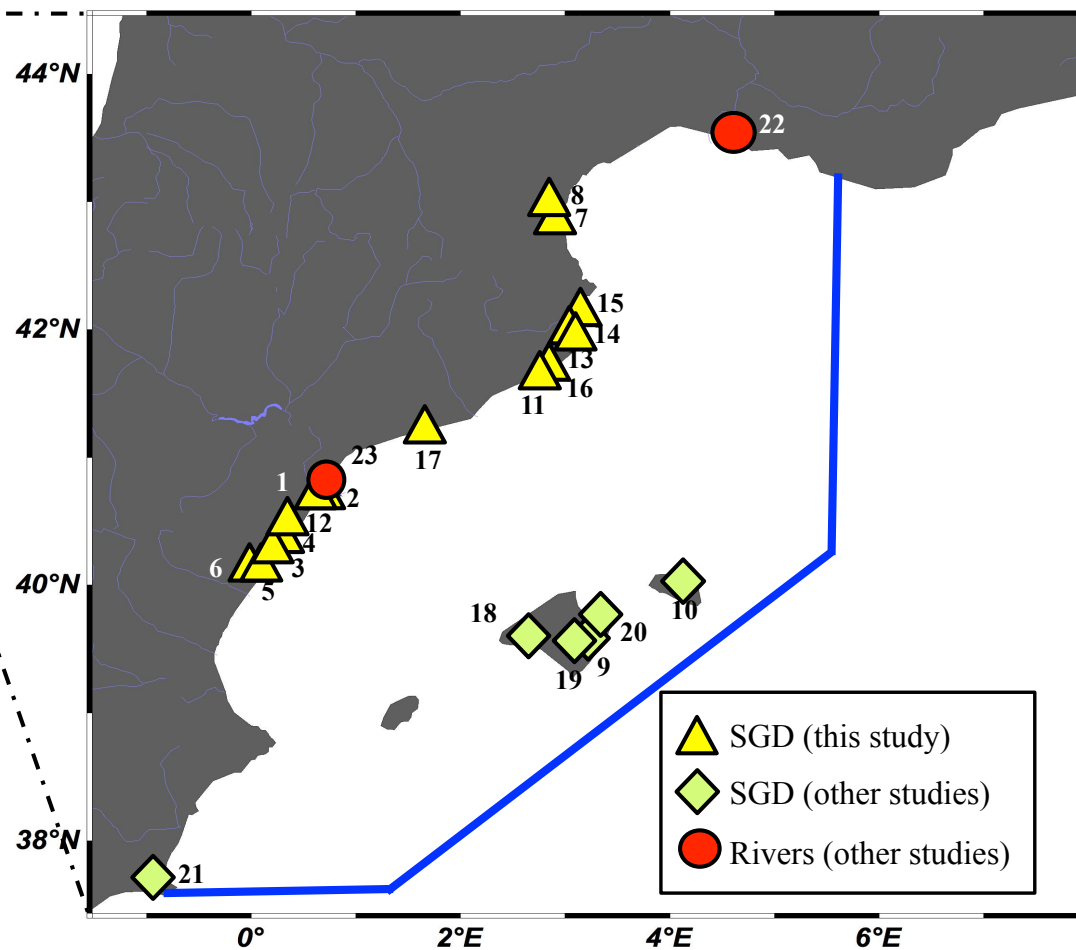
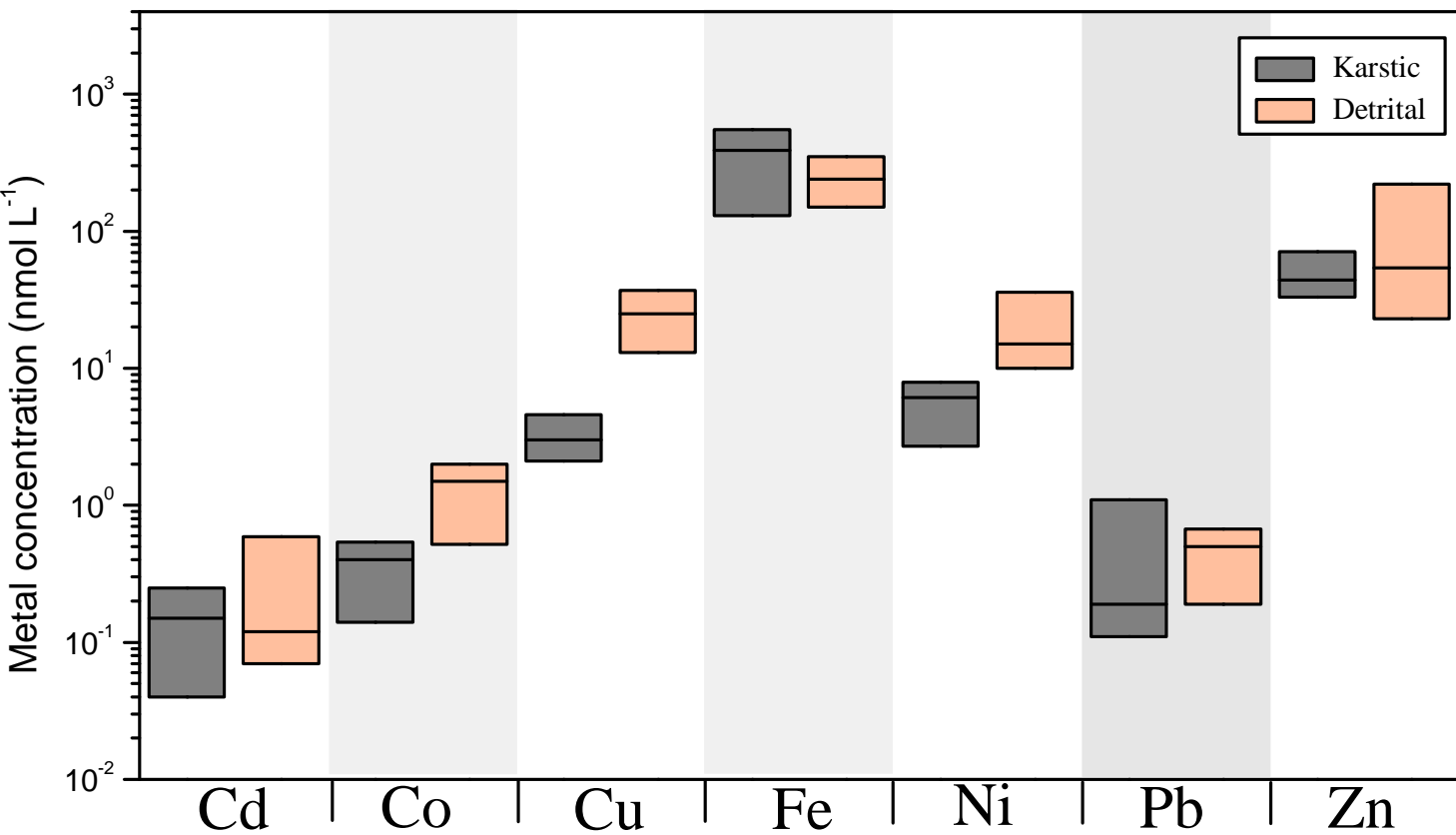
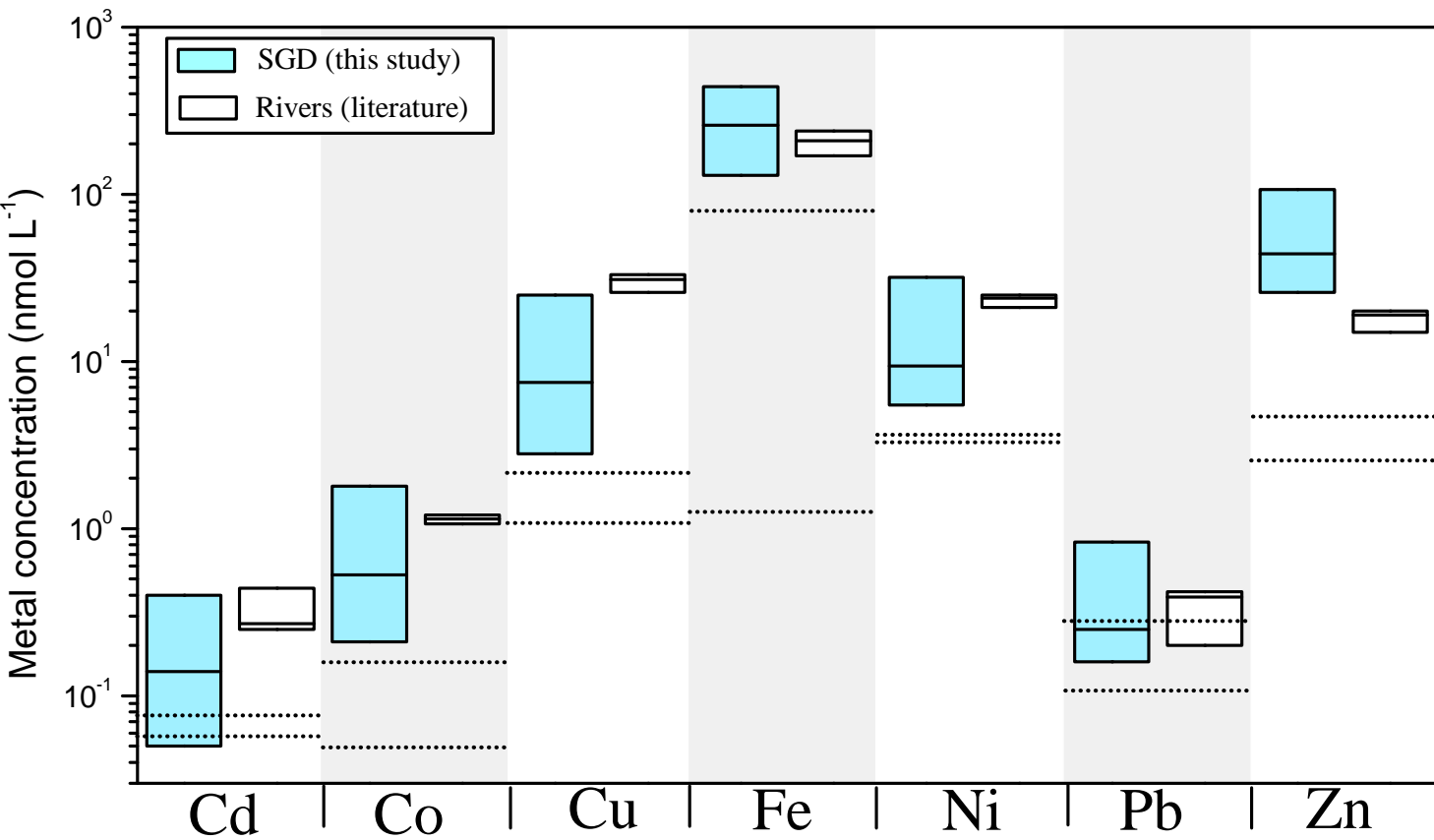
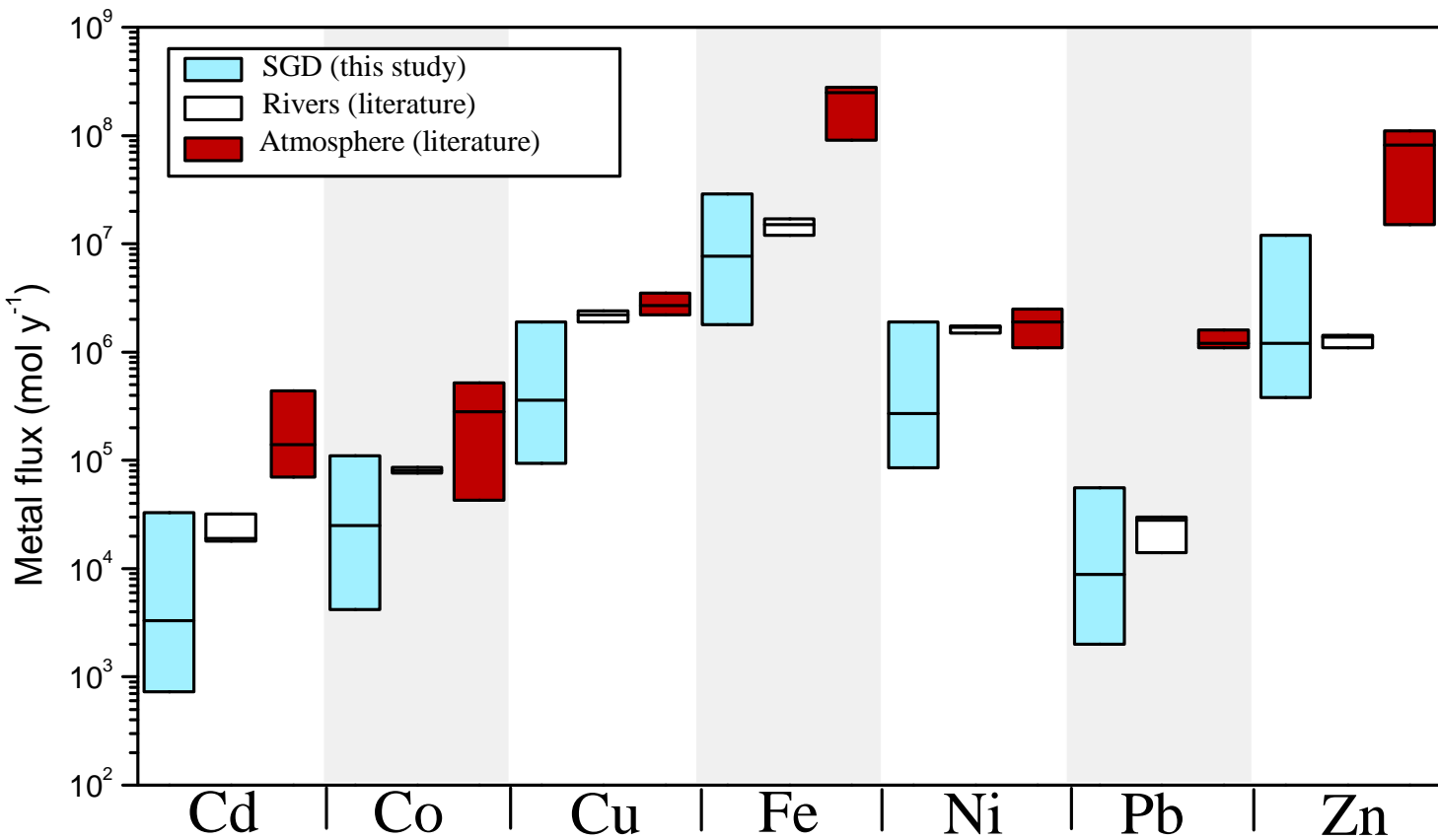


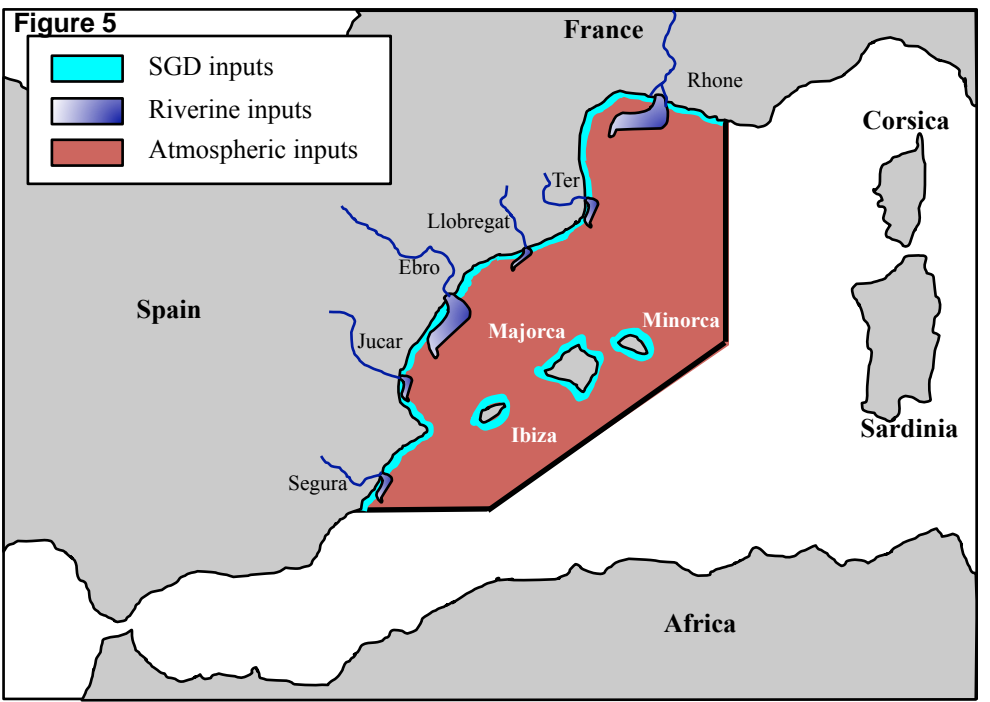
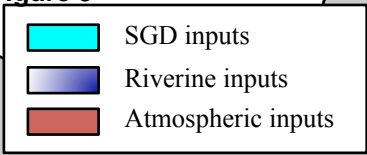
Figure 2



**Figure 3**

**Figure 4**

**Figure 5**



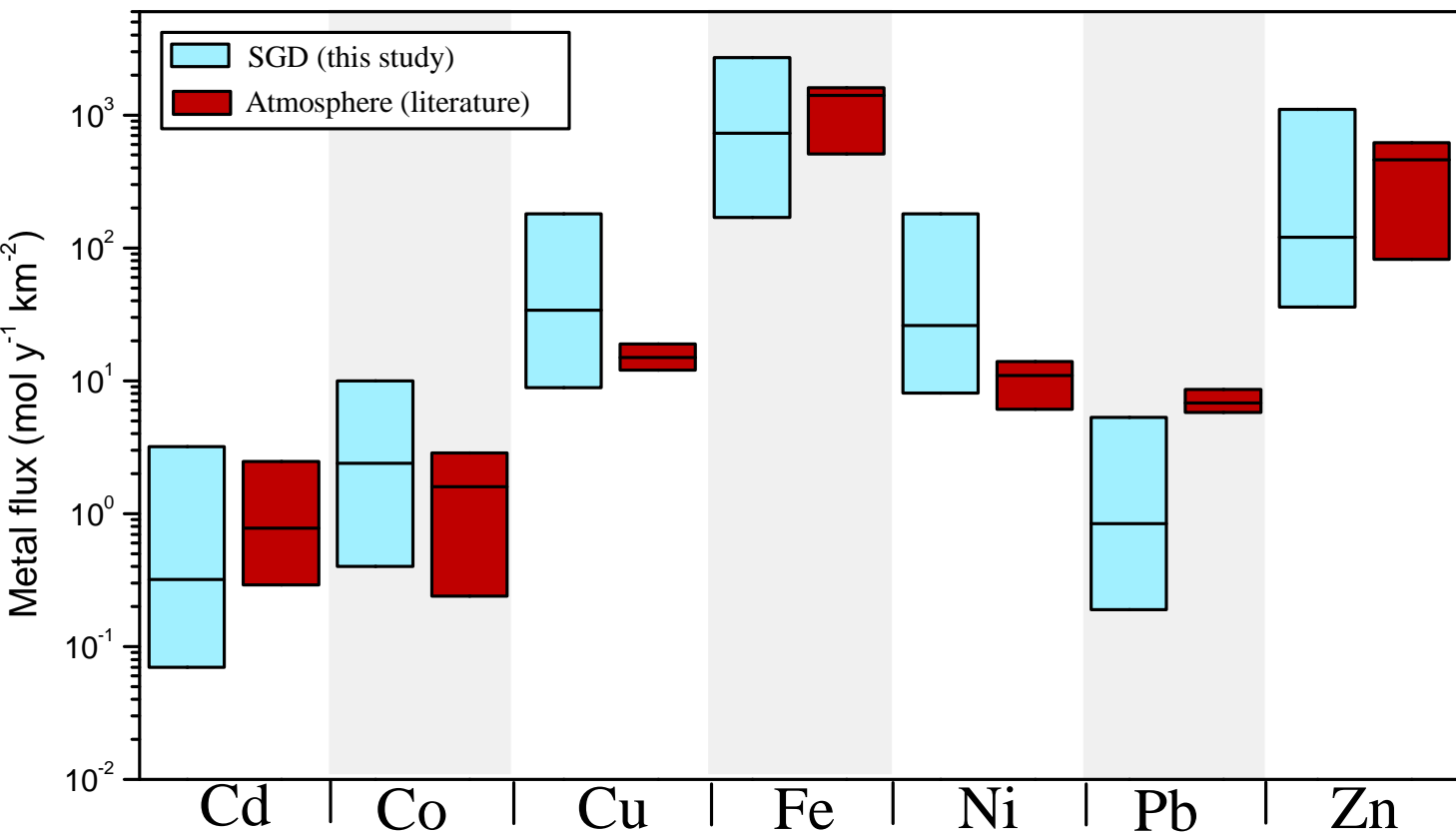
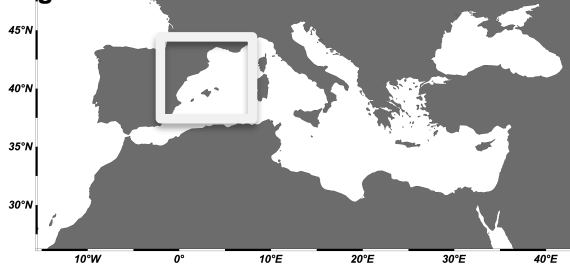
**Figure 6**

Figure 1 black and white



**Karstic SGD**

*This study:*

1. Garbí
  2. Suís
  3. Badum
  4. Font Dins
  5. Font Centre
  6. Font South
  7. Estramar
  8. La Palme
- Other studies:*
9. Sa Nau
  10. Baixamar

**Detrital SGD**

*This study:*

11. Argentona
12. Peníscola
13. Fosca North
14. Fosca South
15. Empuriabrava
16. Arenys
17. Sitges

*Other studies:*

18. Palma Bay
19. Santanyí
20. Romàntica
21. El Gorguel

**Rivers:**

*Other studies:*

22. Rhone
23. Ebro

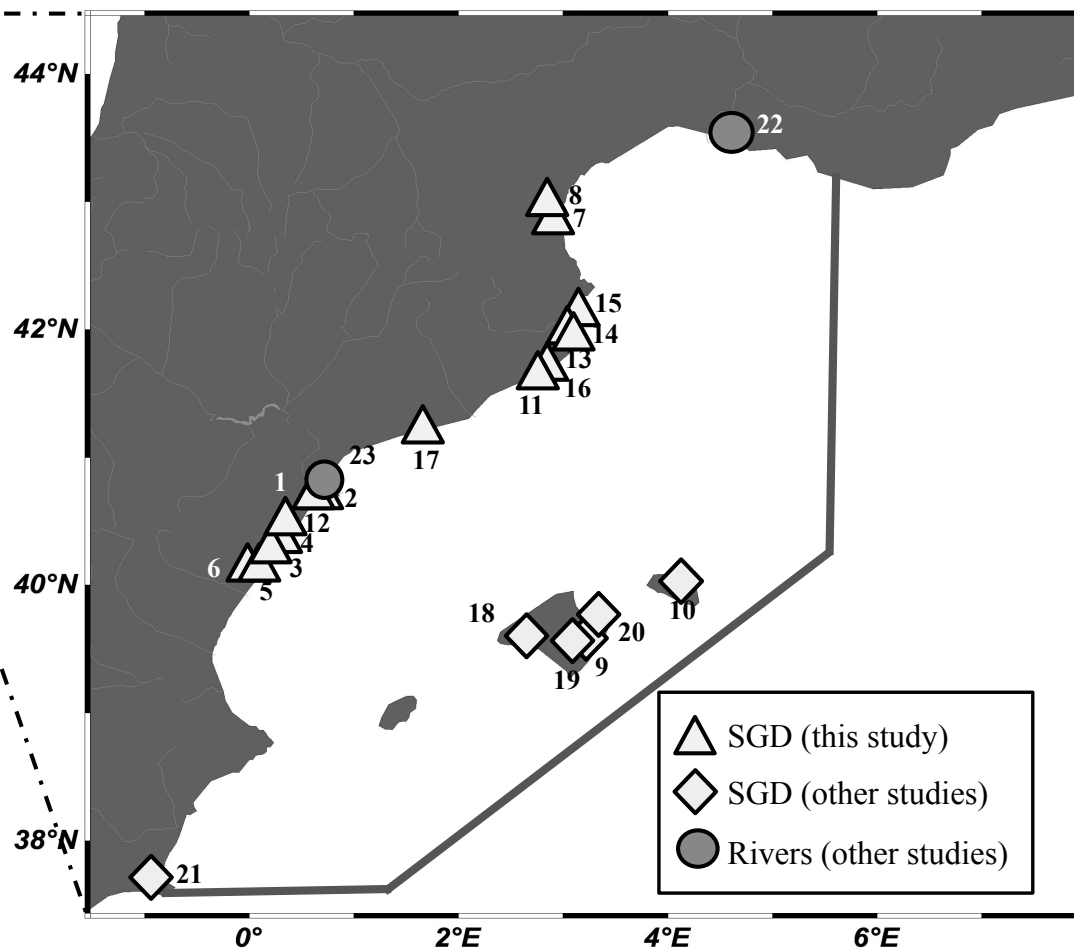


Figure 2 black and white

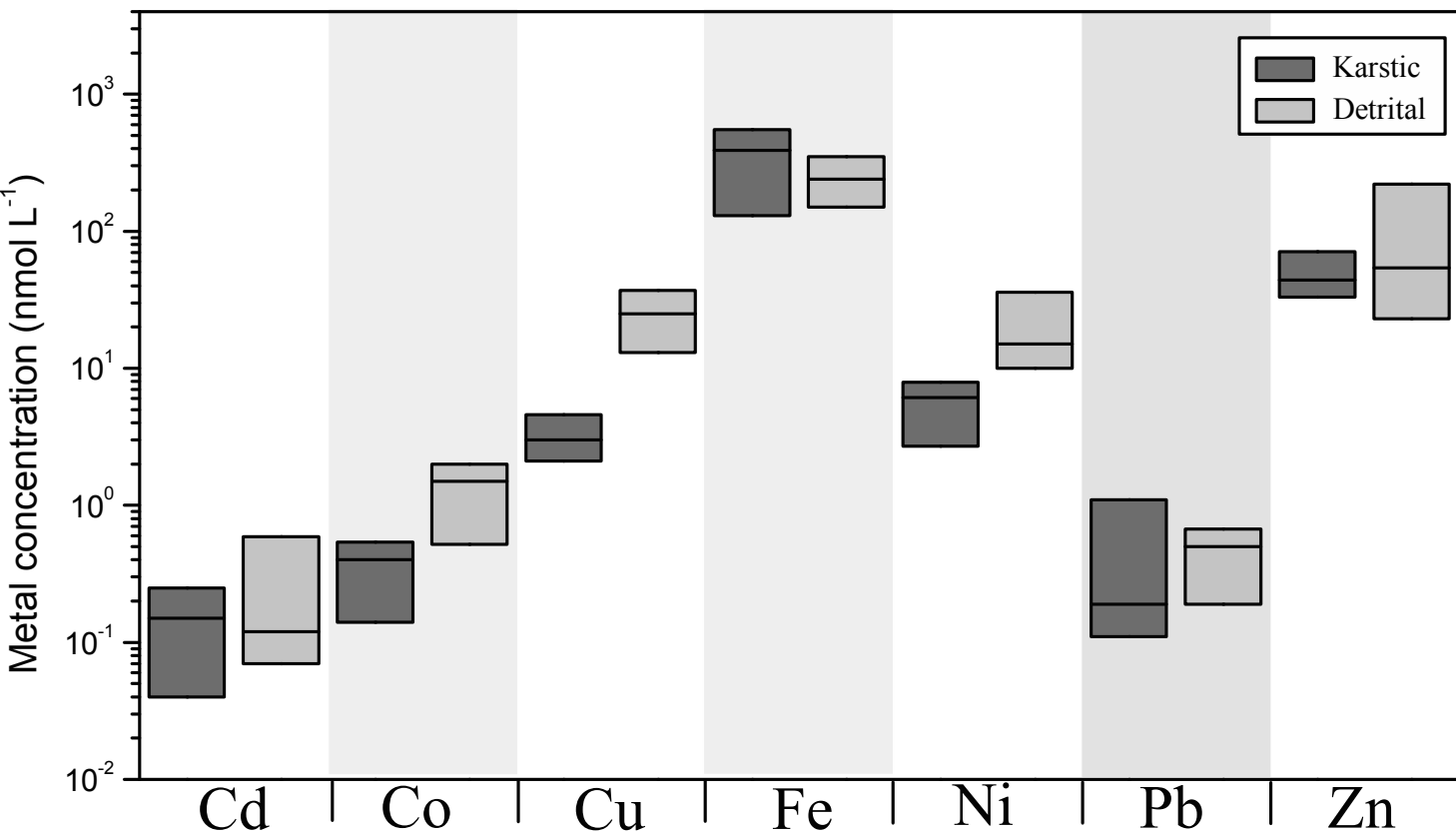




Figure 3 black and white

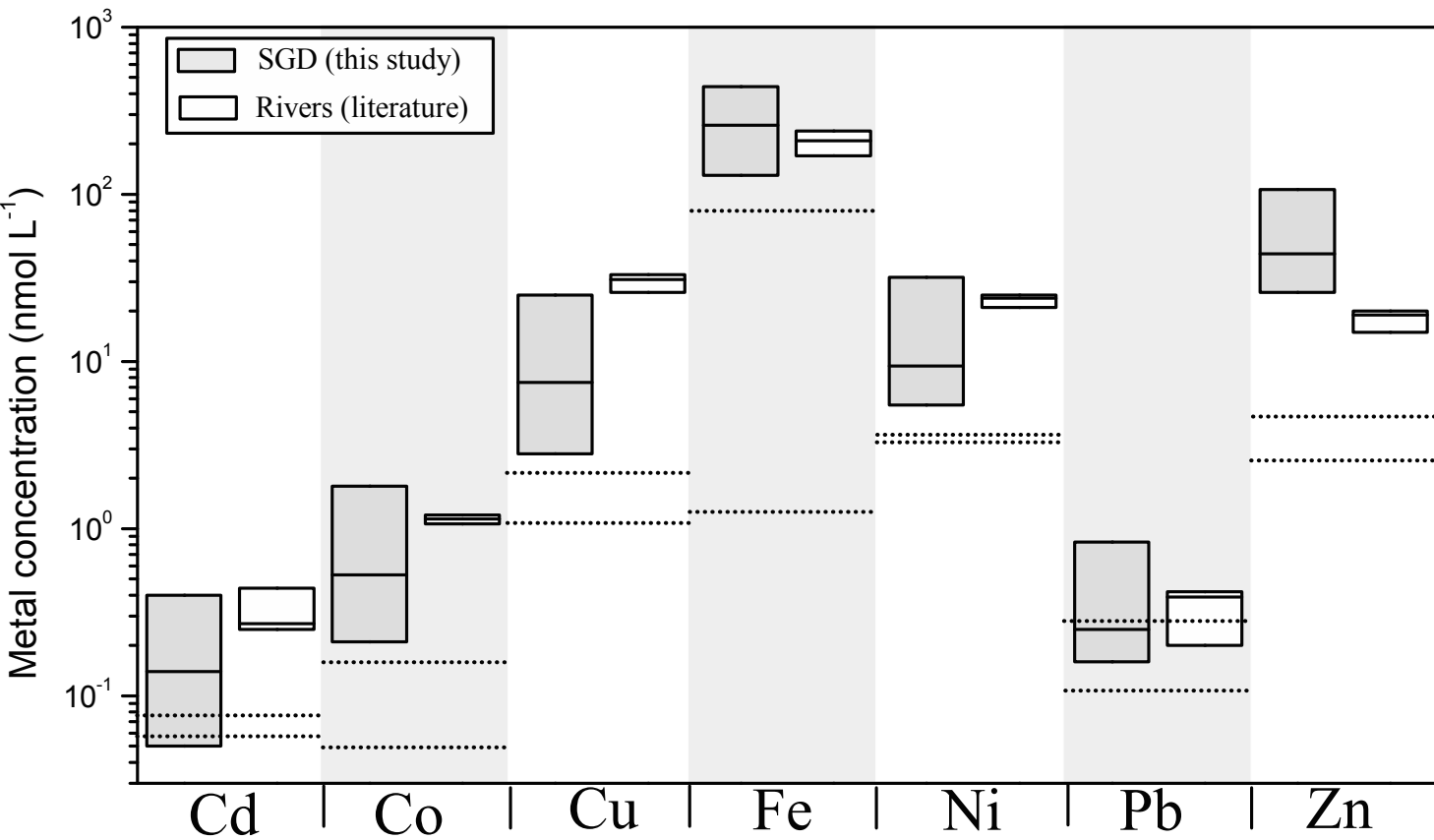
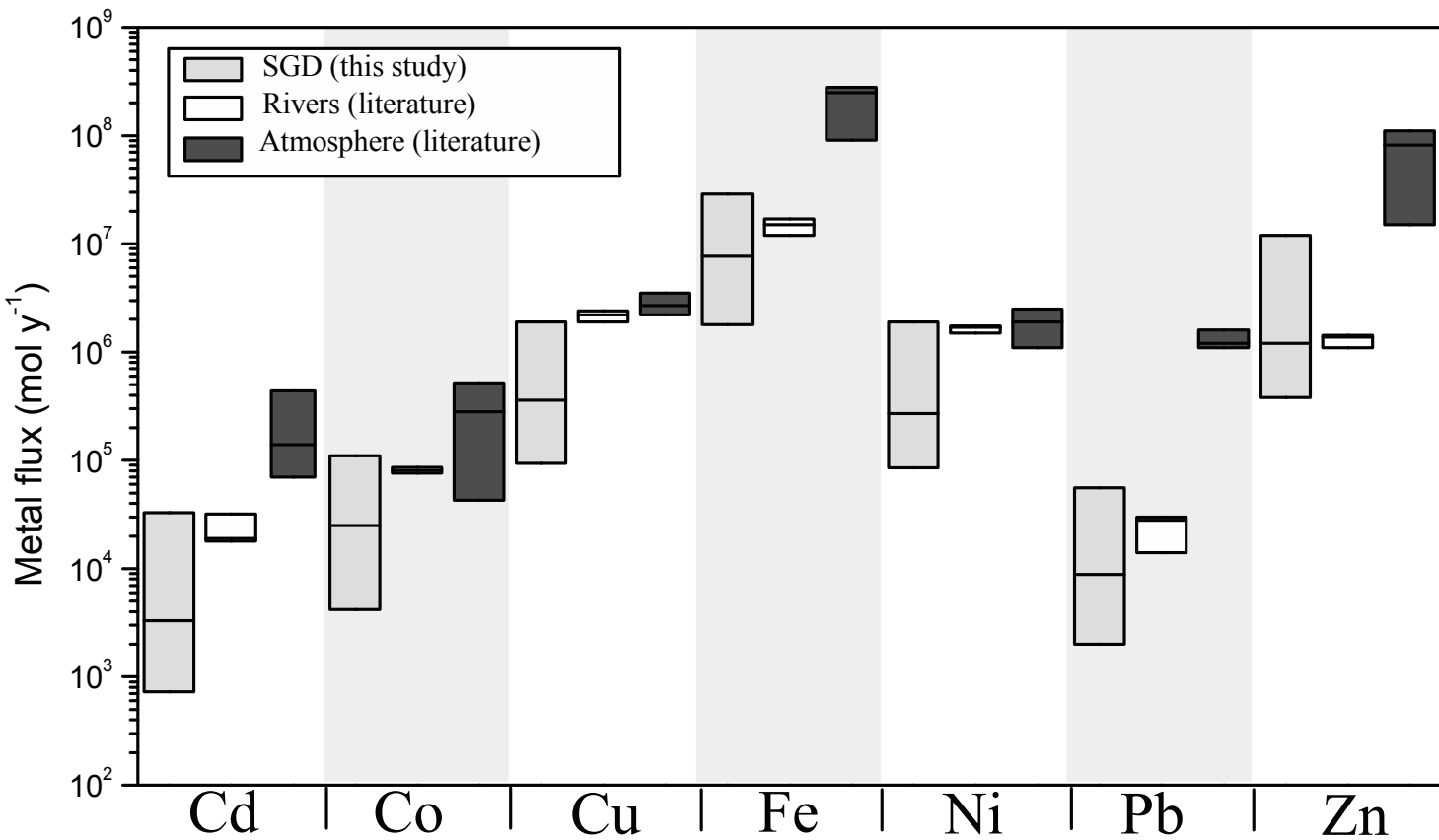


Figure 4 black and white



**Figure 5 black and white**

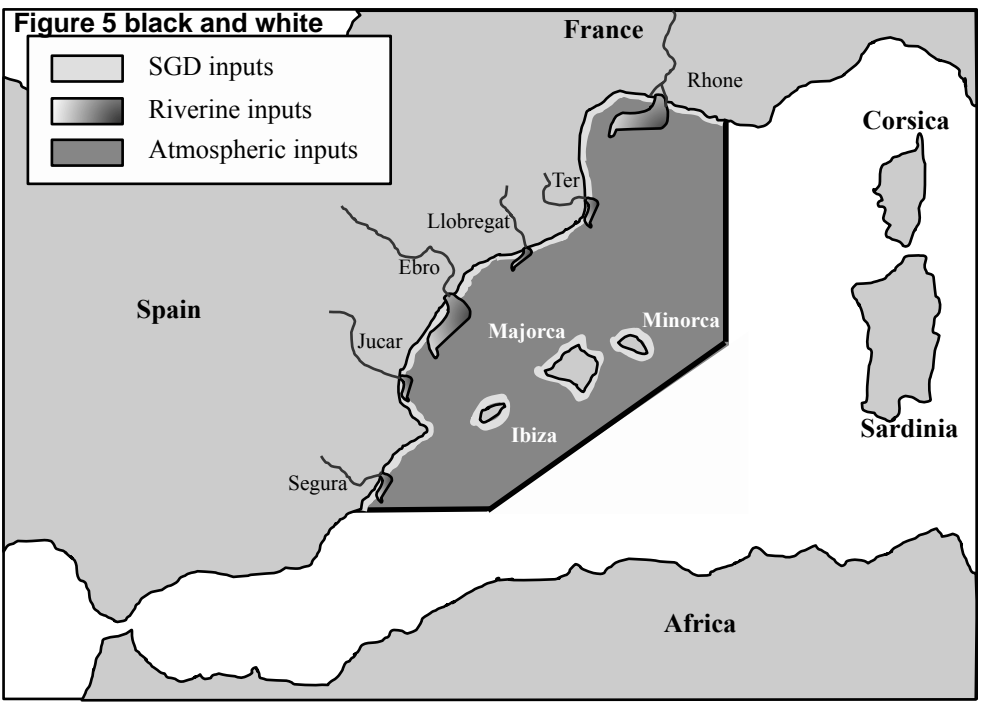
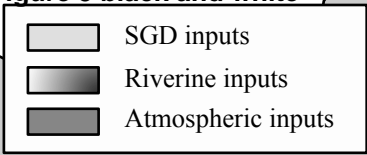
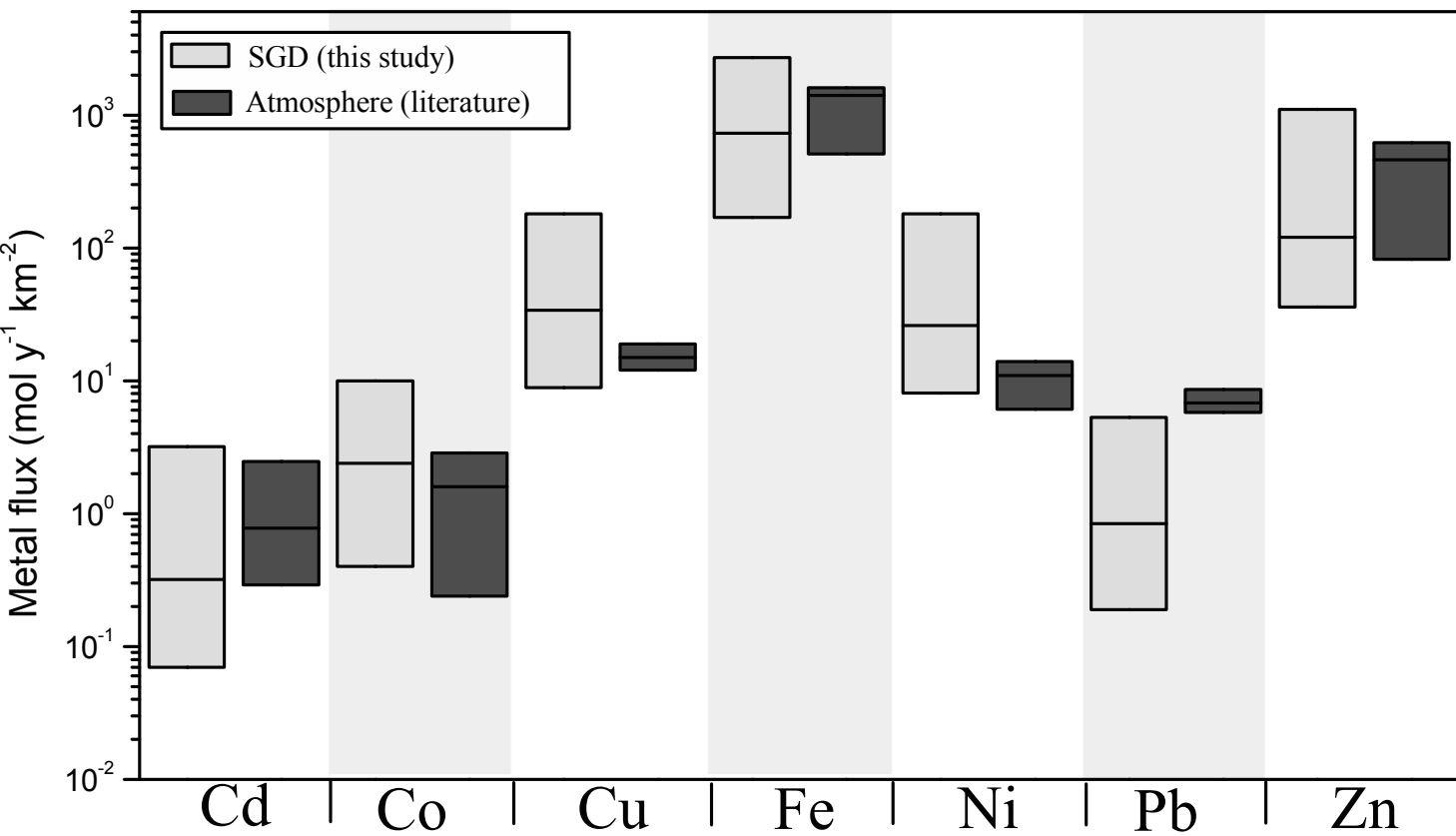
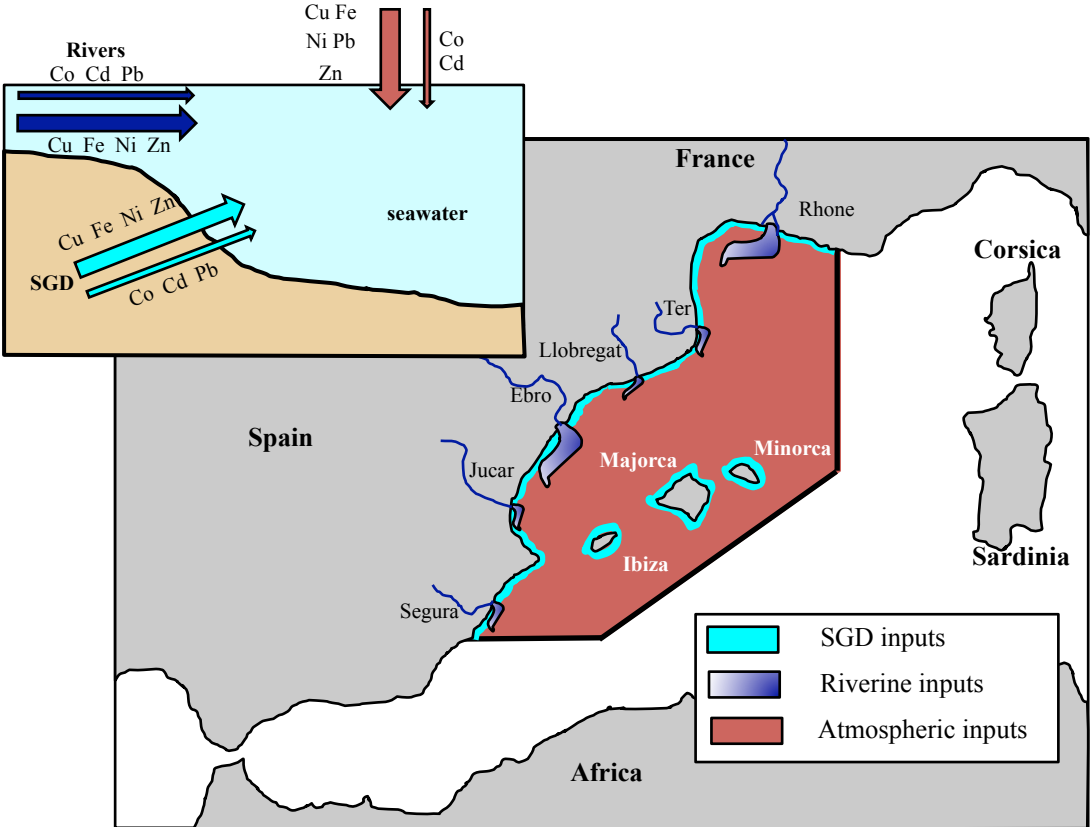


Figure 6 black and white



# Graphical Abstract (for review)



1 **Appendix A:** Karstic and detrital SGD flows reported in the literature for local studies in the NW  
 2 Mediterranean Sea.

		Shore-length	Water flow*
		km	$(10^6 \text{ m}^3 \text{ y}^{-1} \text{ km}^{-1})$
<b>Karstic SGD</b>			
Garcia-Solsona et al., 2010a, in Rodellas et al., 2015a	Alcafar	0.4	0.24
Garcia-Solsona et al., 2010b, in Rodellas et al., 2015a	Badum	2.5	19
Mejías et al., 2012, in Rodellas et al., 2015a	Maestrat	45	8.3
Rodellas et al., 2015b	Port of Maó	18	2.4
Rodellas et al., unpublished	Alfacs	5	13
Stieglitz et al., 2013, in Rodellas et al., 2015a	La palme	6	7.9
Tovar-Sánchez et al., 2014, in Rodellas et al., 2015a	Sa Nau	0.08	21
	Median		8.3
	1 <sup>st</sup> -3 <sup>rd</sup> quartiles		5.2 - 16
<b>Detrital SGD</b>			
Baudron et al., 2015	Mar Menor	22	25
Ollivier et al., 2008, in Rodellas et al., 2015a	Gulf of Lyon	300	29
Rodellas et al., 2012, in Rodellas et al., 2015a	Peníscola	3	6.3
Rodellas et al., 2014, in Rodellas et al., 2015a	Palma Bay	4.4	4.6
Tovar-Sánchez et al., 2014, in Rodellas et al., 2015a	Romàntica	0.15	0.40
Tovar-Sánchez et al., 2014, in Rodellas et al., 2015a	Santanyí	0.07	1.4
Trezzi et al. 2016	El Gorguel	0.7	20
	Median		6.3
	1 <sup>st</sup> -3 <sup>rd</sup> quartiles		3.0 - 23

3 \* SGD flows are normalized to the shore length of each study area (when reported flows were not shore-normalized,  
 4 SGD flows were divided by the shore length or the bay mouth width).  
 5  
 6

7 **Appendix B.** Data on dissolved metal concentrations in the Rhone and the Ebro Rivers reported in the  
 8 literature  
 9

**Dissolved metal concentrations (nmol L<sup>-1</sup>)**

		<b>Cd</b>	<b>Co</b>	<b>Cu</b>	<b>Fe</b>	<b>Ni</b>	<b>Pb</b>	<b>Zn</b>
<b>Elbaz-Poulichet et al. (1989)</b>	Rhone	0.48	1.2	32	n.a.	23	0.50	21
<b>Elbaz-Poulichet et al. (1996)</b>	Rhone	0.27	n.a.	35	n.a.	27	0.42	n.a.
<b>Guieu et al., (1991)</b>	Ebro	0.4	n.a.	30	n.a.	24	0.15	n.a.
<b>Guieu et al., (1993)</b>	Rhone	0.25	1.1	33	232	24	0.40	20
<b>Guieu et al. (1997)</b>	Rhone + Ebro	0.27	1.1	35	184	25	0.38	18
<b>Ollivier et al. (2011)</b>	Rhone	n.a.	n.a.	33	n.a.	17	0.33	41
<b>UNEP (2003) and references</b>	Rhone	0.25	n.a.	0.31	n.a.	15	0.22	17
<b>within</b>	Rhone	0.44	n.a.	30	n.a.	24	0.40	20
	Rhone	n.a.	n.a.	35	n.a.	n.a.	0.43	n.a.
	Ebro	0.13	n.a.	20	n.a.	21	0.12	8.4
	Ebro	0.54	n.a.	28	n.a.	26	0.14	9.2
	Ebro	n.a.	n.a.	15	n.a.	20	0.75	n.a.
	Median	0.27		31		24	0.39	19
	1 <sup>st</sup> -3 <sup>rd</sup> quartiles	0.25 – 0.44		26 - 33		21 - 25	0.20 – 0.42	15 - 20
	Mean		1.1		210			
	$\sigma$		0.07		34			

10 n.a. = not available;

**Appendix C.** Data on atmospheric dissolved metal fluxes to the Mediterranean Sea reported in the literature.

		Dissolved fraction of the total atmospheric deposition (%)						
		Cd	Co	Cu	Fe	Ni	Pb	Zn
<b>Guieu et al., 1997</b>		69	42	31 - 48	4 - 17	44 - 52	30-59	35 - 75
		Atmospheric dissolved metal fluxes (mol km <sup>-2</sup> y <sup>-1</sup> )						
		Cd	Co	Cu	Fe	Ni	Pb	Zn
<b>Bonnet and Guieu (2006)*</b>	NW Med	n.a.	n.a.	n.a.	2100	n.a.	n.a.	n.a.
<b>Chester et al., (1999)</b>	NW Med	n.a.	0.41	23	n.a.	4.6	8.6	n.a.
<b>Guerzoni et al. (1999)</b>	C Med	1.7	n.a.	59	140	21	15	340
<b>Guieu et al. (1993)*</b>	NW Med	8.0	3.0	12	1600	11	8.6	840
<b>Guieu et al. (1997)</b>	NW Med	4.9	1.3	17	1500	7.7	6.8	580
<b>Guieu et al. (2010)*</b>	Med	0.23	n.a.	n.a.	1300	n.a.	3.1	84
<b>Migon et al. (1991)*</b>	NW Med	1.0	n.a.	12	n.a.	n.a.	23	76
<b>Migon et al. (1997)*</b>	NW Med	0.40	n.a.	14	n.a.	11	6.7	680
<b>Ridame et al. (1999)*</b>	NW Med	0.34	n.a.	6.5	260	3.3	1.9	43
<b>Sandroni and Migon (2002)</b>	NW Med	0.52	n.a.	18	n.a.	16	5.8	600
	Median	0.78		15	1400	11	6.8	460
	1 <sup>st</sup> -3 <sup>rd</sup> quartiles	0.39 – 2.4		12 - 19	510 - 1600	6.1 - 14	5.8 – 8.6	82 - 620
	Mean		1.6					
	σ		1.3					

\* Data of dissolved metal fluxes were not reported; they have been calculated for this study from mean fluxes of the total fraction of metals, by using the percentages of partitioning between dissolved and particulate fractions reported in Guieu et al., (1997). For metals characterized by a range of percentages of dissolved fraction, the mean values of the dissolved metal fluxes, calculated considering minimum and maximum percentages of partitioning, are reported.

n.a. = not available;

NW Med = North Western Mediterranean; C Med = Central Mediterranean; Med = Mediterranean.