

Vertical export flux of metals in the Mediterranean Sea

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Abstract:

We examined metal (Al, V, Cr, Mn, Fe, Ni, Cu, Zn, Cd and Pb) and particulate organic carbon (OC) concentrations of the marine vertical export flux at the DYFAMED time-series station in the Northwestern Mediterranean Sea. We present here the first data set of natural and anthropogenic metals from sediment trap moorings deployed at 1000 m-depth between 2003 and 2007 at the DYFAMED site. A highly significant correlation was observed between most metal concentrations, whatever the nature and emission source of the metal. Cu, Zn and Cd exhibit different behaviors, presumably due to their very high solubility and complexation with organic ligands. The observed difference of atmospheric and marine fluxes in terms of temporal variability and elemental concentration suggests that dense water convection and primary production and not atmospheric deposition control the marine vertical export flux. This argument is strengthened by the fact that significant Saharan dust events did not result in concomitant marine vertical export fluxes nor did they generate significant changes in metal concentrations of trapped particles.

Highlights

► Dense water convection and surface primary production control the vertical export flux of metals ► Atmospheric deposition events do not trigger significant vertical export fluxes ► all metals whether of natural or crustal origin are accumulated in the mixed layer until they are exported at the same time

Keywords : Trace metals ; sediment trap ; Mediterranean Sea ; vertical export flux ; ballasting

1. Introduction

Identifying the factors controlling the vertical export flux of particulate matter from the surface ocean to the deep sea is of paramount importance to understand the mechanisms leading to the sequestration of carbon (Jickells et al., 1998). The question of whether the incorporation of suspended minerals drives the vertical export flux of particulate organic carbon (OC, used hereinafter for the particulate fraction only) in the ocean is still under debate (Armstrong et al., 2002 and Passow, 2004). The Mediterranean Sea is an ideal site to address this question. Strong physical forcing, intense coastal-pelagic interactions, short water residence times and an equally strong influence of natural and anthropogenic continental sources on the marine biogeochemical cycles of metals make the Mediterranean Sea particularly sensitive to environmental and climatic changes (Martin and Milliman, 1997, Krahnmann and Schott, 1998, Béthoux and Gentili, 1999 and Duarte et al., 1999). This particular sensitivity justifies that the Mediterranean Sea is a privileged ecosystem for the investigation of marine responses to anthropogenic metal inputs and warming climate (Durrieu de Madron et al., 2011). The atmosphere of the Northwestern Mediterranean Sea is characterized by a European signature disrupted by episodic Saharan dust events (Chester et al., 1997 and Heimbürger et al., 2010b). Atmospheric metal inputs to the Northwestern Mediterranean Sea originate from natural and anthropogenic emissions sources. The major source of natural metals in this region is the Saharan desert. Episodic but intense pulses characterize this particular source (Chester et al., 1997, Guerzoni et al., 1999, Marty et al., 2002, Heimbürger et al., 2010b and Ternon et al., 2010). Anthropogenic metals are mainly carried with air masses from Northern and Central Europe. As a result, metal concentrations in Mediterranean surface waters are higher than in the open ocean,

67 and those of the inflowing North Atlantic Ocean (Morley et al., 1997). Metal
68 distribution patterns in the water column suggest that their biogeochemical cycling is
69 mainly governed by atmospheric inputs (Béthoux et al., 1990; Migon et al., 2002;
70 Heimbürger et al., 2011). Three independent studies (Martín et al., 2009; Angelidis et
71 al., 2011; Heimbürger et al., 2012) show a recent increase of anthropogenic metals
72 in Mediterranean deep marine sediment records. This increasing metal trend in
73 sedimentary records presumably reflects the evolution of anthropogenic metal
74 emissions along the densely populated Mediterranean coast (~300 inhabitants per
75 km² (UNEP/MEDPOL, 2004; Laubier, 2005), in addition to metal inputs from long-
76 ranged sources.

77 However, the problem remains of knowing which parameter controls the temporal
78 variability of the vertical export flux of metal to marine sediments. Previous studies
79 (Fowler et al., 1987; Migon et al., 2002) have shown that biological and
80 biogeochemical processes occurring at the surface control the temporal variability of
81 vertical OC export fluxes in the Northwestern Mediterranean Sea. Miquel et al.
82 (1994; 2011) pointed out that the vertical mixing of the water column is a key factor
83 determining the magnitude of the vertical OC export flux.

84 The ballasting theory pioneered by (Armstrong et al. (2002); Armstrong et al. (2009))
85 suggests another mechanism, in which mineral material (atmospheric dust, biogenic
86 silica, and carbonate shells) determines the occurrence of vertical OC fluxes.
87 However, Passow (2004) proposed that, despite their conspicuous ballasting role,
88 mineral particles may not cause vertical OC fluxes. On the contrary, vertical OC
89 fluxes would determine the vertical export of mineral material. With the present paper
90 we aim to contribute to this debate by examining natural and anthropogenic metal
91 concentrations of the vertical export flux captured by a sediment trap moored at
92 1000m-depth at the DYFAMED site, Northwestern Mediterranean Sea.

93

94 **2. Methods**

95 **2.1. Study site**

96 The DYFAMED (DYnamique des Flux Atmosphériques en Méditerranée) time-series
97 station (2350m-depth, 43°25'N, 7°52'E; Fig. 1) is a long-term monitoring station in
98 the open Ligurian Sea (Northwestern Mediterranean Sea) located 28 nautical miles
99 off continental France. The Ligurian Sea circulation is characterized by a permanent
100 cyclonic gyre (Lévy et al., 1998). The Ligurian Current creates a band ~ 30 km wide

101 and > 250 m deep, which is believed to separate the DYFAMED site from coastal
102 lateral inputs by a strong horizontal density gradient (Niewiadomska et al., 2008).
103 Therefore, atmospheric metal inputs are believed to be by far the most significant
104 source to the open Ligurian Sea (Migon et al., 2002). The DYFAMED site has been
105 used several times for the study of interactions between atmospheric deposition and
106 open surface waters (e.g. DYFAMED and MEDFLUX programs; see special issues
107 Deep-Sea Research II 49, 11 (2002) and 56, 18 (2009), respectively). DYFAMED is
108 now viewed as a reference site for monitoring of ongoing changes in the
109 Northwestern Mediterranean Sea.

110

111 **2.2. Sampling**

112 Automated time-series sediment traps were moored at 1000-m depth at the
113 DYFAMED site between March 2003 and February 2007. Conical sediment traps
114 (Technicap PPS-5, height 2.3m, collection area 1m²) were equipped with a
115 programmable 24-cup collector. The sampling cups contained a solution of 2%
116 buffered formaldehyde in filtered seawater (0.22µm) to prevent *in situ* microbial
117 degradation and grazing by swimmers. After recovery, the samples were stored in
118 the dark at 4°C. Swimmers were removed by successive sieving through 1500 and
119 600µm and followed by hand-picking under the binocular microscope. The remaining
120 samples were then desalted by rinsing on a Nuclepore filter (porosity 1µm) with
121 buffered (pH 7) deionized Milli-Q[®] Millipore water (resistivity: 18MΩ.cm) three times
122 (JGOFS, 1996) and freeze-dried prior to analysis (Miquel et al., 1994; Miquel et al.,
123 2011). Samples were weighed using a high precision balance (Sartorius).

124

125 **2.3. Analysis**

126 Sediment trap samples were mineralized according to the following protocol: The
127 organic matrix was destroyed by oxidation (HNO₃) while the mineral aluminosilicate
128 matrices were destroyed with HF. Every freeze-dried sample was weighed in 7mL
129 Teflon flasks, and dissolved as follows: 1) each flask was filled with 1mL HNO₃ 65%
130 (suprapur, Merck), sealed and placed in a larger Teflon bottle (60mL). This
131 apparatus was left 6 hours in an oven at 150°C, after which bottles and flasks were
132 brought to room temperature and left open under laminar flow hood until a brown dry
133 residue remained. 2) 500µL HNO₃ 65% and 500µL HF 40% were added to the

134 remainder. The flasks and bottles were closed and put in an oven 6 hours at 150°C,
135 prior to open evaporation at room temperature under laminar flow hood, until a white
136 dry residue was obtained. This residue was ultrasonically dissolved in 5mL HNO₃
137 0.1N and then diluted with HNO₃ 0.1N to 15mL.

138 Digested and dissolved metals were analyzed by ICP-OES, using a Perkin-Elmer
139 Optima 3000, axial torch instrument. An ultrasonic nebulizer (CETAC) was used for
140 sample introduction to improve the sensitivity (Desboeufs et al., 2003) to 0.01 to 0.1
141 ppb levels depending on the metal. A plasma power of 1250W and a sample flow of
142 1 mL.min⁻¹ were used. An external calibration was performed with multi-elemental
143 standard solutions made by mixing 1g.L⁻¹ mono-elemental solutions provided by
144 Merck (Darmstadt, Germany). The accuracy was checked using dilutions of multi-
145 elemental commercial solutions and SLRS-4 as certified reference material (CRM).
146 We also monitored the analysis with CRM geo-standards: GBW (National Research
147 Center for Certified Reference Materials, China), BCSS-1 and PACS (National
148 Research Council, Ottawa, Canada). A summary of analytical performances is given
149 in Table 1.

150 Metal concentrations (Al, V, Cr, Mn, Fe, Ni, Cu, Zn, Cd and Pb) were analyzed for
151 samples collected from March 2003 to February 2007. However, years 2005 and
152 2006 were affected by higher currents than usual. Currents >12cm.s⁻¹ are more likely
153 to bias quantitative collection of settling particles by sediment traps (Baker et al.,
154 1988; Scholten et al., 2001; Buesseler et al., 2007). This situation occurred from 22
155 February to 23 June 2005, and during most of the year 2006. Vertical export fluxes
156 during those periods might be underestimated (Miquel et al., 2011) and the quality of
157 the trapped particles in terms of OC content and metal concentration has to be
158 observed critically.

159

160 **2.4. Data treatment and statistical analysis**

161 To our knowledge no certified reference material for sediment trap material exists
162 today and complete procedural blanks are hard if not impossible to realize. We
163 carefully examined the raw data in order to investigate for possible artifacts and
164 contamination. To do so we used enrichment factors (EFs) to trace the
165 anthropogenic component of samples, either from anthropogenic inputs or
166 contamination during sampling. We chose EFs standardized to Al, which is the most

167 commonly used soil dust reference. These ratios are usually defined for a given
 168 element as (e.g. (Herut et al., 2001; Heimbürger et al., 2010b):

169

$$170 \quad EF = (M_{\text{sample}} / Al_{\text{sample}}) / (M_{\text{background}} / Al_{\text{background}}) \quad (1)$$

171

172 where $(M_{\text{sample}} / Al_{\text{sample}})$ is the metal concentration of the sample relative to the Al
 173 concentration. This ratio is normalized to the ratio $(M_{\text{background}} / Al_{\text{background}})$ of Earth's
 174 continental crust (Wedepohl, 1995). Average metal concentrations in soil dust or
 175 rocks are very difficult to define accurately, due to the inhomogeneous composition
 176 of worldwide soils. Moreover, the $(M_{\text{background}} / Al_{\text{background}})$ ratio may be dependent on
 177 grain size fractionation and chemical alteration during atmospheric transport,
 178 biogeochemical cycling in the euphotic zone and settling of particles through the
 179 water column. Such modifications might involve the solubilization of certain metals
 180 from particles, photo-chemically induced redox reactions and aggregation processes
 181 (Desboeufs et al., 2001). The use of EFs is permissible if they are used for the
 182 comparison of different enrichments standardized to the same $Al_{\text{background}}$ value
 183 (Herut et al., 2001; Heimbürger et al., 2010b). We calculated EFs for each metal to
 184 distinguish anthropogenic influences from natural ones. Suspiciously high EFs
 185 occurred occasionally for Cu, Zn, Cd and Pb, always and only for the first samples of
 186 a separate sediment trap deployment. Those metals are particularly prone to
 187 contamination, thus handling, maintenance and setting of the sediment trap mooring
 188 lines and their deployment might have corrupted them, although the collection of
 189 settling particles always started at least 24 hours after completion of the deployment
 190 of the mooring. We removed all of those occasional outliers from the data set.

191 Principal component analysis (PCA) was applied to extract the geochemical
 192 signatures of the chemical composition of the vertical export flux and to get insights
 193 into the underlying factors accounting for them. The analysis was performed by
 194 means of the Z-scores transformation of the raw data:

195

$$196 \quad Z\text{-score} = (X_i - X_{\text{avg}}) / X_{\text{std}} \quad (2)$$

197

198 where X_i is a given value of a variable in a sample, X_{avg} is the average of that
 199 variable and X_{std} is its standard deviation. Z-scores allow keeping the relative
 200 variation of the original data while reducing all variables to a similar range of

201 variation avoiding scaling effects. The best solution was obtained with a Varimax
202 rotation, which is more restrictive with the variables associated to the principal
203 components (i.e. maximizes the proportion of variance of the variables in the
204 principal components). The square of the factor loadings was used as an estimation
205 of the proportion of variance of each variable for each principal component.
206 Statistical computations were performed with XLSTAT® software from Addinsoft.

207

208 **3. Results and Discussion**

209 Temporal variability of vertical export flux, OC and metal concentrations are
210 compared at 1000m-depth (Fig.2.). Mineralization processes and grazing are
211 important features in the upper water column, whereas, at 1000m-depth, vertical
212 export fluxes are considered to be net fluxes with minimal alteration (Martin et al.,
213 1987; Guidi et al., 2009).

214 Mean metal concentrations and vertical metal export fluxes at the DYFAMED site
215 and various other moorings in the Mediterranean and Black Sea are shown in
216 Table 2. The variability of metal and OC concentrations is relatively low (RSD = 21-
217 46 %) compared to the variability of vertical export flux (RSD = 147 %). This implies
218 that the temporal variability of TM and OC fluxes (calculated as the product of TM, or
219 OC, and vertical export flux) is almost entirely governed by the variability of the
220 vertical export flux. This is also the case for other Mediterranean sediment trap
221 moorings, suggesting that this is a general feature. Vertical export fluxes, OC and
222 metal concentrations are roughly in the same ranges as values presented by Migon
223 (2002) and Heimbürger et al. (2012), and also comparable to finding in other basins
224 of the Mediterranean Sea (Theodosi et al., 2010; Roussiez et al., 2012; Theodosi et
225 al., 2012) and the Black Sea (Theodosi et al., 2013). Miquel et al. (2011) suggested
226 that under a one-dimensional scenario, ~38% of OC leaving the 200m-depth horizon
227 is remineralized before reaching the 1000m-depth horizon. OC concentrations during
228 the selected sampling period varied between 2 and 19% (Fig. 2), a range typically
229 observed during the 20-year DYFAMED time-series (Miquel et al., 2011).

230

231 **3.1. Seasonal variability of the marine vertical export flux**

232 The vertical export flux at DYFAMED follows a well-known seasonal pattern (Miquel
233 et al., 1994; Migon et al., 2002; Ternon et al., 2010; Miquel et al., 2011; Heimbürger

234 et al., 2013). This pattern was repeated over the duration of the sampling period and
235 characterized by the following known sequence:

236 In winter (December to February), the cooling and evaporation of surface waters
237 lead to the formation of dense water. The convection of dense water leads to rapid
238 downward transport of dissolved (Copin-Montégut and Avril, 1993; Avril, 2002) and
239 particulate matter (flush-down effect), including metals (Béthoux and Gentili, 1999;
240 Heimbürger et al., 2013). The vertical export flux during dense water convection
241 contains a higher portion of atmospherically-deposited mineral material, which has
242 been accumulated in the surface layer during the preceding stratified period (Migon
243 et al., 2002; Heimbürger et al., 2010a). As a result, the OC concentration is the
244 lowest. The seasonal pattern of the vertical export flux shows reproducible peaks in
245 January-February, e.g. 2004 and 2005 (Fig. 2). During the mesotrophic period
246 (March to May), the vertical export flux is driven by primary production. Nutrients
247 brought to surface waters by the previous dense water convection trigger
248 phytoplanktonic blooms in spring, and generate moderate vertical export fluxes, e.g.
249 2003 and 2004 (Fig.2). The spring vertical export flux is characterized by moderate
250 OC concentrations, as a result of the combination of biogenic material and mineral
251 material. The intensity of the vertical export flux under mesotrophic conditions
252 directly depends on the intensity of the spring bloom conditioned by the dense water
253 convection in winter (Marty and Chiavérini, 2010).

254 Under oligotrophic stratified conditions (June to November, approximately), the
255 vertical export flux is minimal ($\sim 40 \text{ mg}\cdot\text{m}^{-2}\cdot\text{d}^{-1}$) at the DYFAMED site (Sarhou and
256 Jeandel, 2001; Migon et al., 2002; Sternberg et al., 2007). During this period, there is
257 only little to no production of fecal pellets, which are known for their capacity to
258 transfer matter and elements to depth (e.g. (Fowler and Knauer, 1986; Marty et al.,
259 1994; Carroll et al., 1998)). Vertical export flux during this period results almost
260 entirely from regenerated production (Marty et al., 2002). A higher percentage of
261 small-sized phytoplankton is exported out of the euphotic zone because grazing is
262 low (Guidi et al., 2009). The lower vertical export flux recorded in oligotrophic
263 conditions exhibits the highest OC concentrations (Fig. 2).

264 The described seasonal pattern of the vertical export flux may be interrupted by
265 occasional bursts, caused by meanders passing the Ligurian current, fall blooms,
266 and intense meteorological conditions. Two examples are given here:

267 1.) Slightly higher vertical export fluxes were observed in July 2005. Episodes of cold
268 northwesterly winds (Mistral) observed during this period (data from Météo-France)
269 have likely mixed the surface layer and advected nutrient-rich waters from below
270 (Andersen and Prieur, 2000; Marty et al., 2008).

271 2.) Small increases of the vertical export flux were recorded between October and
272 December. For example, a peak was observed in fall 2005 (Fig. 2), while vertical
273 export fluxes were negligible in 2003 and 2004 during the same period. Strong
274 easterly winds were observed early October 2005 and yielded a decrease of sea
275 surface temperature of 3.6°C (from 20.9 to 17.3°C) within 5 days at the Météo-
276 France buoy ODAS located nearby the mooring line. Such a rapid temperature
277 decrease suggests wave-induced mixing below the surface mixed layer. The mixing
278 with nutrient-rich waters from below the thermocline may have supplied nutrients to
279 the depleted surface layer and triggered a fall bloom. This fall bloom was probably
280 dominated by nano- and picophytoplankton (Heimbürger et al., 2010a) and resulted
281 consequently only in a small increase of the vertical export flux (Marty et al., 2009).
282 This seasonal pattern suggests that, apart from dense water convection episodes
283 associated in spatially restricted Mediterranean areas (among which is the Ligurian
284 Sea), the vertical export of atmospherically-deposited material is almost entirely
285 driven by the magnitude and variability of primary production. This statement is in
286 agreement with many studies that pointed out the prominent role of primary
287 production in the removal of mineral material (e.g. (Fowler et al., 1987; Buat-Menard
288 et al., 1989; Jickells et al., 1998; Grotti et al., 2001; Hamm, 2002; Migon et al., 2002).
289 Marty and Chiavérini (2010) stated that the efficiency of the vertical transfer under
290 mesotrophic conditions directly depends on the intensity of the water column mixing
291 and the subsequent diatom bloom. However, several recent papers (e.g. (Armstrong
292 et al., 2002; Francois et al., 2002; Klaas and Archer, 2002; Armstrong et al., 2009;
293 Lee et al., 2009; Ternon et al., 2010) have postulated that mineral particles,
294 originating mainly from atmospheric dust deposition and biogenic minerals
295 (carbonates and silica) control the sedimentation rate of biogenic material by
296 ballasting, particularly when zooplankton fecal pellet production is low (Lee et al.,
297 2009). This process presumably increases the density of OC aggregates and,
298 therefore, their sinking rates. It was also suggested that mineral particles protect OC
299 from oxidation and remineralization (De La Rocha and Passow, 2007).

300

301 3.2. Metal concentrations of the marine vertical export flux

302 The present paper contributes to the ongoing debate of whether atmospheric
303 deposition or primary production/dense water convection controls the marine vertical
304 export flux. We examined sediment trap samples from the DYFAMED site, which
305 have been analyzed previously for OC and Al (Ternon et al., 2010), but not for the
306 selection of anthropogenic and natural metals here presented here. The authors
307 concluded that atmospheric deposition events drive the marine vertical export flux.
308 The outstanding feature of the present dataset is that nearly all metals, whether of
309 crustal or anthropogenic origin, are highly correlated (Table 3). This suggests that all
310 metals are exported to depth at the same time, independently of their different
311 depositional seasonal pattern. However, this does not hold true for Cd, Zn and Cu,
312 which suggests that these metals are less efficiently associated with sinking
313 particles. Metal solubility can be proposed as an explanation: Despite possible
314 adsorption onto lithogenic material such as metal oxide surfaces at seawater pH (Fu
315 and Allen, 1992), Cd is among the most soluble metals studied here (Migon, 2005).
316 This also applies to Zn (Kersten et al., 1991). The ability of Cu to complex with
317 dissolved organic ligands (Muller, 1996) might also lead to lower contribution to the
318 pool of sinking particles. The solubility of those three metals might explain losses in
319 sediment traps.

320 An alternative explanation could be related to the processing of sediment trap
321 samples. Rinsing the particles by deionized water may have led to osmotic bursting
322 of planktonic cells, thereby releasing metals within the cytoplasm of algal cells. Zinc,
323 Cu, and Cd reside in phytoplankton cytoplasm to a significantly greater extent than
324 most of the other metals that were assessed (these other metals are typically bound
325 to cell walls and membranes; (Sunda, 2012)). The discrepancy between these two
326 groups of metals can likely be explained by this artifact.

327

328 3.3. Atmospheric metal inputs from natural and anthropogenic sources

329 Pb concentrations are significantly correlated with those of Al, V, Cr, Mn, Fe, and Ni.
330 This is presumably due to its strong affinity for suspended particulate matter,
331 principally Al, Fe and Mn oxides, organic matter, carbonates and clay (Kersten et al.,
332 1991). Among the highly correlated metals (Al, V, Cr, Mn, Fe, Ni, and Pb), one can
333 find crustal (Al, Fe), intermediate (Cr, Mn), and anthropogenic elements (V, Ni, and
334 Pb). Natural and anthropogenic metals depict distinct seasonal deposition patterns

335 related to their different emission sources (Heimbürger et al., 2010b). For example,
336 the deposition of crustal metals is strongly associated with Saharan dust episodes
337 (Bonnet and Guieu, 2006; Heimbürger et al., 2010b; TERNON et al., 2010). Saharan
338 dust events are generally observed in spring and summer in the western
339 Mediterranean (Moulin et al., 1997; Heimbürger et al., 2010b). Atmospheric
340 deposition of anthropogenic metals does not exhibit this pulsed character, and most
341 of the anthropogenic inputs occur in winter, when polluted air masses from Northern
342 Europe influence the Ligurian Sea (Barnaba and Gobbi, 2004; Duncan and Bey,
343 2004; Heimbürger et al., 2010b). Anthropogenic metals have various emission
344 sources that are temporally variable. This may also lead to different seasonal
345 patterns of their atmospheric deposition. For example, V and Ni emissions result
346 mainly from oil combustion, whereas major Pb emissions results from steel
347 metallurgy plants, mining complexes in Eastern Europe, leaded petrol carried by
348 long-range atmospheric transport from North Africa, Middle East or Eastern Europe
349 (Bollhöfer and Rosman, 2001; Migon et al., 2008). Individual metal deposition to the
350 Northwestern Mediterranean Sea surface is temporally variable, according to the
351 nature and the individual seasonal patterns of their emission sources (Heimbürger et
352 al., 2010b).

353 Different seasonal variations in the supply of atmospheric deposition to surface
354 waters and the rate of particle removal from surface waters result in rather constant
355 metal concentrations of the vertical export flux through the year. Similar observations
356 were made for dust deposition at the BATS time-series (Jickells et al., 1998).
357 Compared to the BATS time-series site (Sargasso Sea), the DYFAMED time-series
358 site (Northwestern Mediterranean Sea) receives much higher loads of atmospheric
359 metal deposition and the water column is mixed every winter by dense water
360 convection. Vertical export flux in the Mediterranean Sea is driven by dense water
361 convection in winter (flush-down effect) and by primary production in spring (Miquel
362 et al., 1994; Migon et al., 2002; Miquel et al., 2011).

363 We hypothesized that atmospheric metal deposition accumulates in the marine
364 surface layer in the absence of dense water convection and low biological activity
365 (under stratified oligotrophic conditions). Indeed, individual dust particles have,
366 based upon Stokesian calculations (Stokes, 1901), a negligible settling velocity
367 ($<5 \text{ m.d}^{-1}$; (Buat-Menard et al., 1989)). Therefore, the transfer of particulate metals
368 from the sea surface to 1000m-depth without the driving force of hydrology or biology

369 would require at least 200 days. This is consistent with particulate metal residence
370 times calculated at the BATS time-series site (Jickells et al., 1984). This time being
371 longer than the oligotrophic period (on average, ~ 5 months in the Northwestern
372 Mediterranean Sea), atmospheric deposition (dissolved matter and particles that do
373 not dissolve) cannot be removed from surface waters without packaging onto large
374 organic particles or aggregates, incorporation into fecal pellets (Fowler and Knauer,
375 1986; Wang and Fisher, 1998), or adsorption onto planktonic debris and fecal pellets
376 during their sinking (Fisher et al., 1991).

377

378 3.4. Saharan dust inputs

379 In spite of Stokesian considerations, we investigated if field observations could
380 suggest that atmospheric deposition of mineral loads is capable of causing vertical
381 export fluxes, either by direct sinking of mineral particles, or indirectly by atmospheric
382 fertilization of surface waters. Ternon et al. (2010) concluded that atmospheric
383 deposition events drive the marine vertical export flux at the DYFAMED time-series
384 site. Their interpretation is based on the fact that "...for this 4-years time-series, high
385 OC fluxes were related to high marine lithogenic fluxes (their Fig. 8), forming high
386 export events...". Both variables, OC flux and the marine lithogenic flux, are
387 calculated as the product of the marine vertical export flux and the concentration of
388 OC and Al, respectively. That means that both flux variables contain a similar
389 variable, and are therefore not independent. If we examine their atmospheric data
390 closely we can identify 4 Saharan dust events (atmospheric flux of $>1000\text{mg}\cdot\text{m}^{-2}\cdot\text{d}^{-1}$).
391 Only one single Saharan dust event actually resulted in significant marine vertical
392 export flux, taking the same threshold value. This exceptionally strong input of
393 mineral dust observed over the Ligurian Sea occurred in February 2004, when
394 $22,210\text{ mg}\cdot\text{m}^{-2}$ were deposited during a single event (Bonnet and Guieu, 2006).
395 Marine vertical export fluxes increased during this period (Ternon et al., 2010). This
396 Saharan dust event occurred during the dense water convection period and the
397 marine vertical export fluxes remained elevated for the entire dense water
398 convection period (Heimbürger et al., 2013). It is thus difficult to clearly determine
399 what was the driving force (hydrology or atmospheric deposition) for this vertical
400 export flux event. None of the 3 other Saharan dust events that occurred during our
401 sampling period (Ternon et al., 2010) actually resulted in significant marine vertical
402 export flux. For instance, a significant atmospheric dust episode that occurred during

403 oligotrophic stratified conditions in summer 2006 over the Ligurian Sea (Heimbürger
404 et al., 2010b; Ternon et al., 2010) did not yield increased marine vertical export
405 fluxes.

406

407 3.5. Metal enrichment factor assessment

408 To further investigate the relationship of atmospherically-deposited particles and the
409 marine vertical export flux we chose to study their chemical composition using EFs.
410 Anthropogenic sources can be distinguished from natural ones using EFs. We
411 calculated EFs for each metal relative to the Al concentration ($M_{\text{sample}} / Al_{\text{sample}}$) and
412 normalized to the ratio ($M_{\text{background}} / Al_{\text{background}}$) of Earth's continental crust
413 (Wedepohl, 1995). Summary statistics of EFs and EF of Mediterranean aerosols are
414 given in Table 4. EFs of all metal of the marine vertical export flux (1.23 to 8.93) are
415 much lower compared to those of Mediterranean aerosols (2.59-597) (Heimbürger et
416 al., 2010b). This, and the fact that vertical export flux metal EFs show only very low
417 temporal variability, suggest again a common transport mechanism for all studied
418 metals and that intense deposition events are smoothed out. The consistently lower
419 metal EFs of the marine vertical export flux compared to those of Mediterranean
420 aerosols may also indicate that a part of the atmospheric deposition is solubilized
421 and may enrich dissolved metal concentration of the Mediterranean surface waters
422 (Heimbürger et al., 2011).

423

424 3.6. Principal components analysis

425 We applied principal component analysis after z-score transformation and Varimax
426 rotation to extract the geochemical signatures of the chemical composition of the
427 vertical export flux and to get insights into the underlying factors accounting for them.
428 The square of the factor loadings was used as an estimation of the proportion of
429 variance of each variable for each principal component (Table 5). Factor 1 explains
430 58 % of the variation with the main contribution of OC and all metals except Cu, Zn
431 and Cd. This means that over half of the variability of the entire data set can be
432 described by this factor, which composed by the variables Al, V, Cr, Mn, Fe, Ni, and
433 Pb. We suggest that the concomitant vertical export of those metals is the process
434 that gives the vertical export flux this distinct geochemical signature. The negative
435 OC value explains the relative dilution effect of the OC contribution to metal
436 concentrations of the vertical export flux. Factor 2 explains 21 % of the variation and

437 is principally determined by OC, Cu and Zn. This confirms once again that all metals
438 (except Cu, Zn and Cd, see discussion above) are accumulated in the surface
439 waters, homogenized and exported to depth at the same time.

440 Aggregation and coagulation processes, combined with sedimentation, strongly
441 impact the amount of mineral matter that is packaged with biogenic material. They
442 also impact the sinking velocity of exported particles and, therefore, the fate and
443 biogeochemical cycling of inorganic material (including metals) in the water column
444 (Armstrong et al., 2002; Burd and Jackson, 2009). Those processes presumably
445 occurred at the DYFAMED station only when biogenic material was present in
446 sufficient concentration. However, our results suggest that dense water convection is
447 the major driver of metal vertical export flux and that aggregation cannot occur
448 without a minimal concentration of organic matter. This is consistent with the role of
449 biological production as a factor that determines the occurrence of vertical export
450 fluxes after spring bloom, while atmospheric deposition is likely to supply pelagic
451 waters with mineral material, but seems unable to trigger significant vertical export
452 fluxes.

453

454 **4. Conclusions**

455 Our results suggest that the marine vertical export flux of metals is controlled by
456 hydrology and biology, and not by atmospheric deposition. This statement is in
457 agreement with studies by (Deuser et al. (1983); Jickells et al. (1984); Buat-Menard
458 et al., 1989; 1998; Passow (2004)) and De La Rocha and Passow (2007). For
459 instance, Deuser et al. (1983) noticed early on the decoupling of atmospheric
460 deposition and marine vertical export flux at the BATS time-series site. At the BATS
461 time-series site, the removal of mineral particles from the surface ocean is controlled
462 by biology. We show that the vertical export flux at the DYFAMED time-series site is
463 controlled by both hydrology and biology. The hydrology of the Northwestern
464 Mediterranean Sea is strongly constrained by meteorological conditions (winter
465 temperature, wind events, rain events) and it conditions biology (Marty and
466 Chiavérini, 2010). As a consequence, the marine vertical export flux in the
467 Northwestern Mediterranean Sea is strongly dependent on climatic and
468 meteorological conditions as well. Therefore, the understanding of the
469 interannual/decadal variability of vertical export fluxes of elements in relation with
470 climatic and meteorological changes requires i) reliable measurements of vertical

471 export fluxes, including the use of proxies such as ^{234}Th and ^{230}Th to minimize
472 possible bias in the measurements (Rutten et al., 2000; Roy-Barman et al., 2009),
473 and ii) good knowledge of physical (climatic and meteorological) parameters that
474 determine the magnitude of dense water formation, as well as their
475 interannual/decadal variability (Stabholz et al., 2013). This is important in terms of
476 ongoing global change, because any alteration of the climatic/meteorological
477 conditions would significantly impact the marine vertical export flux, and this would
478 ultimately determine the evolution of metal cycling in the Northwestern
479 Mediterranean, independently from changes in the atmospheric (metal) deposition.
480 We showed that the marine vertical export flux of metals to deep marine sediments
481 is driven by dense water convection and primary production. The study metal
482 deposition by means of deep marine sediment records requires therefore a profound
483 understanding of the seasonal and long-term variability of primary production and
484 hydrology.
485 Furthermore, we recommend comparing elemental concentrations rather than
486 elemental fluxes in marine vertical export studies.

487

488

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498

499 Tables

500 **Table 1** Certified reference material (CRM) validation results, expressed in $\mu\text{g}\cdot\text{g}^{-1}$.
501 The median relative standard deviation (RSD, in %) is calculated from full replicates
502 including the mineralization step, 10 for GBW, 5 for BCSS-1 and PACS. The median
503 recovery observed between certified and measured values is expressed in %.

504 Values noted * are close to the detection limit. Mean RSD values can be used to
505 determine the uncertainty of the analytical method.

506

507 **Table 2.** Mean metal concentrations and fluxes at the DYFAMED site and various
508 other moorings in the Mediterranean and Black Sea. Variability of metal
509 concentrations is relatively low compared to the variability of vertical export flux.

510 *values have been calculated from the available data given in the cited papers

511

512 **Table 3.** Pearson intercorrelation matrix of the z-scores of OC and metal
513 concentrations of sediment trap material from 2003-2007 (number of variables 11,
514 number of observations 91, missing values have been pairwise deleted). Values in
515 bold are different from 0 with a significance level $\alpha=0.05$.

516

517 **Table 4.** Enrichments factors of all metals of the vertical export flux and EFs of
518 Mediterranean aerosols (Heimbürger et al., 2010b).

519

520 **Table 5.** Factor loadings after Varimax rotation. Factor 1 explains 58 % of the
521 variation with the main contribution of OC and all metals except Cu, Zn and Cd. The
522 negative OC value explains the relative dilution effect of the OC contribution to metal
523 concentrations of the vertical export flux. Factor 2 explains 21 % of the variation and
524 is principally determined by OC, Cu and Zn.

525

526 **Figure captions**

527 **Figure 1** Map of the Northwestern Mediterranean Sea and the location of the time-
528 series sampling station DYFAMED.

529

530 **Figure 2** Temporal variability of the vertical export flux ($\text{mg}\cdot\text{m}^{-2}\cdot\text{d}^{-1}$), particulate metal
531 (Al, V, Cr, Mn, Fe, Ni, Cu, Zn, Cd and Pb) and organic carbon (OC) concentrations
532 ($\mu\text{g}\cdot\text{g}^{-1}$ and %, respectively) of the sediment trap moored at 1000m-depth at the
533 DYFAMED time-series site between 2003 and 2007. The vertical export flux is
534 shown in each inset as bar plots (right axis). Particulate metal and OC
535 concentrations are shown as black line with dots (left axis).

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References

540

541

Andersen, V., Prieur, L., 2000. One-month study in the open NW Mediterranean Sea

542

(DYNAPROC experiment, May 1995): overview of the hydrobiogeochemical

543

structures and effects of wind events. *Deep Sea Research Part I: Oceanographic*

544

Research Papers, 47(3): 397-422.

545

Angelidis, M.O., Radakovitch, O., Veron, A., Aloupi, M., Heussner, S., Price, B., 2011.

546

Anthropogenic metal contamination and sapropel imprints in deep Mediterranean

547

sediments. *Marine Pollution Bulletin*, 62(5): 1041-1052.

548

Armstrong, R.A., Lee, C., Hedges, J.I., Honjo, S., Wakeham, S.G., 2002. A new, mechanistic

549

model for organic carbon fluxes in the ocean based on the quantitative association of

550

POC with ballast minerals. *Deep Sea Research Part II: Topical Studies in*

551

Oceanography, 49(1-3): 219-236.

552

Armstrong, R.A., Peterson, M.L., Lee, C., Wakeham, S.G., 2009. Settling velocity spectra

553

and the ballast ratio hypothesis. *Deep Sea Research II*, 56(18): 1470-1478.

554

Avril, B., 2002. DOC dynamics in the northwestern Mediterranean Sea (DYFAMED site).

555

Deep Sea Research Part II: Topical Studies in Oceanography, 49(11): 2163-2182.

556

Baker, E.T., Milburn, H.B., Tennant, D.A., 1988. Field assessment of sediment trap

557

efficiency under varying flow conditions. *Journal of Marine Research*, 46(3): 573-

558

592.

559

Barnaba, F., Gobbi, G.P., 2004. Aerosol seasonal variability over the Mediterranean region

560

and relative impact of maritime, continental and Saharan dust particles over the basin

561

from MODIS data in the year 2001. *Atmos. Chem. Phys. Discuss.*, 4(4): 4285-4337.

562

Béthoux, J.P., Courau, P., Nicolas, E., Ruiz-Pino, D., 1990. Trace metal pollution in the

563

Mediterranean Sea. *Oceanologica acta*, 13(4): 481-488.

564

Béthoux, J.P., Gentili, B., 1999. Functioning of the Mediterranean Sea: past and present

565

changes related to freshwater input and climate changes. *Journal of Marine Systems*,

566

20(1-4): 33-47.

567

Bollhöfer, A., Rosman, K.J.R., 2001. Isotopic source signatures for atmospheric lead: the

568

Northern Hemisphere. *Geochimica et Cosmochimica Acta*, 65(11): 1727-1740.

569

Bonnet, S., Guieu, C., 2006. Atmospheric forcing on the annual iron cycle in the western

570

Mediterranean Sea: A 1-year survey. *Journal of Geophysical Research-Oceans*,

571

111(C9).

572

Buat-Menard, P., Davies, J., Remoudaki, E., Miquel, J.C., Bergametti, G., Lambert, C.E.,

573

Ezat, U., Quétel, C., La Rosa, J., Fowler, S.W., 1989. Non-steady-state biological

574

removal of atmospheric particles from Mediterranean surface waters. *Nature*,

575

340(6229): 131-134.

576

Buesseler, K.O., Antia, A.N., Chen, M., Fowler, S.W., Gardner, W.D., Gustafsson, O.,

577

Harada, K., Michaels, A.F., Rutgers van der Loeff, M., Sarin, M., Steinberg, D.K.,

578

Trull, T., 2007. An assessment of the use of sediment traps for estimating upper ocean

579

particle fluxes. *Journal of Marine Research*, 65(3): 345-416.

580

Burd, A.B., Jackson, G.a., 2009. Particle Aggregation. *Annual Review of Marine Science*,

581

1(1): 65-90.

582

Carroll, M.L., Miquel, J.-C., Fowler, S.W., 1998. Seasonal patterns and depth-specific trends

583

of zooplankton fecal pellet fluxes in the Northwestern Mediterranean Sea. *Deep Sea*

584

Research Part I: Oceanographic Research Papers, 45(8): 1303-1318.

585

Chester, R., Nimmo, M., Corcoran, P.A., 1997. Rain water aerosol trace metal relationships

586

at Cap Ferrat: A coastal site in the western Mediterranean. *Marine Chemistry*, 58(3-

587

4): 293-312.

- 588 Copin-Montégut, G., Avril, B., 1993. Vertical distribution and temporal variation of
589 dissolved organic carbon in the North-Western Mediterranean Sea. *Deep Sea*
590 *Research Part I: Oceanographic Research Papers*, 40(10): 1963-1972.
- 591 De La Rocha, C.L., Passow, U., 2007. Factors influencing the sinking of POC and the
592 efficiency of the biological carbon pump. *Deep Sea Research II*, 54(5-7): 639-658.
- 593 Desboeufs, K.V., Losno, R., Colin, J., 2003. Figures of merit of pneumatic and ultrasonic
594 sample introduction systems in inductively coupled plasma-multichannel-based
595 emission spectrometry in an ultra-clean environment. *Anal Bioanal Chem*, 375(4):
596 567-573.
- 597 Desboeufs, K.V., Losno, R., Colin, J.L., 2001. Factors influencing aerosol solubility during
598 cloud processes. *Atmospheric Environment*, 35(20): 3529-3537.
- 599 Deuser, W.G., Brewer, P.G., Jickells, T.D., Commeau, R.F., 1983. Biological Control of the
600 Removal of Abiogenic Particles from the Surface Ocean. *Science*, 219(4583): 388-
601 391.
- 602 Duarte, C.M., Agusti, S., Kennedy, H., Vaque, D., 1999. The Mediterranean climate as a
603 template for Mediterranean marine ecosystems: the example of the northeast Spanish
604 littoral. *Progress In Oceanography*, 44(1-3): 245-270.
- 605 Duncan, B.N., Bey, I., 2004. A modeling study of the export pathways of pollution from
606 Europe: Seasonal and interannual variations (1987–1997). *J. Geophys. Res.*,
607 109(D8): D08301.
- 608 Durrieu de Madron, X., Guieu, C., Sempéré, R., Conan, P., Cossa, D., D'Ortenzio, F.,
609 Estournel, C., Gazeau, F., Rabouille, C., Stemmann, L., Bonnet, S., Diaz, F., Koubbi,
610 P., Radakovitch, O., Babin, M., Baklouti, M., Bancon-Montigny, C., Belviso, S.,
611 Bensoussan, N., Bonsang, B., Bouloubassi, I., Brunet, C., Cadiou, J.F., Carlotti, F.,
612 Chami, M., Charmasson, S., Charrière, B., Dachs, J., Doxaran, D., Dutay, J.C., Elbaz-
613 Poulichet, F., Eléaume, M., Eyrolles, F., Fernandez, C., Fowler, S., Francour, P.,
614 Gaertner, J.C., Galzin, R., Gasparini, S., Ghiglione, J.F., Gonzalez, J.L., Goyet, C.,
615 Guidi, L., Guizien, K., Heimbürger, L.E., Jacquet, S.H.M., Jeffrey, W.H., Joux, F., Le
616 Hir, P., Leblanc, K., Lefèvre, D., Lejeusne, C., Lemé, R., Loÿe-Pilot, M.D., Mallet,
617 M., Méjanelle, L., Mélin, F., Mellon, C., Mérigot, B., Merle, P.L., Migon, C., Miller,
618 W.L., Mortier, L., Mostajir, B., Mousseau, L., Moutin, T., Para, J., Pérez, T.,
619 Petrenko, A., Poggiale, J.C., Prieur, L., Pujo-Pay, M., Pulido, V., Raimbault, P., Rees,
620 A.P., Ridame, C., Rontani, J.F., Ruiz Pino, D., Sicre, M.A., Taillandier, V.,
621 Tamburini, C., Tanaka, T., Taupier-Letage, I., Tedetti, M., Testor, P., Thébault, H.,
622 Thouvenin, B., Touratier, F., Tronczynski, J., Ulses, C., Van Wambeke, F.,
623 Vantrepotte, V., Vaz, S., Verney, R., 2011. Marine ecosystems' responses to climatic
624 and anthropogenic forcings in the Mediterranean. *Progress In Oceanography*, 91(2):
625 97-166.
- 626 Fisher, N.S., Nolan, C.V., Fowler, S.W., 1991. Scavenging and retention of metals by
627 zooplankton fecal pellets and marine snow. *Deep Sea Research Part A*.
628 *Oceanographic Research Papers*, 38(10): 1261-1275.
- 629 Fowler, S.W., Buat-Ménard, P., Yokoyama, Y., Ballestra, S., Holm, E., Nguyen, H.V., 1987.
630 Rapid removal of Chernobyl fallout from the Mediterranean surface waters by
631 biological activity. *Nature*, 329(6134): 56-58.
- 632 Fowler, S.W., Knauer, G.A., 1986. Role of large particles in the transport of elements and
633 organic compounds through the oceanic water column. *Progress In Oceanography*,
634 16(3): 147-194.
- 635 Francois, R., Honjo, S., Krishfield, R., Manganini, S., 2002. Factors controlling the flux of
636 organic carbon to the bathypelagic zone of the ocean. *Global Biogeochem. Cycles*,
637 16(4): 1087.

- 638 Fu, G., Allen, H.E., 1992. Cadmium adsorption by oxic sediment. *Water Research*, 26(2):
639 225-233.
- 640 Grotti, M., Soggia, F., Abemoschi, M.L., Rivaro, P., Magi, E., Frache, R., 2001. Temporal
641 distribution of trace metals in Antarctic coastal waters. *Marine Chemistry*, 76(3): 189-
642 209.
- 643 Guerzoni, S., Molinaroli, E., Rossini, P., Rampazzo, G., Quarantotto, G., De Falco, G.,
644 Cristini, S., 1999. Role of desert aerosol in metal fluxes in the Mediterranean area.
645 *Chemosphere*, 39(2): 229-246.
- 646 Guidi, L., Stemann, L., Jackson, G.A., Ibanez, F., Claustre, H., Legendre, L., Picheral, M.,
647 Gorsky, G., 2009. Effects of phytoplankton community on production, size and export
648 of large aggregates: A world-ocean analysis. *Limnology and Oceanography*, 54(6):
649 1951-1963.
- 650 Hamm, C.E., 2002. Interactive aggregation and sedimentation of diatoms and clay-sized
651 lithogenic material. *Limnol. Oceanogr.*, 47(6): 1790-1795.
- 652 Heimbürger, L.E., Cossa, D., Marty, J.-C., Migon, C., Averty, B., Dufour, A., Ras, J., 2010a.
653 Methylmercury distributions in relation to the presence of nano- and
654 picophytoplankton in an oceanic water column (Ligurian Sea, North-western
655 Mediterranean). *Geochimica Et Cosmochimica Acta*, 74(19): 5549-5559.
- 656 Heimbürger, L.E., Cossa, D., Thibodeau, B., Khripounoff, A., Mas, V., Chiffoleau, J.-F.,
657 Schmidt, S., Migon, C., 2012. Natural and anthropogenic trace metals in sediments of
658 the Ligurian Sea (Northwestern Mediterranean). *Chemical Geology*, 291(0): 141-151.
- 659 Heimbürger, L.E., Lavigne, H., Migon, C., D'Ortenzio, F., Estournel, C., Coppola, L.,
660 Miquel, J.-C., 2013. Temporal variability of vertical export flux at the DYFAMED
661 time-series station (Northwestern Mediterranean Sea). *Progress in Oceanography*,
662 119(0): 59-67.
- 663 Heimbürger, L.E., Migon, C., Cossa, D., 2011. Impact of atmospheric deposition of
664 anthropogenic and natural trace metals on Northwestern Mediterranean surface
665 waters: A box model assessment. *Environmental Pollution*, 159(6): 1629-1634.
- 666 Heimbürger, L.E., Migon, C., Dufour, A., Chiffoleau, J.F., Cossa, D., 2010b. Trace metal
667 concentrations in the North-western Mediterranean atmospheric aerosol between 1986
668 and 2008: Seasonal patterns and decadal trends. *Science of The Total Environment*,
669 408(13): 2629-2638.
- 670 Herut, B., Nimmo, M., Medway, A., Chester, R., Krom, M.D., 2001. Dry atmospheric inputs
671 of trace metals at the Mediterranean coast of Israel (SE Mediterranean): sources and
672 fluxes. *Atmospheric Environment*, 35(4): 803-813.
- 673 JGOFS, 1996. Protocols for the Joint Global Ocean Flux Study (JGOFS) core measurements.
- 674 Jickells, T.D., Deuser, W.G., Knap, A.H., 1984. The sedimentation rates of trace elements in
675 the Sargasso Sea measured by sediment trap. *Deep Sea Research Part A*.
676 *Oceanographic Research Papers*, 31(10): 1169-1178.
- 677 Jickells, T.D., Dorling, S., Deuser, W.G., Church, T.M., Arimoto, R., Prospero, J.M., 1998.
678 Air-borne dust fluxes to a deep water sediment trap in the Sargasso Sea. *Global*
679 *Biogeochemical Cycles*, 12(2): 311-320.
- 680 Kersten, M., Kriews, M., Förstner, U., 1991. Partitioning of trace metals released from
681 polluted marine aerosols in coastal seawater. *Marine Chemistry*, 36(1-4): 165-182.
- 682 Klaas, C., Archer, D.E., 2002. Association of sinking organic matter with various types of
683 mineral ballast in the deep sea: Implications for the rain ratio. *Global Biogeochem.*
684 *Cycles*, 16(4): 1116.
- 685 Krahnmann, G., Schott, F., 1998. Longterm increases in Western Mediterranean salinities and
686 temperatures: anthropogenic and climatic sources. *Geophysical Research Letters*,
687 25(22): 4209-4212.

- 688 Laubier, L., 2005. Mediterranean Sea and humans: Improving a conflictual partnership.,
689 Handbook of Environmental Chemistry, pp. 3-27.
- 690 Lee, C., Armstrong, R.A., Cochran, J.K., Engel, A., Fowler, S.W., Goutx, M., Masqué, P.,
691 Miquel, J.C., Peterson, M., Tamburini, C., Wakeham, S., 2009. MedFlux:
692 Investigations of particle flux in the Twilight Zone. *Deep Sea Research II*, 56(18):
693 1363-1368.
- 694 Lévy, M., Memery, L., Andre, J.M., 1998. Simulation of primary production and export
695 fluxes in the Northwestern Mediterranean Sea. *Journal of Marine Research*, 56(1):
696 197-238.
- 697 Martín, J., Sanchez-Cabeza, J.A., Eriksson, M., Levy, I., Miquel, J.C., 2009. Recent
698 accumulation of trace metals in sediments at the DYFAMED site (Northwestern
699 Mediterranean Sea). *Marine Pollution Bulletin*, 59(4-7): 146-153.
- 700 Martin, J.H., Knauer, G.A., Karl, D.M., Broenkow, W.W., 1987. VERTEX: carbon cycling in
701 the northeast Pacific. *Deep Sea Research I*, 34(2): 267-285.
- 702 Martin, J.M., Milliman, J.D., 1997. EROS 2000 (European River Ocean System). The
703 western Mediterranean: An introduction. *Deep Sea Research II*, 44(3-4): 521-529.
- 704 Marty, J.-C., 2002. The DYFAMED time-series program (French-JGOFS). *Deep Sea*
705 *Research II*, 49(11): 1963-1964.
- 706 Marty, J.-C., Garcia, N., Raimbault, P., 2008. Phytoplankton dynamics and primary
707 production under late summer conditions in the NW Mediterranean Sea. *Deep Sea*
708 *Research Part I: Oceanographic Research Papers*, 55(9): 1131-1149.
- 709 Marty, J.C., Chiavérini, J., 2010. Hydrological changes in the Ligurian Sea (NW
710 Mediterranean, DYFAMED site) during 1995–2007 and biogeochemical
711 consequences. *Biogeosciences*, 7: 2117-2128.
- 712 Marty, J.C., Chiavérini, J., Pizay, M.D., Avril, B., 2002. Seasonal and interannual dynamics
713 of nutrients and phytoplankton pigments in the western Mediterranean Sea at the
714 DYFAMED time-series station (1991-1999). *Deep Sea Research II*, 49(11): 1965-
715 1985.
- 716 Marty, J.C., Goutx, M., Guigue, C., Leblond, N., Raimbault, P., 2009. Short-term changes in
717 particulate fluxes measured by drifting sediment traps during end summer
718 oligotrophic regime in the NW Mediterranean Sea. *Biogeosciences*, 6(5): 887-899.
- 719 Marty, J.C., Nicolas, E., J.C., M., Fowler, S.W., 1994. Particulate fluxes of organic
720 compounds and their relationship to zooplankton fecal pellets in the northwestern
721 Mediterranean Sea. *Marine Chemistry*, 46: 387 - 405.
- 722 Migon, C., 2005. Trace Metals in the Mediterranean Sea. In: Saliot, A. (Ed.), *The*
723 *Mediterranean Sea*. Springer, Berlin, Heidelberg, New York.
- 724 Migon, C., Robin, T., Dufour, A., Gentili, B., 2008. Decrease of lead concentrations in the
725 Western Mediterranean atmosphere during the last 20 years. *Atmospheric*
726 *Environment*, 42(4): 815-821.
- 727 Migon, C., Sandroni, V., Marty, J.-C., Gasser, B., Miquel, J.-C., 2002. Transfer of
728 atmospheric matter through the euphotic layer in the northwestern Mediterranean:
729 seasonal pattern and driving forces. *Deep Sea Research II*(49): 2125-2141.
- 730 Miquel, J.-C., Martín, J., Gasser, B., Rodriguez-y-Baena, A., Toubal, T., Fowler, S.W., 2011.
731 Dynamics of particle flux and carbon export in the northwestern Mediterranean Sea:
732 A two decade time-series study at the DYFAMED site. *Progress In Oceanography*,
733 91(4): 461-481.
- 734 Miquel, J.C., Fowler, S.W., La Rosa, J., Buat-Ménard, P., 1994. Dynamics of the Downward
735 Flux of Particles and Carbon in the Open Northwestern Mediterranean-Sea. *Deep Sea*
736 *Research I*, 41(2): 243-261.

- 737 Morley, N.H., Burton, J.D., Tankere, S.P.C., Martin, J.M., 1997. Distribution and behaviour
738 of some dissolved trace metals in the western Mediterranean Sea. *Deep Sea Research*
739 *II*, 44(3-4): 675-691.
- 740 Moulin, C., Guillard, F., Dulac, F., Lambert, C.E., 1997. Long-term daily monitoring of
741 Saharan dust load over ocean using Meteosat ISCCP-B2 data: 1. Methodology and
742 preliminary results for 1983–1994 in the Mediterranean. *Journal of Geophysical*
743 *Research: Atmospheres*, 102(D14): 16947-16958.
- 744 Muller, F.L.L., 1996. Interactions of copper, lead and cadmium with the dissolved, colloidal
745 and particulate components of estuarine and coastal waters. *Marine Chemistry*, 52(3–
746 4): 245-268.
- 747 Niewiadomska, K., Claustre, H., Prieur, L., d'Ortenzio, F., 2008. Submesoscale physical-
748 biogeochemical coupling across the Ligurian Current (northwestern Mediterranean)
749 using a bio-optical glider. *Limnology and Oceanography*, 53(5): 2210-2225.
- 750 Passow, U., 2004. Switching perspectives: Do mineral fluxes determine particulate organic
751 carbon fluxes or vice versa? *Geochemistry Geophysics Geosystems*, 5: 5.
- 752 Roussiez, V., Heussner, S., Ludwig, W., Radakovitch, O., Durrieu de Madron, X., Guieu, C.,
753 Probst, J.-L., Monaco, A., Delsaut, N., 2012. Impact of oceanic floods on particulate
754 metal inputs to coastal and deep-sea environments: A case study in the NW
755 Mediterranean Sea. *Continental Shelf Research*, 45(0): 15-26.
- 756 Roy-Barman, M., Lemaître, C., Ayrault, S., Jeandel, C., Souhaut, M., Miquel, J.C., 2009. The
757 influence of particle composition on Thorium scavenging in the Mediterranean Sea.
758 *Earth and Planetary Science Letters*, 286(3-4): 526-534.
- 759 Rutten, A., de Lange, G.J., Ziveri, P., Thomson, J., van Santvoort, P.J.M., Colley, S.,
760 Corselli, C., 2000. Recent terrestrial and carbonate fluxes in the pelagic eastern
761 Mediterranean; a comparison between sediment trap and surface sediment.
762 *Palaeogeography, Palaeoclimatology, Palaeoecology*, 158(3-4): 197-213.
- 763 Sarthou, G., Jeandel, C., 2001. Seasonal variations of iron concentrations in the Ligurian Sea
764 and iron budget in the Western Mediterranean Sea. *Marine Chemistry*, 74(2-3): 115-
765 129.
- 766 Scholten, J.C., Fietzke, J., Vogler, S., van der Loeff, M.M.R., Mangini, A., Koeve, W.,
767 Waniek, J., Stoffers, P., Antia, A., Kuss, J., 2001. Trapping efficiencies of sediment
768 traps from the deep Eastern North Atlantic: the Th-230 calibration. *Deep Sea*
769 *Research II*, 48(10): 2383-2408.
- 770 Stabholz, M., Durrieu de Madron, X., Canals, M., Khripounoff, A., Taupier-Letage, I.,
771 Testor, P., Heussner, S., Kerhervé, P., Delsaut, N., Houpert, L., Lastras, G.,
772 Dennielou, B., 2013. Impact of open-ocean convection on particle fluxes and
773 sediment dynamics in the deep margin of the Gulf of Lions. *Biogeosciences*, 10(2):
774 1097-1116.
- 775 Sternberg, E., Jeandel, C., Miquel, J.-C., Gasser, B., Souhaut, M., Arraes-Mescoff, R.,
776 Francois, R., 2007. Particulate barium fluxes and export production in the
777 northwestern Mediterranean. *Marine Chemistry*, 105(3–4): 281-295.
- 778 Stokes, G.G., 1901. *Mathematical and Physical papers*, Cambridge University Press,
779 Cambridge, pp. 413.
- 780 Sunda, W., 2012. Feedback interactions between trace metal nutrients and phytoplankton in
781 the ocean. *Frontiers in Microbiology*, 3.
- 782 Ternon, E., Guieu, C., Loÿe-Pilot, M.-D., Leblond, N., Bosc, E., Gasser, B., Miquel, J.-C.,
783 Martín, J., 2010. The impact of Saharan dust on the particulate export in the water
784 column of the North Western Mediterranean Sea. *Biogeosciences*, 7: 809-826.

- 785 Theodosi, C., Markaki, Z., Tselepides, A., Mihalopoulos, N., 2010. The significance of
 786 atmospheric inputs of soluble and particulate major and trace metals to the eastern
 787 Mediterranean seawater. *Marine Chemistry*, 120(1-4): 154-163.
- 788 Theodosi, C., Parinos, C., Gogou, A., Kokotos, A., Stavrakakis, S., Lykousis, V.,
 789 Hatzianestis, J., Mihalopoulos, N., 2012. Downward fluxes of elemental carbon,
 790 metals and polycyclic aromatic hydrocarbons in settling particles from the deep
 791 Ionian Sea (NESTOR site), Eastern Mediterranean. *Biogeosciences Discuss.*, 9(12):
 792 19165-19197.
- 793 Theodosi, C., Stavrakakis, S., Koulaki, F., Stavrakaki, I., Moncheva, S., Papathanasiou, E.,
 794 Sanchez-Vidal, A., Koçak, M., Mihalopoulos, N., 2013. The significance of
 795 atmospheric inputs of major and trace metals to the Black Sea. *Journal of Marine*
 796 *Systems*, 109–110(0): 94-102.
- 797 UNEP/MEDPOL, 2004. United Nations Environment Program: Mediterranean Action Plan
 798 MED POL Transboundary diagnostic analysis (TDA) for the Mediterranean Sea.,
 799 Athens.
- 800 Wang, W.X., Fisher, N.S., 1998. Excretion of trace elements by marine copepods and their
 801 bioavailability to diatoms. *Journal of Marine Research*, 56(3): 713-729.
- 802 Wedepohl, H.K., 1995. The composition of the continental crust. *Geochimica Et*
 803 *Cosmochimica Acta*, 59(7): 1217-1232.
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CRM	Metal	Al	V	Cr	Mn	Fe	Ni	Cu	Zn	Cd	Pb
GBW	Measured	78900	107	57	3106	39100	163	498	152	0.2	27
	RSD	3	5	7	6	6	9	5	6	30*	8
	Certified	72800	112	58.4	3330	46000	150	424	160		29.3
	Recovery	108	96	97	93	85	109	117	95		92
BCSS-1	Measured	67600	93	105	231	30900	63	27	108	0.4	22
	RSD	3	5	5	5	6	5	8	12	7	18
	Certified	62600	94.4	123	229	33400	55.3	18.5	119	0.25	22.7
	Recovery	108	98	86	101	93	113	147	91	163*	98
PACS	Measured	70200	132	106	469	43400	57	508	824	3	400
	RSD	2	5	2	1	1	9	2	6	4	5
	Certified	64700	127	113	470	48700	44.1	452	824	2.38	404
	Recovery	108	104	94	100	89	130	112	100	109	99
Mean	Mean RSD	3	5	5	4	4	8	5	8	6	10
	Mean recovery	108	99	92	98	89	117	125	95	109	96

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Study	Location	Study period	Sediment trap depth (m)	this study		Migon et al., 2002	Heimbürger et al., 2013	Roussiez et al., 2012	Theodosi et al., 2010	Theodosi et al., 2013			Theodosi et al., 2013				
				WMED	DYFAMED	WMED	WMED	GoL	EMED	EMED			Black Sea				
				1000		200	2005-06 (20m. a.b.)	30m.a.b.	1715	700	1200	2000	930	1930			
				S	RSD (%)	RSD (%)				RSD (%)	RSD (%)	S	RSD (%)	S	RSD (%)		
Metal concentration ($\mu\text{g g}^{-1}$)	Al	4 1 1	7 0 0	5 6 0	0 0 0	7 8 22	58400			433 204	4150 1290	4 1 1	2 1 1	4 6 7	9 0 0	14 4	
		7 2 2	5 0 0	7 2 2	9 6 33	94	76	20.5	100 110 110	120 180 150	4 9 30	5 1 2	5 4 56	7 7 7	3 2 95		
	V	6 2 4	4 4 4	9 2 2	3 5 2	3 2 0	4 1 22	26300	1400	226 520	2190	0 2 0	0 0 0	0 0 0	0 0 0	0 0 0	59
		5 1 1	5 3 25	57	38	21 18 86	17 13 76	5 0 67	9 5 38	2 1 2	1 1 2	1 1 1	1 1 1	0 1 11			
	Cr	7 1 1	6 8 24	47	27	6.85	26 16 62	33 17 52	4 1 0	5 38	7 3 6	2 2 42	4 8 21	0 6 5	3 6 16		
		1 5 1	1 6 37	107	113	27.4	0.11	0.17	0.11	1.0 1.2 120	1.5 1.3 87	1. 1. 13	2. 2. 91	4. 8. 21	0 6 5	3 6 16	
	Mn	0. 0. 2	1 1 0	43	0.11	0.17	0.11	1.0 1.2 120	1.5 1.3 87	1. 1. 13	2. 2. 91	4. 8. 21	0 6 5	3 6 16			
		8 8 21	44	37	4.66	38 12 32	40 13 33	3 6 37	5 5 7	3 3 2							
	Cd	1 1 14	0 5 7	77 77 100	105*	63*	57*	5 3*	1 2 0*	5 2*							
		5 4															
Vertical metal export flux ($\mu\text{g m}^{-2} \text{d}^{-1}$)	Al	5 9 7	7 6 16	389 422	2 3 109	6132*			260 220	2200 2200 100	2 1 0	2 3 7	1 1 7	0 0 0	71		
		4 2 7	9 1 1	1 4 16	9 1 3	11.3*	3.7 3.2 86	3 4 106	2. 2. 10	2. 3. 12	1. 1. 10	9 9 0					
	V	4 4 15	7 5 4	9.87*			5.4 5.1 94	6 10 182	3. 2. 94	6. 7. 11	4. 3. 76						
		1 1 13	4 3 9	82.4*			36 30 83	32 36 113	2 2 7	4 2 92	1 1 8	2 2 92	1 1 8	6 89			
	Cr	2 4 8	7 17 0	2762*			150 140	1400 1500 107	1 1 5	7 10 0	6 9 0	0 0 11	0 0 9	0 0 90			
		6 8 0	4 13 9	5.99*			1.7 1.7 100	1.4 1.9 136	1. 1. 12	4. 4. 10	3. 2. 82						
	Ni	6 7 8	7 8 11	4.94*			1.9 1.9 100	2.1 2.5 119	2. 2. 1	8. 7. 0	6. 5. 98						
		1 1 11	3 9 2	18.712.1 65	11.2*				0. 0. 0	2 5 0	8 7 20	3 3 10	0 0 0				
	Mn	0 0 3	2 3 15	0.080.06 75	0.0116*		0.04 0.04	0.04 0.04	0 0 4	80	6. 5. 91	1. 1. 8	6. 5. 91	1. 1. 8	6 89		
		4 9 6	0 6 75	4. 62 *			2.2 1.7 77	1 0 5	9 6 84								
Fe	3 5 7	0 13 3	4.9 4.9 100														
	6 0 3																

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R^2	OC	Al	V	Cr	Mn	Fe	Ni	Cu	Zn	Cd	Pb
OC	1										
Al	-0.71	1									
V	-0.72	0.98	1								
Cr	-0.62	0.91	0.94	1							
Mn	-0.66	0.75	0.80	0.83	1						
Fe	-0.65	0.98	0.96	0.92	0.74	1					
Ni	-0.45	0.81	0.85	0.94	0.79	0.84	1				
Cu	0.35	-0.22	-0.17	-0.14	-0.04	-0.18	0.01	1			
Zn	0.44	-0.34	-0.29	-0.25	-0.27	-0.29	-0.13	0.72	1		
Cd	0.60	-0.37	-0.36	-0.36	-0.42	-0.30	-0.26	0.20	0.31	1	
Pb	-0.24	0.53	0.61	0.67	0.72	0.58	0.72	0.39	0.14	-0.12	1

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	V	Cr	Mn	Fe	Ni	Cu	Zn	Cd	Pb
Mean	2.28	3.61	1.98	1.23	4.76	8.93	4.87	4.81	3.14
SD	0.16	0.54	0.52	0.06	0.60	2.97	2.30	2.79	0.62
RSD	7	15	26	5	13	33	47	58	20
MIN	1.91	2.62	0.62	1.08	2.78	3.80	1.91	1.20	1.75
MAX	2.65	5.02	2.92	1.47	6.68	16.42	12.39	17.76	4.62
N	91	91	91	91	89	86	83	88	89
EF of MED aerosol*			2.59	2.63	66.9	172	164	597	109

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	F1	F2
OC	-0.65	0.53
Al	0.92	-0.25
V	0.96	-0.18
Cr	0.96	-0.10
Mn	0.89	-0.08
Fe	0.93	-0.17
Ni	0.92	0.07
Cu	0.00	0.89
Zn	-0.18	0.84
Cd	-0.38	0.45
Pb	0.77	0.46

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843 Highlights for “*Vertical export flux of metals in the Mediterranean Sea*”

844 Lars-Eric HEIMBÜRGER^(1, 2, 3,*), Christophe MIGON^(1, 2), Rémi LOSNO⁽⁴⁾, Juan-Carlos

845 MIQUEL⁽⁵⁾, Benoît THIBODEAU^(1, 2, 6), Marion STABHOLZ⁽⁷⁾, Aurélie DUFOUR^(1, 2) & Nathalie

846 LEBLOND^(1, 2)

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848 (1) Dense water convection and surface primary production control the vertical export flux of
849 metals

850 (2) Atmospheric deposition events do not trigger significant vertical export fluxes

851 (3) all metals whether of natural or crustal origin are accumulated in the mixed layer until
852 they are exported at the same time

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Accepted manuscript

Figure 1

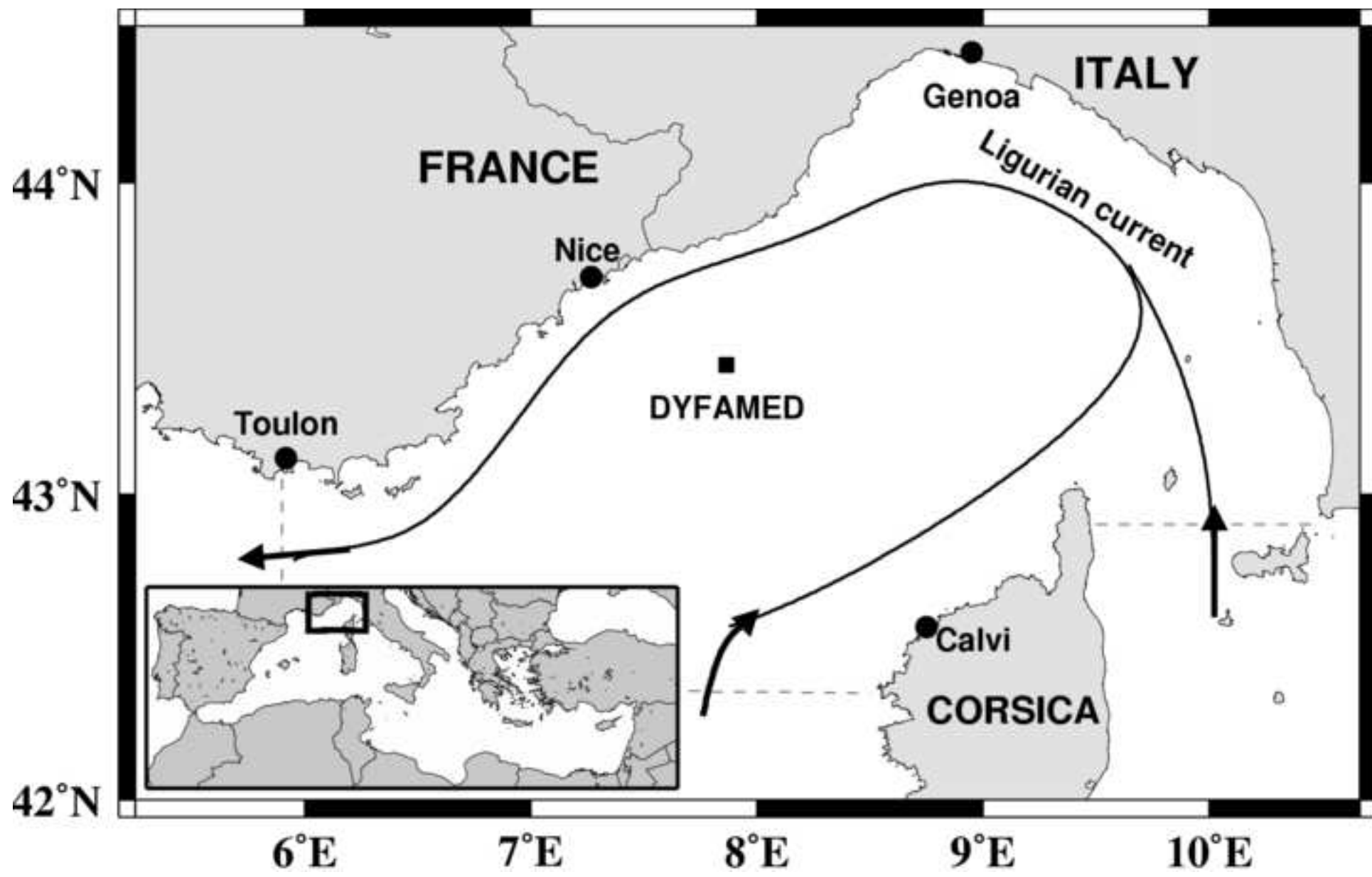


Figure 2