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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 106 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 29th, 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,

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Prof -Hein de Baar,
Associated Editor of Marine Chemistry

Barcelona, July 29th, 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; Gonneea 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: *Lne 185: Based on what method (228Ra mass balance). Please mention.*

Answer 4: Done: We have added "by using Ra isotopes and ^{222}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; Gonneea 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.

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

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Key words: submarine groundwater discharge (SGD), trace metals, micronutrients, Mediterranean Sea, rivers, atmospheric deposition

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 mol y^{-1}): Cd: 0.0007 - 0.03, Co: 0.004 -0.11, Cu: 0.09 - 1.9, Fe: 1.8 - 29, Ni: 0.09 - 1.9, Pb: 0.002 - 0.06, Zn: 0.38 - 12. These fluxes were compared to dTM fluxes from riverine discharge and atmospheric deposition, demonstrating that SGD is a major source of dTM to the NW Mediterranean Sea. Whilst riverine inputs are limited to the surrounding of river mouths and atmospheric fluxes are distributed throughout the whole basin mainly during sporadic depositional events, SGD represents a permanent, albeit seasonally variable, source of metals to most of the coastal areas. SGD-driven dTM inputs may be even more significant, in relative terms, in other coastal regions of the Mediterranean Sea where rivers are scarce, as it is the case of the African coast and many islands. This study highlights the relevance of SGD as a source of dTM to the Mediterranean Sea and the need of its consideration in the calculation of metal budgets in the basin and in the investigation of biogeochemical cycles in coastal areas.

1 Introduction

The availability of bioactive trace metals (e.g. Fe, Mn, Co, Ni, Cu, Zn and Cd) plays an important role in supporting primary productivity in the oceans (Bruland et al., 1991; Morel and Price, 2003; Sunda, 2012). Understanding the biogeochemical cycling of these micronutrients requires a detailed knowledge of their diverse sources and sinks. The main continental sources of trace metals to the ocean are riverine discharge (e.g. Bewers and Yeats, 1989; Jeandel and Oelkers, 2015; Martin and Whitfield, 1983; Oelkers et al., 2011), atmospheric deposition (e.g. Bowie et al., 2002; Duce et al., 1991; Jickells, 1995; Mackey et al., 2012; Mahowald et al., 2005), benthic fluxes from sediments (e.g. Elrod et al., 2004; Jeandel et al., 2011) and submarine groundwater discharge (SGD), although the latter has received attention only recently (e.g. Beck et al., 2007, 2009; Charette and Buesseler, 2004; Windom et al., 2006). SGD includes both fresh meteoric groundwater and recirculated seawater through permeable sediments of the coastal aquifer. Indeed, the mixing interface between fresh and salty water is a chemical reaction zone called the subterranean estuary, where groundwater can become enriched or depleted in chemical compounds before discharging into the sea (Moore, 1999). The chemical composition of SGD is influenced by several factors, such as the geological matrix and the geochemical conditions of the coastal aquifers (Charette et al., 2005; Mcallister et al., 2015; Santos et al., 2012), the potential impact of human activities (Beck et al., 2009; de Sieyes et al., 2008; Trezzi et al., 2016) and the type of discharge (e.g. karstic or detrital) (Tovar-Sánchez et al., 2014b).

Globally SGD has been estimated to be 3 to 4 times higher than riverine discharge into the oceans (Kwon et al., 2014). In the Mediterranean Sea, a semi-enclosed oligotrophic basin, SGD is comparable or even larger (up to 16 times) than the riverine water flow (Rodellas et al., 2015a). In this basin, the role of SGD in biogeochemical cycles is also

prominent since the estimated SGD-driven macronutrient fluxes (DIN, DIP and DSi) are comparable or even higher than the riverine and atmospheric fluxes (Rodellas et al., 2015a). The relevance of SGD in delivering dissolved trace metals (dTM) to the Mediterranean Sea has been highlighted in some local areas, characterized by the absence of riverine discharge (Rodellas et al., 2014; Tovar-Sánchez et al., 2014b; Trezzi et al., 2016).

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

2 Methodology

2.1 The NW Mediterranean Sea

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

Ocean, that leads to oligotrophic conditions in the whole basin (Béthoux et al., 1998). Climate conditions of the Mediterranean Sea generally consist of dry summers and rainy autumns and winters, with larger mean annual precipitation in the north and western parts of the basin.

The study area comprises the NW Mediterranean zone (Eastern Spanish coast, including the Balearic Islands, and French Mediterranean coast, up to Marseille city), encompassing a coastline of about 3,500 km and a surface area of about 180,000 km^2 (Figure 1). The Rhone and the Ebro are the main rivers in this area, representing more than the 70% of the total riverine discharge to the Western Mediterranean Sea, with mean water flows of $54 \cdot 10^9$ and $13 \cdot 10^9$ m^3 y^{-1}, respectively (Ludwig et al., 2009). Groundwater inputs occur via both detrital and karstified coastal aquifers. Fractured karstified carbonated aquifers constitute a large portion (about the 40%) of the French and Spanish coasts, including the Balearic Islands (Bakalowicz, 2015, 1999; Instituto Geologico Minero de España (IGME), 1986).

2.2 Sampling

Groundwater samples representative of the water discharging into the sea (i.e. SGD end-members) were collected between November 2013 and June 2015 at several locations along the Spanish and French Mediterranean coasts: 10 samples were collected from karstic systems and 8 from detrital systems (Figure 1; Table 1). The karstic waters corresponded to 3 different coastal carbonate aquifers and were collected mostly from flowing coastal springs associated with fractures (Garbí, Suís, Badum, Font Centre, Font South, Estramar, La Palme). One of these springs (Garbí, located close to the Ebro delta) was sampled three times (December 2013; July 2014;

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

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

2.3 Analysis

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

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

2.4 Calculations of continental trace metal fluxes

Metal concentrations in SGD end-members and magnitudes of SGD water flows to the NW Mediterranean Sea are required in order to quantify the SGD-driven dTM fluxes to the study area. We differentiated karstic from detrital SGD systems, because the hydrogeological setting of the aquifer and the discharge type (i.e. rapid discharges through fractures in karstified carbonates and slow diffuse ~~diffusive~~ flows through permeable sediments in detrital aquifers) can affect the chemical composition of SGD (Tovar-Sánchez et al., 2014b).

SGD water flows into the NW Mediterranean Sea have been quantified by using Ra isotopes and ^{222}Rn as tracers of the process in several locations of the Spanish and

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

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

estimation of the flux.

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

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

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

3 Results and Discussion

3.1 Metal characterization of SGD

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

The variability of trace metal concentrations in SGD systems depends on the geological composition of the coastal aquifers, the possible groundwater contamination through anthropogenic activities (Beck et al., 2009; Trezzi et al., 2016), the residence time of groundwater in the aquifers and the mixing of freshwater and seawater in the subterranean estuary (Beck et al., 2007; Moore, 1999). In karstic SGD, the ranges of dTM concentrations (in nmol L^{-1}) were <0.04 – 3.1 for Cd, <0.06 – 4.0 for Co, 0.68 – 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 detrital SGD, the ranges of dTM concentrations (in nmol L^{-1}) were <0.04 – 14 for Cd, 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, and 13 – 2100 for Zn.

Figure 2 shows the comparison between metal concentrations in karstic and detrital SGD end-members, for which ranges between the 1st and the 3rd quartiles were reported. Detrital SGD was distinctively more enriched in Co, Cu and Ni than karstic SGD. For the other trace metals (Cd, Fe, Pb and Zn), the ranges of concentrations in karstic and detrital SGD were comparable, although the median values of Fe were higher in karstic SGD (up to 1.5 times) and the median values of Pb were higher in detrital SGD (up to 2.5 times). 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; Gonneea 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.

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

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

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

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

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

Pb in rivers were higher than in SGD. 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). ~~different pH/redox conditions in subterranean estuaries with respect to surface estuaries.~~ The comparison of dTM concentrations in SGD and rivers confirmed that SGD must be evaluated as a potential source of metals to the coastal ocean, given that dTM concentrations of SGD end-members are at least similar to those of rivers for most of the metals. Thus, the volume of riverine and SGD water discharges will determine the relative significance of these two inputs of dTM to the coastal sea.

3.2 Comparison of trace metal fluxes into the NW Mediterranean Sea

Trace metal inputs through SGD are ~~also~~ 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.

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

SGD-driven dTM fluxes (in 10^6 mol y^{-1}) to the NW Mediterranean Sea are (0.0007 – 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) for Ni, (0.002 – 0.06) for Pb and (0.38 - 12) for Zn. Trace metals inputs through SGD can be subjected to seasonal variability. Unfortunately, detailed information about temporal characterization of SGD (metal concentrations and/or water flow) in each coastal aquifer considered in the work is not available. 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.

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

Dissolved trace metal fluxes from rivers to the NW Mediterranean Sea (in 10^6 mol y^{-1}), calculated using data from the literature as explained in Section 2.4, are (0.02 – 0.03) 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 – 0.03) for Pb and (1.1 – 1.4) for Zn.

Dissolved trace metal fluxes from atmospheric deposition to the NW Mediterranean Sea (in 10^6 mol y^{-1}), calculated with literature data as explained in Section 2.4, are (0.07 - 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, (1.1 - 1.6) for Pb and (15 - 110) for Zn.

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

3.3 Spatial and temporal influence of the continental trace metal fluxes

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

coastal geochemical cycles. Conversely to SGD and riverine discharge, which are short-scale coastal processes, atmospheric deposition occurs over the whole NW Mediterranean basin. Consequently, even if the atmospheric dTM fluxes calculated in Section 3.2 are clearly higher than those through SGD, the real contribution of these two inputs to the coastal sea should be evaluated dividing the calculated dTM fluxes by the respective areas of influence. For the atmospheric deposition, the area of influence is the total study area (180,000 km^2). In the case of SGD, several local studies have highlighted that this process usually does not reach a distance offshore higher than 2-3 km (on the base of Ra isotopes and/or salinity differences in coastal seawater) and that inputs of macronutrients and metals through SGD decrease towards the open seawater, being concentrated in the first hundreds of meters (Gonneea et al., 2014; Mejías et al., 2012; Moore, 2003; Rodellas et al., 2014; Trezzi et al., 2016; Windom et al., 2006). Dissolved trace metals supplied to this coastal seawater can also be removed from the water column by means of biogeochemical processes (Bruland and Lohan, 2003). Therefore, if we consider a distance of 3 km offshore as an upper limit affected by SGD and multiply it by the 3,500 km of coastline of the study area, a maximum area of influence for SGD of about 10,500 km^2 is obtained. Thus, we calculate the area-weighted SGD-driven dTM fluxes, which are a lower limit (at least for Cu, Fe, Ni and Zn) of the possible SGD contribution to the coastal area. In the case of Cd, Co and Pb, the obtained SGD values are not necessarily a lower limit, since for the samples characterized by no detectable metal concentrations, the limit of detection itself was considered in the calculations (see Section 2.4). The comparison of these SGD-driven fluxes with the atmospheric dTM fluxes (in mol y^{-1} km^{-2}) highlights that SGD inputs to the coastal sea are comparable or higher than atmospheric deposition for all the metals studied here, with the exception of Pb (Figure 6).

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

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

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

3.4 Relevance of SGD for the global Mediterranean Sea

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

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

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

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

3.5 Biogeochemical implications of SGD

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

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

4 Conclusions

This study is a first effort to estimate regional inputs of dTM (Cd, Co, Cu, Fe, Ni, Pb and Zn) through SGD to the oligotrophic Mediterranean Sea. SGD-driven dTM fluxes, calculated for the NW basin and compared to riverine discharge and atmospheric deposition, reveal that SGD is a significant source of dTM to the coastal Mediterranean Sea. The relevance of SGD may be even higher in coastal areas of the Southern and Eastern Mediterranean Sea or in many islands, which are characterized by scarce riverine discharge. Therefore SGD should be taken into account for the assessment of

trace metal budgets and for biogeochemical studies in coastal areas, as some of the metals delivered by this process are crucial micronutrients for primary productivity in the ocean.

Further investigations on trace metal inputs through SGD in the Mediterranean Sea are required in order to improve the estimation of SGD fluxes presented in this study. Indeed, spatial and temporal variability of trace metal concentrations in SGD end-members, as well as relations between concentrations and magnitude of water flows, need to be investigated in a large number of subterranean estuaries. At the same time, the present data set should be expanded with the characterization of metal inputs through SGD in areas that are not well studied at the moment, such the African Coast.

SUPPORTING INFORMATION

Karstic and detrital SGD-driven flows reported in the literature for local studies in the NW Mediterranean Sea (Appendix A); dissolved trace metal concentrations of the Rhone and the Ebro Rivers reported in the literature (Appendix B); atmospheric dissolved trace metal fluxes to the Mediterranean Sea reported in the literature (Appendix C).

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Submarine groundwater discharge: a significant source of dissolved trace metals to the North Western 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 mol y^{-1}): Cd: 0.0007 - 0.03, Co: 0.004 -0.11, Cu: 0.09 - 1.9, Fe: 1.8 - 29, Ni: 0.09 - 1.9, Pb: 0.002 - 0.06, Zn: 0.38 - 12. These fluxes were compared to dTM fluxes from riverine discharge and atmospheric deposition, demonstrating that SGD is a major source of dTM to the NW Mediterranean Sea. Whilst riverine inputs are limited to the surrounding of river mouths and atmospheric fluxes are distributed throughout the whole basin mainly during sporadic depositional events, SGD represents a permanent, albeit seasonally variable, source of metals to most of the coastal areas. SGD-driven dTM inputs may be even more significant, in relative terms, in other coastal regions of the Mediterranean Sea where rivers are scarce, as it is the case of the African coast and many islands. This study highlights the relevance of SGD as a source of dTM to the Mediterranean Sea and the need of its consideration in the calculation of metal budgets in the basin and in the investigation of biogeochemical cycles in coastal areas.

1 Introduction

The availability of bioactive trace metals (e.g. Fe, Mn, Co, Ni, Cu, Zn and Cd) plays an important role in supporting primary productivity in the oceans (Bruland et al., 1991; Morel and Price, 2003; Sunda, 2012). Understanding the biogeochemical cycling of these micronutrients requires a detailed knowledge of their diverse sources and sinks. The main continental sources of trace metals to the ocean are riverine discharge (e.g. Bewers and Yeats, 1989; Jeandel and Oelkers, 2015; Martin and Whitfield, 1983; Oelkers et al., 2011), atmospheric deposition (e.g. Bowie et al., 2002; Duce et al., 1991; Jickells, 1995; Mackey et al., 2012; Mahowald et al., 2005), benthic fluxes from sediments (e.g. Elrod et al., 2004; Jeandel et al., 2011) and submarine groundwater discharge (SGD), although the latter has received attention only recently (e.g. Beck et al., 2007, 2009; Charette and Buesseler, 2004; Windom et al., 2006). SGD includes both fresh meteoric groundwater and recirculated seawater through permeable sediments of the coastal aquifer. Indeed, the mixing interface between fresh and salty water is a chemical reaction zone called the subterranean estuary, where groundwater can become enriched or depleted in chemical compounds before discharging into the sea (Moore, 1999). The chemical composition of SGD is influenced by several factors, such as the geological matrix and the geochemical conditions of the coastal aquifers (Charette et al., 2005; Mcallister et al., 2015; Santos et al., 2012), the potential impact of human activities (Beck et al., 2009; de Sieyes et al., 2008; Trezzi et al., 2016) and the type of discharge (e.g. karstic or detrital) (Tovar-Sánchez et al., 2014b).

Globally SGD has been estimated to be 3 to 4 times higher than riverine discharge into the oceans (Kwon et al., 2014). In the Mediterranean Sea, a semi-enclosed oligotrophic basin, SGD is comparable or even larger (up to 16 times) than the riverine water flow (Rodellas et al., 2015a). In this basin, the role of SGD in biogeochemical cycles is also

prominent since the estimated SGD-driven macronutrient fluxes (DIN, DIP and DSi) are comparable or even higher than the riverine and atmospheric fluxes (Rodellas et al., 2015a). The relevance of SGD in delivering dissolved trace metals (dTM) to the Mediterranean Sea has been highlighted in some local areas, characterized by the absence of riverine discharge (Rodellas et al., 2014; Tovar-Sánchez et al., 2014b; Trezzi et al., 2016).

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

2 Methodology

2.1 The NW Mediterranean Sea

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

Ocean, that leads to oligotrophic conditions in the whole basin (Béthoux et al., 1998). Climate conditions of the Mediterranean Sea generally consist of dry summers and rainy autumns and winters, with larger mean annual precipitation in the north and western parts of the basin.

The study area comprises the NW Mediterranean zone (Eastern Spanish coast, including the Balearic Islands, and French Mediterranean coast, up to Marseille city), encompassing a coastline of about 3,500 km and a surface area of about 180,000 km^2 (Figure 1). The Rhone and the Ebro are the main rivers in this area, representing more than the 70% of the total riverine discharge to the Western Mediterranean Sea, with mean water flows of $54 \cdot 10^9$ and $13 \cdot 10^9$ m^3 y^{-1}, respectively (Ludwig et al., 2009). Groundwater inputs occur via both detrital and karstified coastal aquifers. Fractured karstified carbonated aquifers constitute a large portion (about the 40%) of the French and Spanish coasts, including the Balearic Islands (Bakalowicz, 2015, 1999; Instituto Geologico Minero de España (IGME), 1986).

2.2 Sampling

Groundwater samples representative of the water discharging into the sea (i.e. SGD end-members) were collected between November 2013 and June 2015 at several locations along the Spanish and French Mediterranean coasts: 10 samples were collected from karstic systems and 8 from detrital systems (Figure 1; Table 1). The karstic waters corresponded to 3 different coastal carbonate aquifers and were collected mostly from flowing coastal springs associated with fractures (Garbí, Suís, Badum, Font Centre, Font South, Estramar, La Palme). One of these springs (Garbí, located close to the Ebro delta) was sampled three times (December 2013; July 2014;

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

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

2.3 Analysis

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

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

2.4 Calculations of continental trace metal fluxes

Metal concentrations in SGD end-members and magnitudes of SGD water flows to the NW Mediterranean Sea are required in order to quantify the SGD-driven dTM fluxes to the study area. We differentiated karstic from detrital SGD systems, because the hydrogeological setting of the aquifer and the discharge type (i.e. rapid discharges through fractures in karstified carbonates and slow diffuse flows through permeable sediments in detrital aquifers) can affect the chemical composition of SGD (Tovar-Sánchez et al., 2014b).

SGD water flows into the NW Mediterranean Sea have been quantified by using Ra isotopes and ^{222}Rn as tracers of the process in several locations of the Spanish and

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

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

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

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

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

3 Results and Discussion

3.1 Metal characterization of SGD

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

The variability of trace metal concentrations in SGD systems depends on the geological composition of the coastal aquifers, the possible groundwater contamination through anthropogenic activities (Beck et al., 2009; Trezzi et al., 2016), the residence time of groundwater in the aquifers and the mixing of freshwater and seawater in the subterranean estuary (Beck et al., 2007; Moore, 1999). In karstic SGD, the ranges of dTM concentrations (in nmol L^{-1}) were <0.04 – 3.1 for Cd, <0.06 – 4.0 for Co, 0.68 – 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 detrital SGD, the ranges of dTM concentrations (in nmol L^{-1}) were <0.04 – 14 for Cd, 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, and 13 – 2100 for Zn.

Figure 2 shows the comparison between metal concentrations in karstic and detrital SGD end-members, for which ranges between the 1^{st} and the 3^{rd} quartiles were reported. Detrital SGD was distinctively more enriched in Co, Cu and Ni than karstic SGD. For the other trace metals (Cd, Fe, Pb and Zn), the ranges of concentrations in karstic and detrital SGD were comparable, although the median values of Fe were higher in karstic SGD (up to 1.5 times) and the median values of Pb were higher in detrital SGD (up to 2.5 times). 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; Gonneea 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.

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

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

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

The concentrations of dTM in SGD end-members (obtained unifying the data set on karstic and detrital systems) were compared to those reported in the literature for the Rhone and the Ebro Rivers (Figure 3). For the data set presented in this work, the clearest differences were the higher concentrations of dissolved Zn in SGD and dissolved Cu in the rivers. For the other trace metals, the ranges of concentrations were comparable in SGD and in rivers, although the median concentrations of Cd, Co, Ni and Pb in rivers were higher than in SGD. 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). The comparison of dTM concentrations in SGD and rivers confirmed that SGD must be evaluated as a potential source of metals to the coastal ocean, given that dTM concentrations of SGD end-members are at least similar to those of rivers for most of the metals. Thus, the volume of riverine and SGD water discharges will determine the relative significance of these two inputs of dTM to the coastal sea.

3.2 Comparison of trace metal fluxes into the NW Mediterranean Sea

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.

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

SGD-driven dTM fluxes (in 10^6 mol y^{-1}) to the NW Mediterranean Sea are (0.0007 – 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) for Ni, (0.002 – 0.06) for Pb and (0.38 - 12) for Zn. Trace metals inputs through SGD can be subjected to seasonal variability. Unfortunately, detailed information about temporal characterization of SGD (metal concentrations and/or water flow) in each coastal aquifer considered in the work is not available. 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.

Dissolved trace metal fluxes from rivers to the NW Mediterranean Sea (in 10^6 mol y^{-1}), calculated using data from the literature as explained in Section 2.4, are (0.02 – 0.03) 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 – 0.03) for Pb and (1.1 – 1.4) for Zn.

Dissolved trace metal fluxes from atmospheric deposition to the NW Mediterranean Sea (in 10^6 mol y^{-1}), calculated with literature data as explained in Section 2.4, are (0.07 - 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, (1.1 - 1.6) for Pb and (15 - 110) for Zn.

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

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

3.3 Spatial and temporal influence of the continental trace metal fluxes

The presented comparison between continental inputs of dTM to the NW Mediterranean Sea did not consider the spatial and temporal distribution of SGD, rivers and atmospheric deposition. These distributions are different (Figure 5) and should be taken into account for an appropriate evaluation of the effects of the sources of dTM on coastal geochemical cycles. Conversely to SGD and riverine discharge, which are short-scale coastal processes, atmospheric deposition occurs over the whole NW Mediterranean basin. Consequently, even if the atmospheric dTM fluxes calculated in Section 3.2 are clearly higher than those through SGD, the real contribution of these two inputs to the coastal sea should be evaluated dividing the calculated dTM fluxes by the respective areas of influence. For the atmospheric deposition, the area of influence is the total study area (180,000 km^2). In the case of SGD, several local studies have highlighted that this process usually does not reach a distance offshore higher than 2-3 km (on the base of Ra isotopes and/or salinity differences in coastal seawater) and that inputs of macronutrients and metals through SGD decrease towards the open seawater, being concentrated in the first hundreds of meters (Gonneea et al., 2014; Mejías et al., 2012; Moore, 2003; Rodellas et al., 2014; Trezzi et al., 2016; Windom et al., 2006). Dissolved trace metals supplied to this coastal seawater can also be removed from the water column by means of biogeochemical processes (Bruland and Lohan, 2003). Therefore, if we consider a distance of 3 km offshore as an upper limit affected by SGD and multiply it by the 3,500 km of coastline of the study area, a maximum area of

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

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

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

Temporal variability should also be considered when comparing the different continental inputs of dTM to the NW Mediterranean Sea. Thus, whilst SGD and rivers can be considered a permanent source of dTM to the coastal areas (even if they are affected by water flow fluctuations on annual scale), atmospheric deposition in the Mediterranean Sea has a very high intra-annual and inter-annual variability, with most of the flux concentrated in few strong events during the year (Avila et al., 1998; Guieu et al., 2010). This is particularly true for crustal-derived trace metals (Fe, Co and part of Ni and Cu), whose atmospheric deposition is related principally to Saharan dust events (Heimbürger et al., 2010). Therefore, the relative significance of SGD-driven dTM fluxes to the NW Mediterranean Sea can be actually higher in absence of dust events and lower during the dust events.

3.4 Relevance of SGD for the global Mediterranean Sea

The Mediterranean Sea is one of the most oligotrophic and exploited seas in the world, where the sources of nutrients are limited (Macias et al., 2014). Atmospheric deposition (Guerzoni et al., 1999; Guieu et al., 2010, 1997) and riverine runoff (Ludwig et al., 2009; Macias et al., 2014) have been traditionally considered the main continental sources of nutrients, while other sources such as SGD are not commonly considered or documented. However, the relevance of SGD as a source of macronutrients to the whole Mediterranean basin was recently demonstrated (Rodellas et al., 2015a) and the present study represents the first evidence of the potential relevance of SGD as a source of dTM

(e.g. Cd, Co, Cu, Fe, Ni, Pb and Zn) at regional scale. While this study is particularly focused on the NW Mediterranean Sea, 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 currently prevent the extension of these calculations to the whole Mediterranean Sea. However, some general considerations about the key role of SGD in contributing dTM to the whole Mediterranean Sea can be made.

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

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

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

3.5 Biogeochemical implications of SGD

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

4 Conclusions

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

Further investigations on trace metal inputs through SGD in the Mediterranean Sea are required in order to improve the estimation of SGD fluxes presented in this study. Indeed, spatial and temporal variability of trace metal concentrations in SGD end-members, as well as relations between concentrations and magnitude of water flows, need to be investigated in a large number of subterranean estuaries. At the same time, the present data set should be expanded with the characterization of metal inputs through SGD in areas that are not well studied at the moment, such the African Coast.

SUPPORTING INFORMATION

Karstic and detrital SGD-driven flows reported in the literature for local studies in the NW Mediterranean Sea (Appendix A); dissolved trace metal concentrations of the Rhone and the Ebro Rivers reported in the literature (Appendix B); atmospheric

dissolved trace metal fluxes to the Mediterranean Sea reported in the literature (Appendix C).

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***Research Highlights**

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(s) corrected

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^{-1})						
			Cd	Co	Cu	Fe	Ni	Pb	Zn
Karstic SGD									
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
Suís	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)[+]	Nov 2010	3.2	3.1	4.0	7.2	730	32	0.16	300
Baixamar (Tovar-Sánchez, personal communication)[+]	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^{st}-3^{rd} 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
Detrital SGD									
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)[+]	May 2010	2.1-31.0*	n.a.	n.a.	30	320	38	0.69	73
Santanyí (Tovar-Sanchez et al. 2014)[+]	Nov 2010	10.9-33.7*	0.73	1.64	59	44	32	0.62	1900
Romàntica (Tovar-Sanchez et al. 2014)[+]	Nov 2010	17.8-32.4*	0.44	6.9	23	420	50	0.19	170
El Gorguel (Trezzi et al., 2016)[+]	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^{st}-3^{rd} quartiles)			0.07 - 0.59	0.52 - 2.0	13 - 37	150 - 350	10 - 36	0.19 - 0.67	23 - 220
	Total SGD								
SGD Median			0.14	0.53	7.5	260	9.4	0.25	85
SGD (1^{st}-3^{rd} quartiles)			0.05 - 0.40	0.21 - 1.8	2.8 - 25	130 - 440	5.5 - 32	0.16 - 0.82	16 - 120

[+] 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.

		Dissolved metal fluxes (10^6 mol y^{-1})						
		Cd	**Co**	**Cu**	**Fe**	**Ni**	**Pb**	**Zn**
SGD	Median	0.003	0.02	0.36	7.7	0.27	0.009	1.2
	1^{st}- 3^{rd} 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
Rivers	Median	0.02		2.2		1.7	0.03	1.4
	1^{st}- 3^{rd} 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			
	σ		0.005		2.4			
Atmosphere	Median	0.14		2.7	250	1.9	1.2	82
	1^{st}- 3^{rd} quartiles	0.07 – 0.44		2.2 – 3.5	91 - 280	1.1 – 2.5	1.1 – 1.6	15 - 110
	Mean		0.28					
	σ		0.24					
Total		0.09 – 0.51	0.12 – 0.71	4.2 – 7.7	110 - 330	2.7 – 6.1	1.1 – 1.6	16 - 120

Figure 1

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

Figure 2

Comparison of dTM concentrations in SGD from karstic (orange) and detrital (grey) systems. Ranges between the 1^{st} and the 3^{rd} quartiles and median values of the available dataset are plotted.

Figure 3

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

Figure 4

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

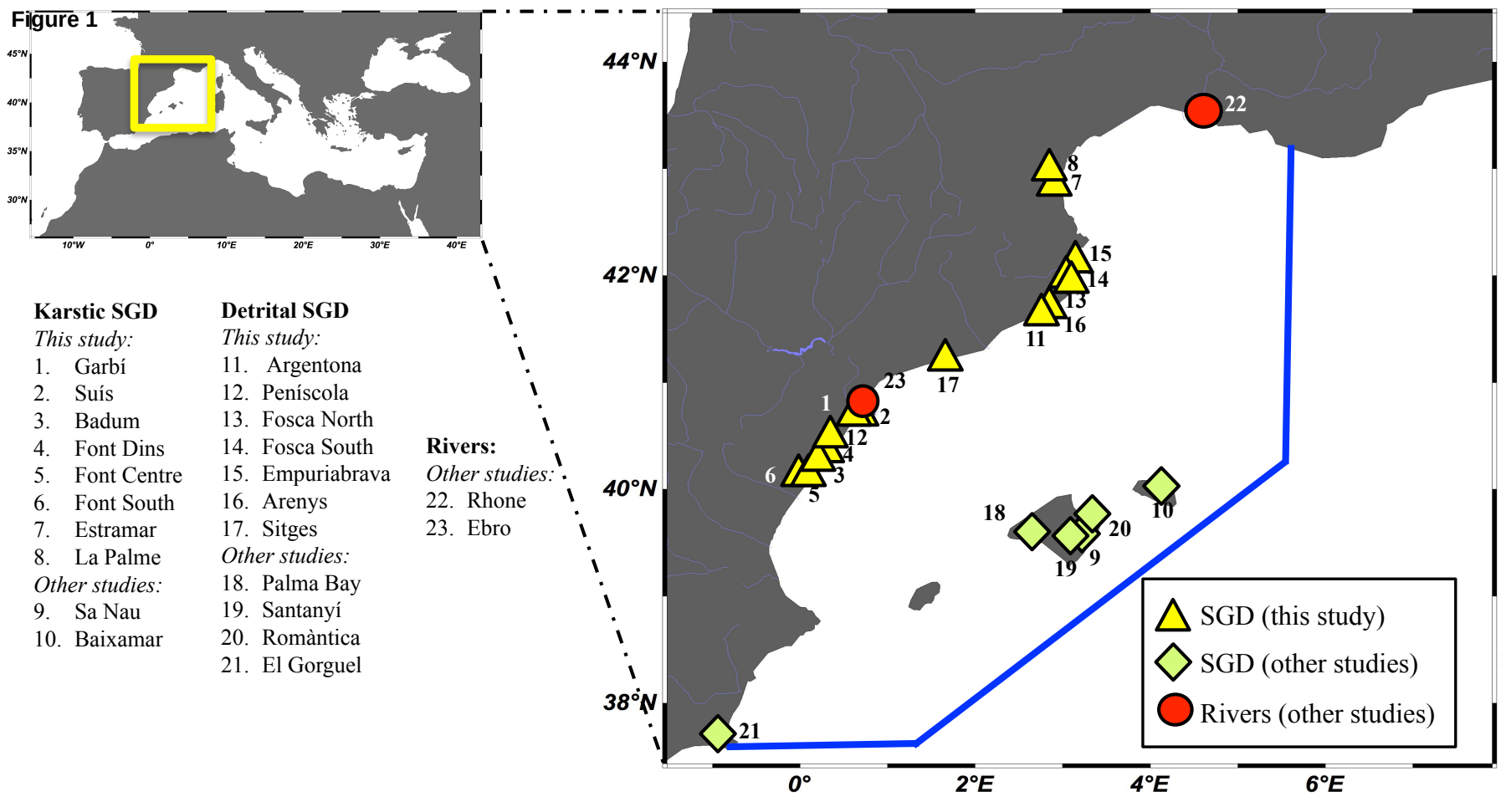
Figure 5

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

Figure 6

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

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

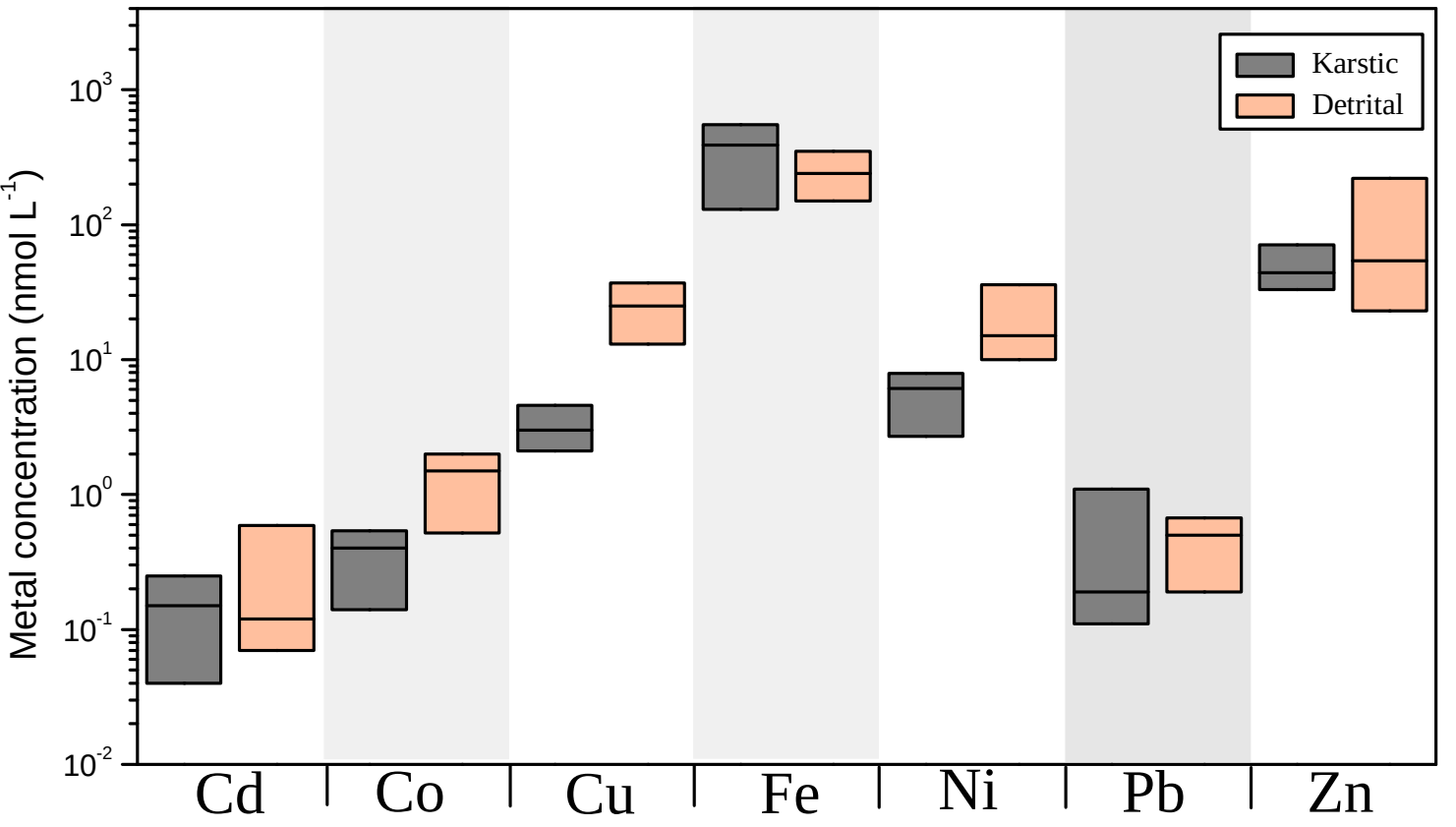

Karstic
Detrital
Metal concentration (nmol L-1)
10^3
10^2
10^1
10^0
10^-1
10^-2
Cd
Co
Cu
Fe
Ni
Pb
Zn

Figure 3

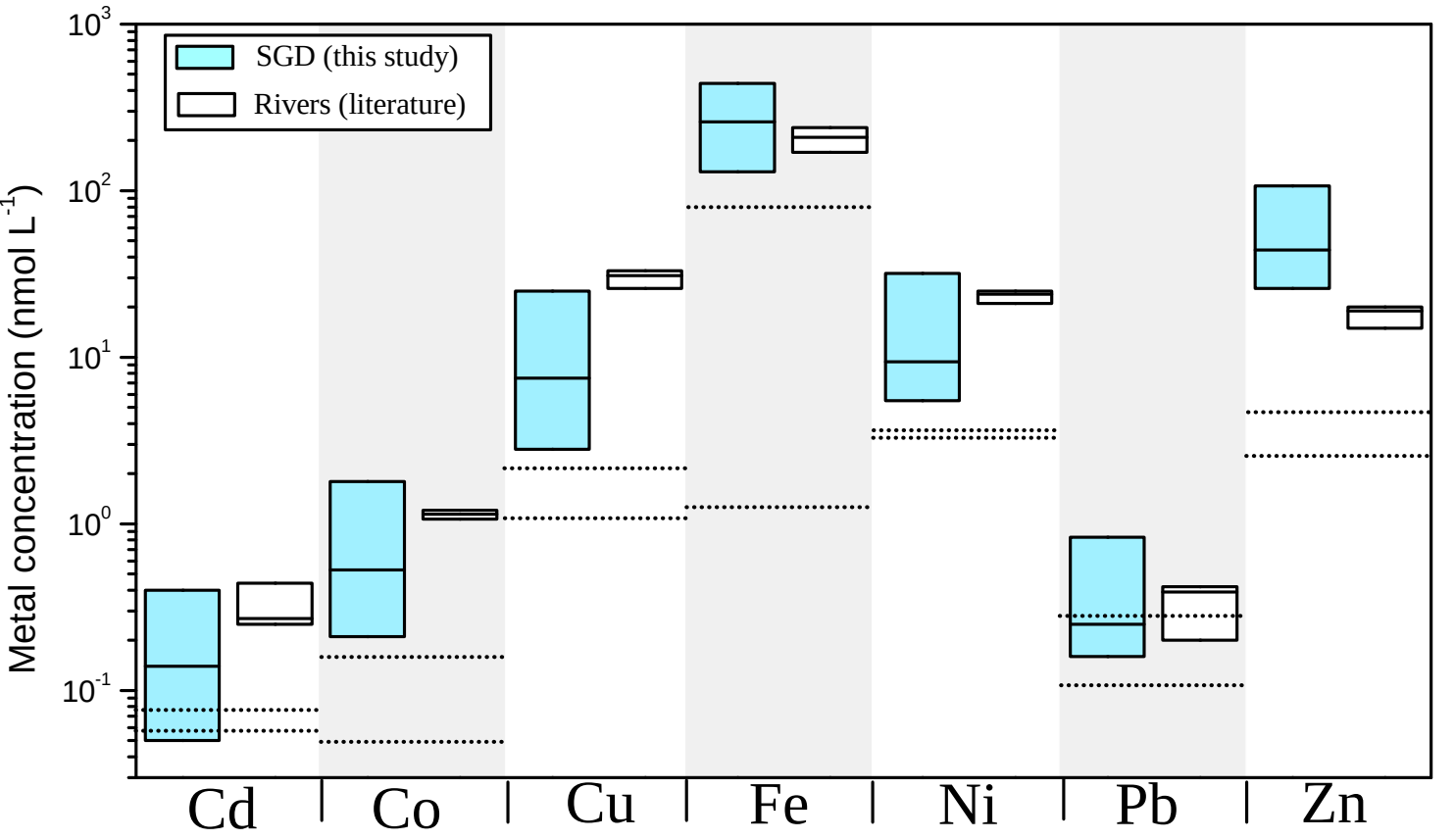

SGD (this study)
Rivers (literature)
Metal concentration (nmol L-1)
10^3
10^2
10^1
10^0
10^-1
Cd
Co
Cu
Fe
Ni
Pb
Zn

Figure 4

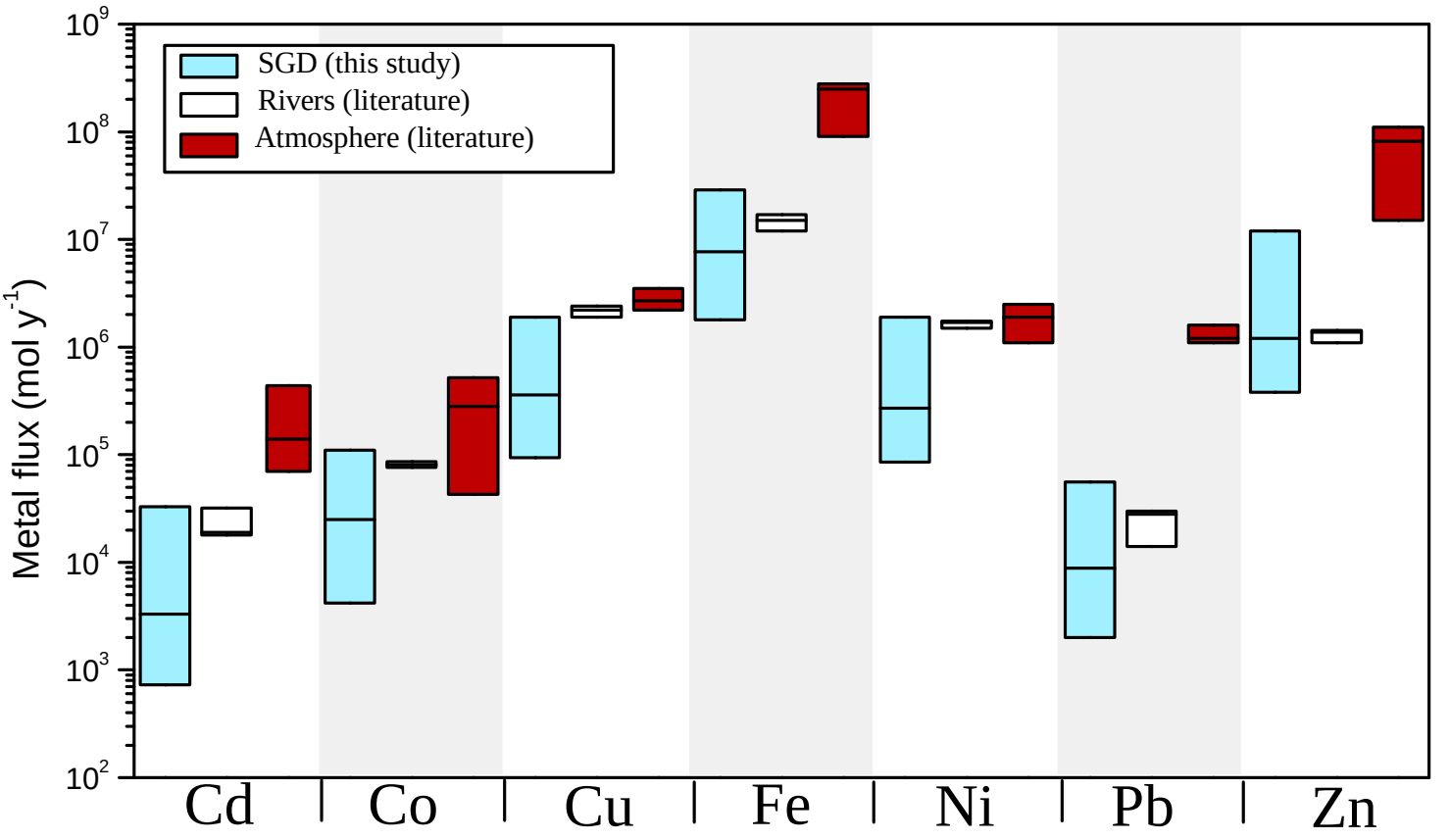

SGD (this study)
Rivers (literature)
Atmosphere (literature)
Metal flux (mol y-1)
10^9
10^8
10^7
10^6
10^5
10^4
10^3
10^2
Cd
Co
Cu
Fe
Ni
Pb
Zn

Figure 5

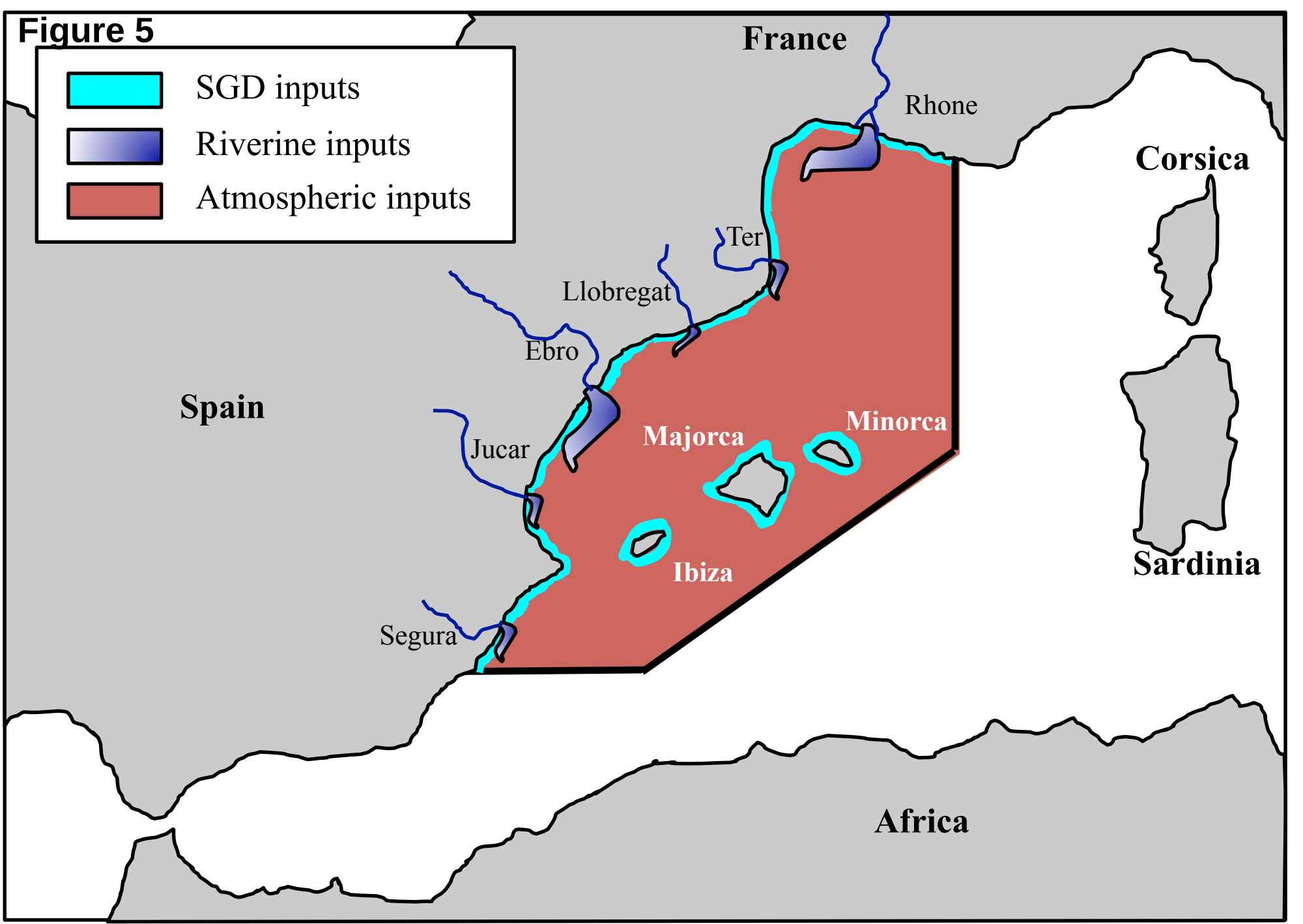

SGD inputs
Riverine inputs
Atmospheric inputs
France
Rhone
Corsica
Ter
Llobregat
Ebro
Spain
Jucar
Majorca
Minorca
Ibiza
Sardinia
Segura
Africa

Figure 6

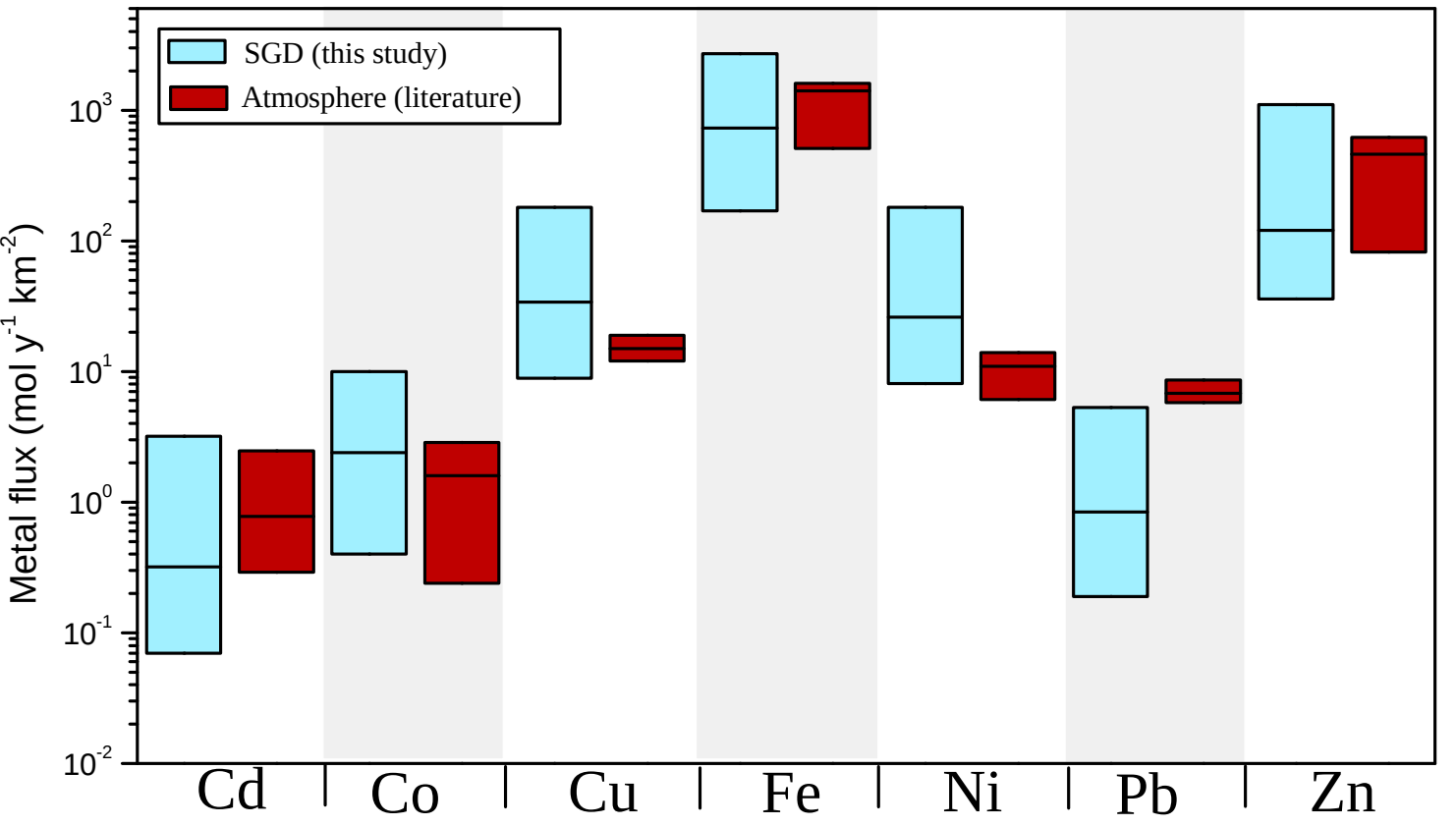
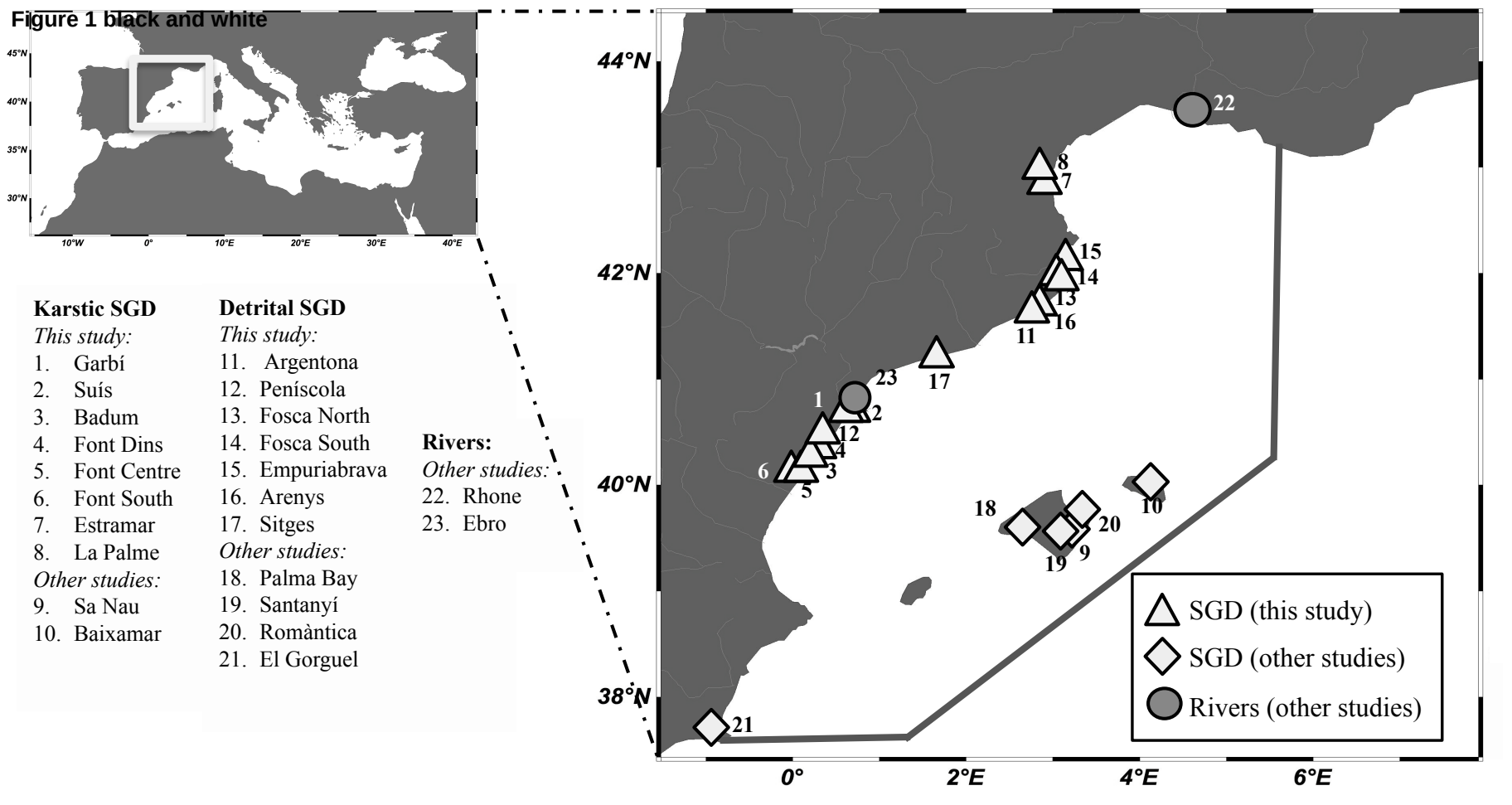

SGD (this study)
Atmosphere (literature)
Metal flux (mol y-1 km-2)
10^3
10^2
10^1
10^0
10^-1
10^-2
Cd
Co
Cu
Fe
Ni
Pb
Zn

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

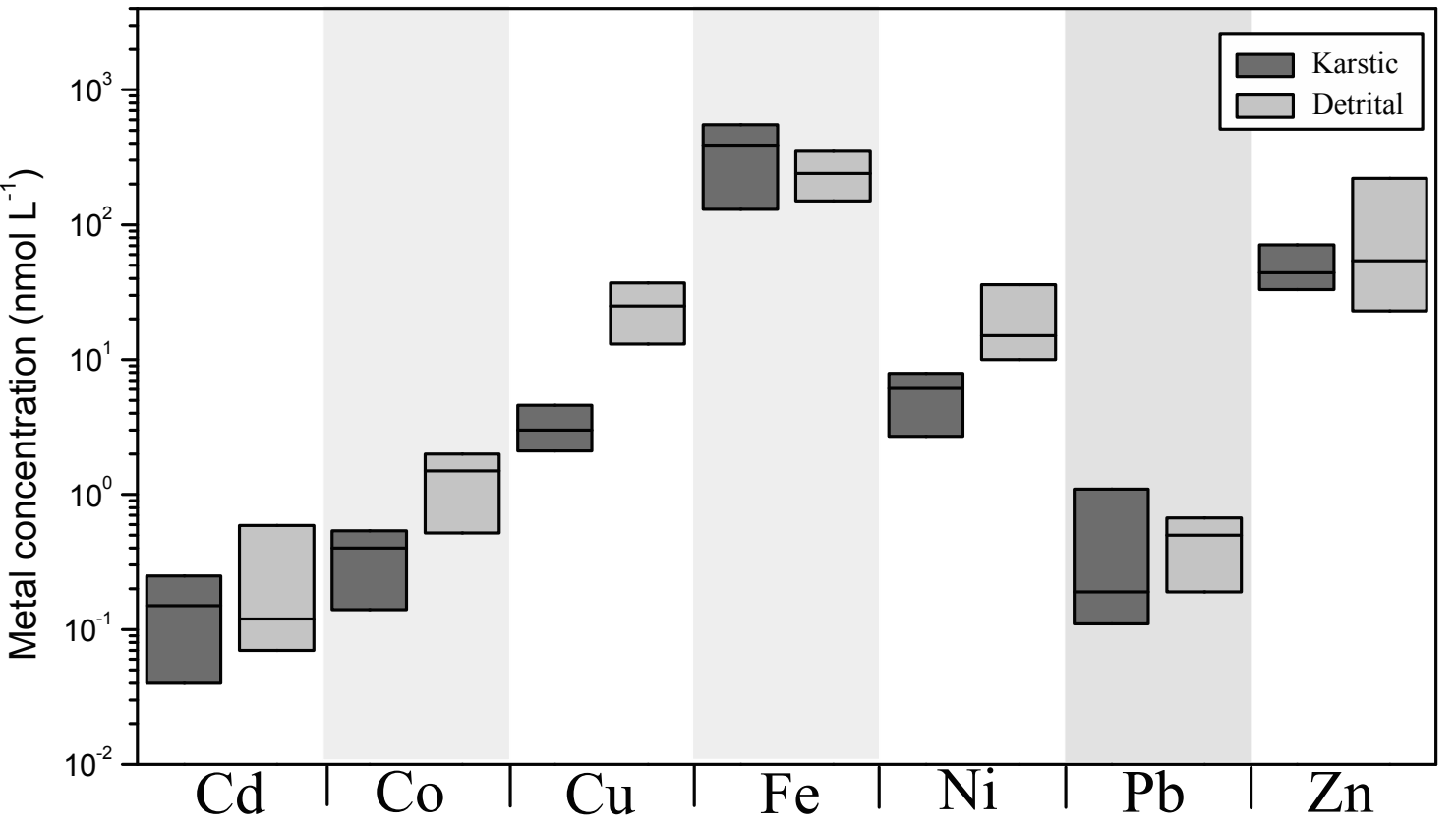


Figure 3 black and white

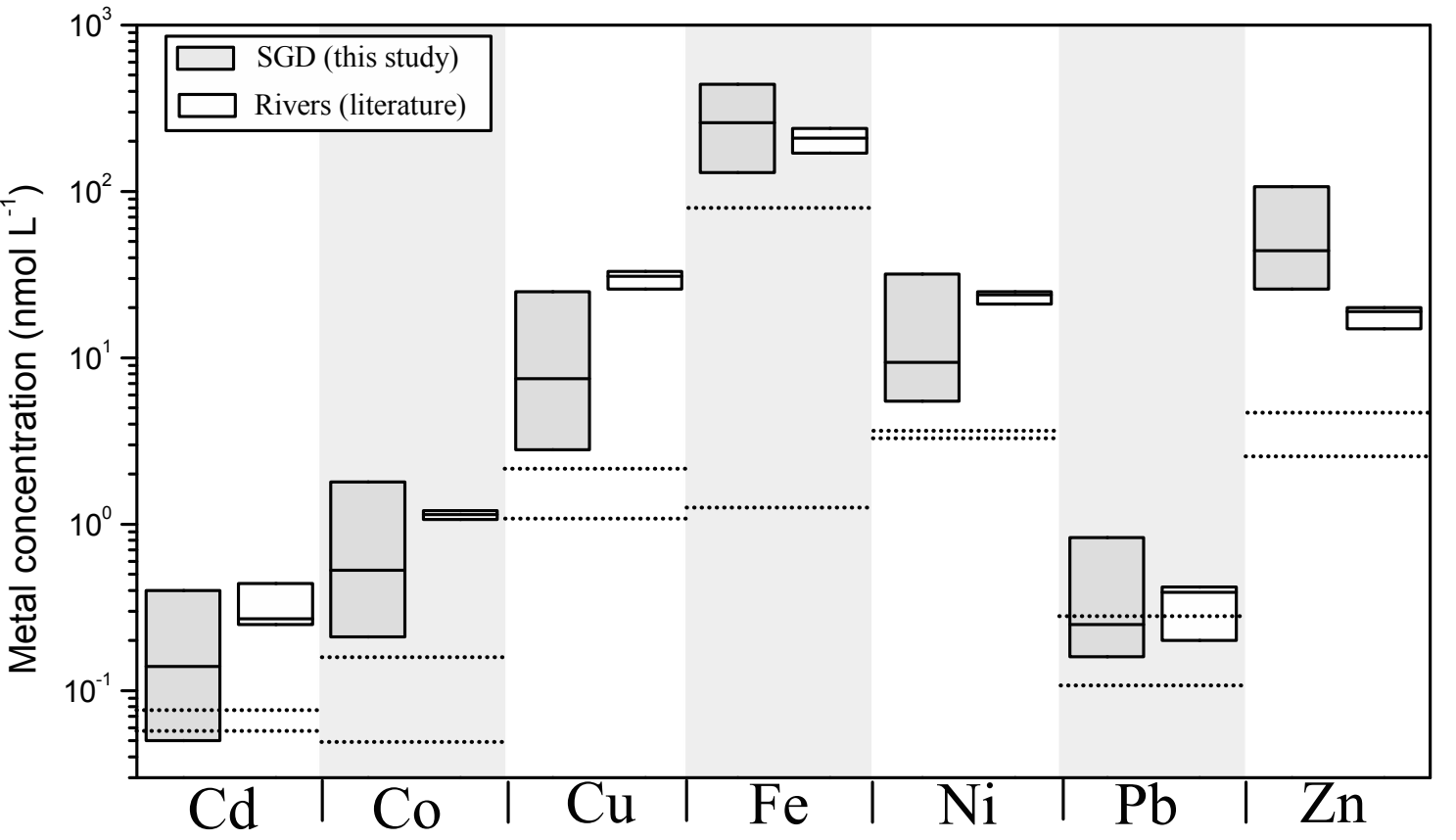
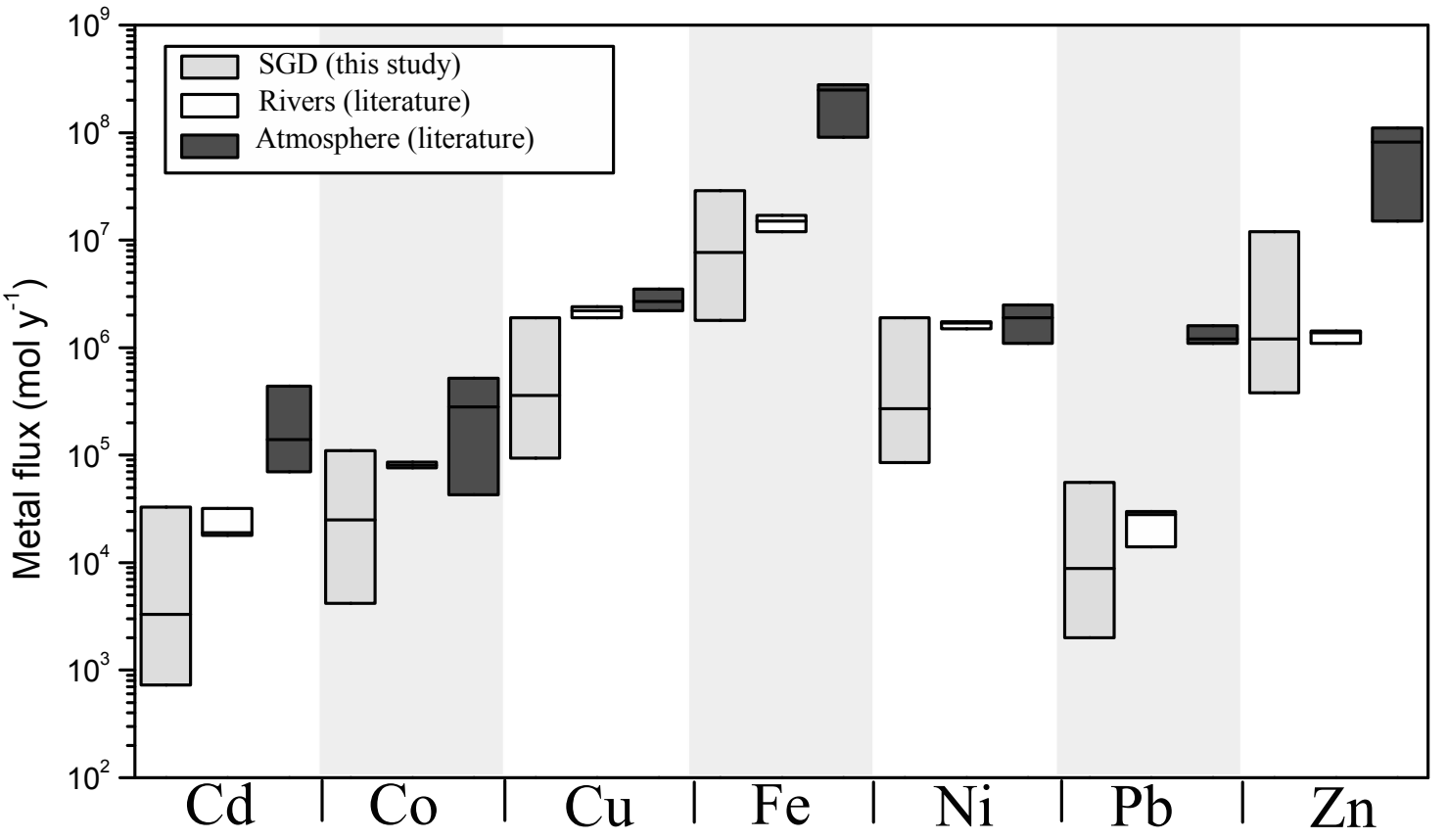


Figure 4 black and white



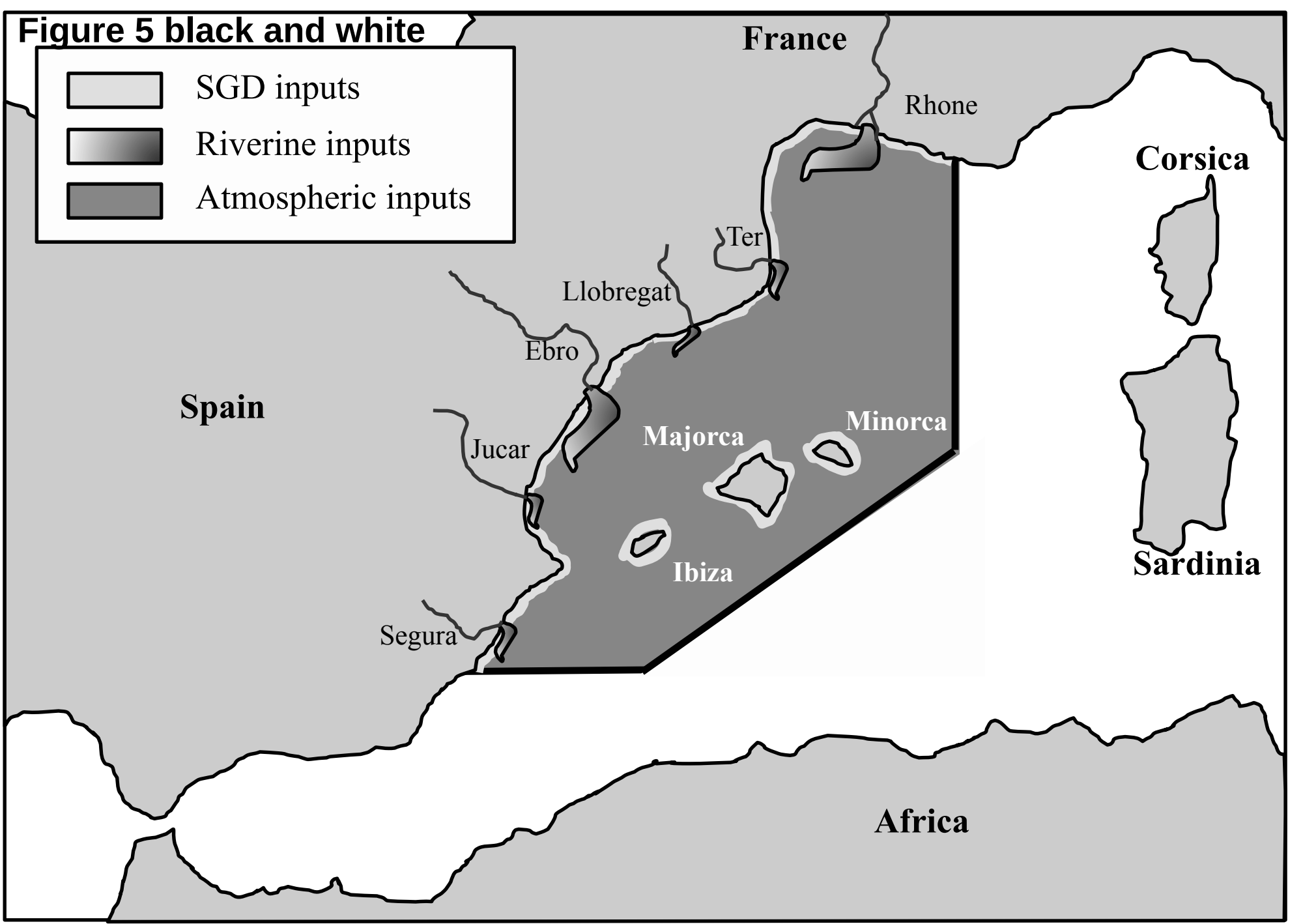
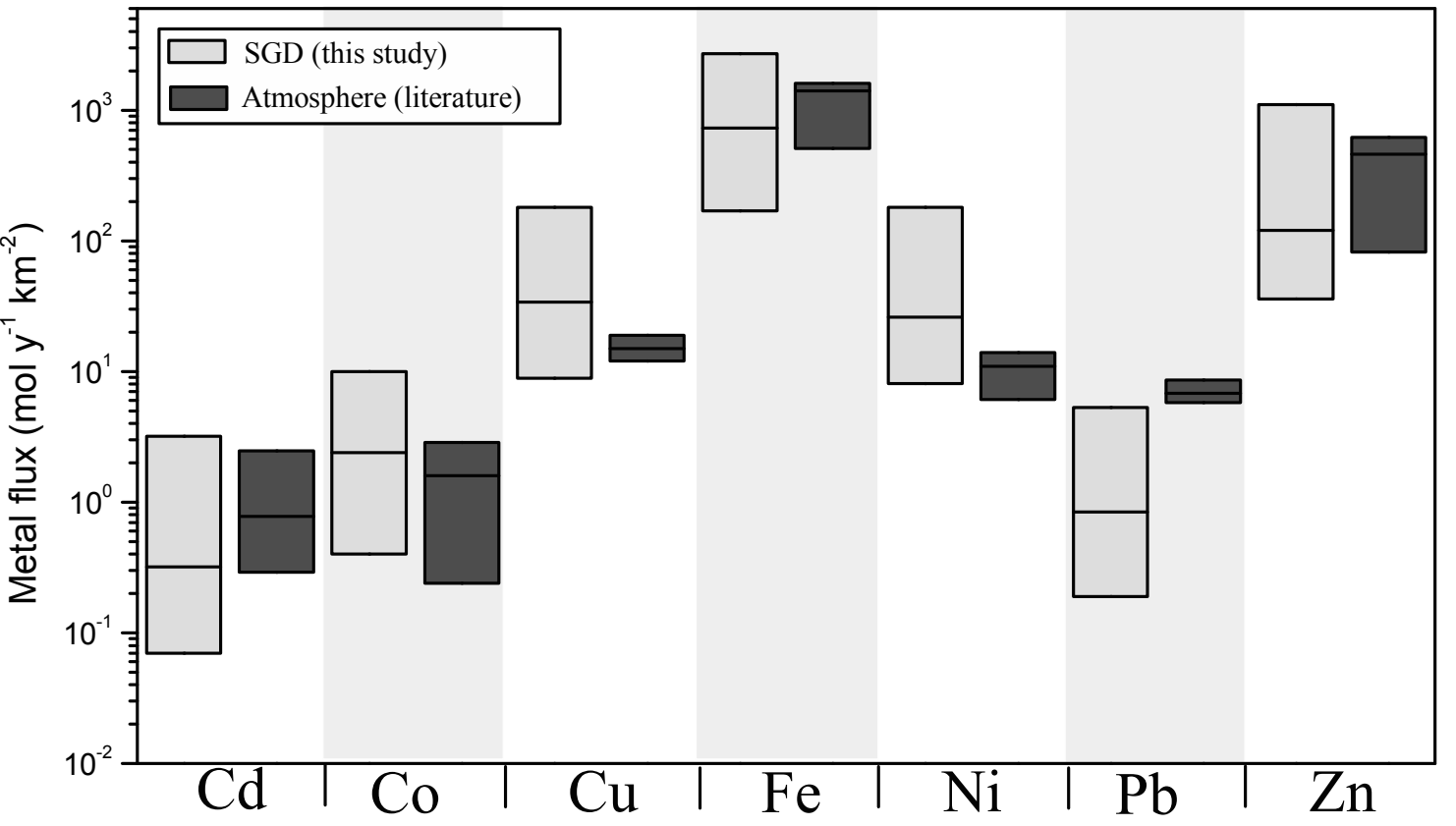
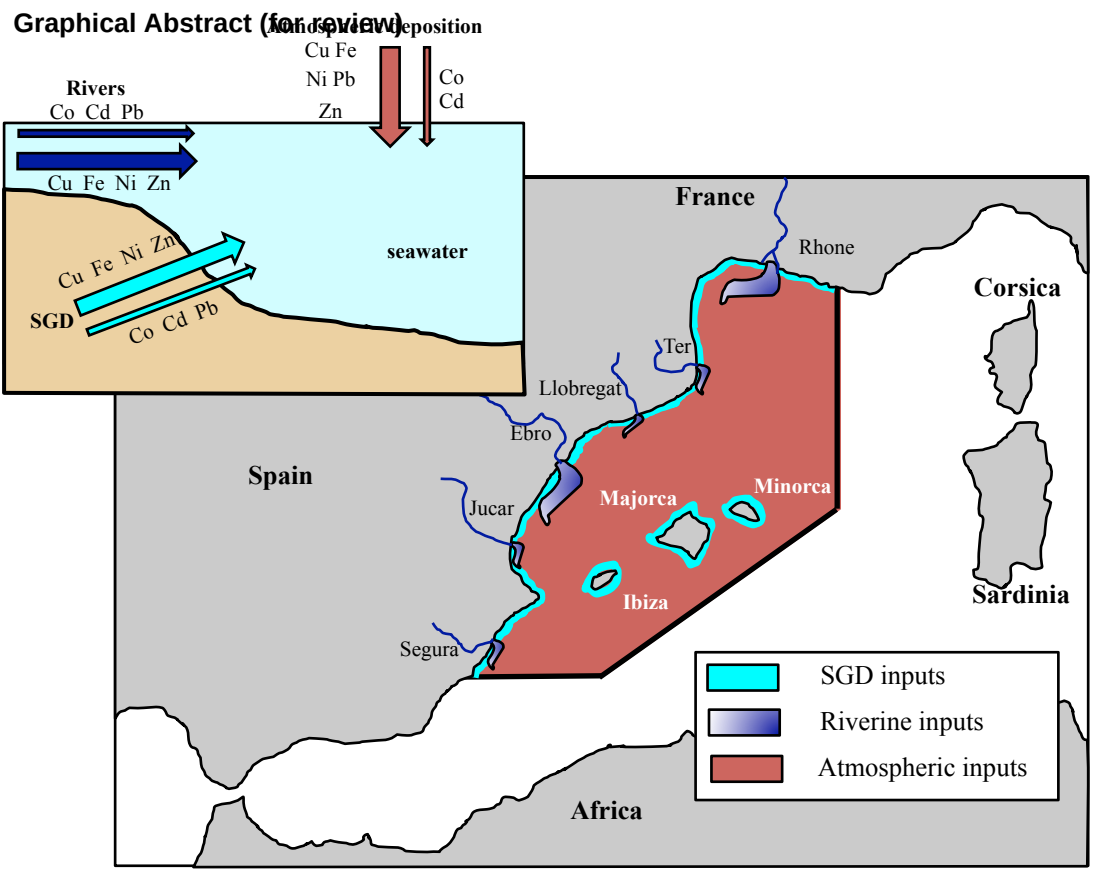


Figure 5 black and white
SGD inputs
Riverine inputs
Atmospheric inputs
France
Rhone
Corsica
Ter
Llobregat
Ebro
Spain
Majorca
Minorca
Jucar
Ibiza
Sardinia
Segura
Africa

Figure 6 black and white



Graphical Abstract (for review)



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

		Shore-lenght	**Water flow***
Karstic SGD		**km**	**(10^6 m^3 y^{-1} km^{-1})**
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^{st}-3^{rd} quartiles		5.2 - 16
Detrital SGD			
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^{st}-3^{rd} quartiles		3.0 - 23

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

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

		Dissolved metal concentrations (nmol L^{-1})						
		Cd	**Co**	**Cu**	**Fe**	**Ni**	**Pb**	**Zn**
Elbaz-Poulichet et al. (1989)	Rhone	0.48	1.2	32	n.a.	23	0.50	21
Elbaz-Poulichet et al. (1996)	Rhone	0.27	n.a.	35	n.a.	27	0.42	n.a.
Guieu et al., (1991)	Ebro	0.4	n.a.	30	n.a.	24	0.15	n.a.
Guieu et al., (1993)	Rhone	0.25	1.1	33	232	24	0.40	20
Guieu et al. (1997)	Rhone + Ebro	0.27	1.1	35	184	25	0.38	18
Ollivier et al. (2011)	Rhone	n.a.	n.a.	33	n.a.	17	0.33	41
UNEP (2003) and references	Rhone	0.25	n.a.	0.31	n.a.	15	0.22	17
within	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^{st}-3^{rd} quartiles	0.25 – 0.44		26 - 33		21 - 25	0.20 – 0.42	15 - 20
	Mean		1.1		210			
	σ		0.07		34			

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**
Guieu et al., 1997		69	42	31 - 48	4 - 17	44 - 52	30-59	35 - 75
		Atmospheric dissolved metal fluxes (mol km^{-2} y^{-1})						
		Cd	**Co**	**Cu**	**Fe**	**Ni**	**Pb**	**Zn**
Bonnet and Guieu (2006)*	NW Med	n.a.	n.a.	n.a.	2100	n.a.	n.a.	n.a.
Chester et al., (1999)	NW Med	n.a.	0.41	23	n.a.	4.6	8.6	n.a.
Guerzoni et al. (1999)	C Med	1.7	n.a.	59	140	21	15	340
Guieu et al. (1993)*	NW Med	8.0	3.0	12	1600	11	8.6	840
Guieu et al. (1997)	NW Med	4.9	1.3	17	1500	7.7	6.8	580
Guieu et al. (2010)*	Med	0.23	n.a.	n.a.	1300	n.a.	3.1	84
Migon et al. (1991)*	NW Med	1.0	n.a.	12	n.a.	n.a.	23	76
Migon et al. (1997)*	NW Med	0.40	n.a.	14	n.a.	11	6.7	680
Ridame et al. (1999)*	NW Med	0.34	n.a.	6.5	260	3.3	1.9	43
Sandroni and Migon (2002)	NW Med	0.52	n.a.	18	n.a.	16	5.8	600
	Median	0.78		15	1400	11	6.8	460
	1st-3rd 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.