Vertical export flux of metals in the Mediterranean Sea

Lars-Eric HEIMBÜRGER[1, 2, 3,*], Christophe MIGON[1, 2], Rémi LOSNO[4], Juan-Carlos MIQUEL[5], Benoît THIBODEAU[1, 2, 6], Marion STABHOLZ[7], Aurélie DUFOUR[1, 2] & Nathalie LEBLOND[1, 2]

(1) Université Pierre et Marie Curie (UPMC), UMR 7093, Observatoire océanologique de Villefranche-sur-Mer, F-06234, Villefranche-sur-Mer, France
(2) CNRS/INSU, UMR 7093, Laboratoire d'Océanographie de Villefranche-sur-Mer, F-06234, Villefranche-sur-Mer, France
(3) IFREMER, Centre de Méditerranée, BP 330, F-83507, La Seyne-sur-Mer, France
(4) LISA, Université Paris 7-Paris 12, CNRS, 61 Avenue du Général de Gaulle, F-94010 Créteil, France
(5) IAEA, Environment Laboratories, 4a Quai Antoine 1er, MC 98000 Monaco
(6) Academy of Sciences, Humanities and Literature, Mainz, c/o Helmholtz Centre for Ocean Research, GEOMAR, Wischhofstrasse 1-3, 24148 Kiel, Germany
(7) CEFREM, CNRS, Université de Perpignan Via Domitia, UMR 5110, 52 avenue Paul Alduy, 66860 Perpignan, France

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

* Corresponding author and present address: L.E. Heimbürger, Geosciences Environment Toulouse (GET), Observatoire Midi-Pyrénées (OMP), 14 Ave. E. Belin, 31400 Toulouse, France; Email: heimburger@get.obs-mip.fr

Abstract
We examined metal (Al, V, Cr, Mn, Fe, Ni, Cu, Zn, Cd and Pb) and particulate organic carbon (OC) concentrations in 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 1000m-depth between 2003 and 2007 at the DYFAMED site. A highly significant correlation was observed between most metals, 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.

1. Introduction

Identifying the factors controlling the vertical export fluxes of particulate matter from surface water to 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; 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; Krahmann and Schott, 1998; Béthoux and Gentili, 1999; 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; 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; 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,

and those of the inflowing North Atlantic Ocean (Morley et al., 1997). Metal distribution patterns in the water column suggest that their biogeochemical cycling is mainly governed by atmospheric inputs (Béthoux et al., 1990; Migon et al., 2002; Heimbürger et al., 2011). Three independent studies (Martín et al., 2009; Angelidis et al., 2011; Heimbürger et al., 2012) show a recent increase of anthropogenic metals in Mediterranean deep marine sediment records. This increasing metal trend in sedimentary records reflects presumably the evolution of anthropogenic metal emissions along the densely populated Mediterranean coast (~300 inhabitants per km^2 (UNEP/MEDPOL, 2004; Laubier, 2005), in addition to metal inputs from long-ranged sources.

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

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

2. Methods

2.1. Study site

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

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

2.2. Sampling

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

2.3. Analysis

Sediment trap samples were mineralized according to the following protocol: The organic matrix was destroyed by oxidation (HNO_3) while the mineral aluminosilicate matrices were destroyed with HF. Every freeze-dried sample was weighed in 7mL Teflon flasks, and dissolved as follows: 1) each flask was filled with 1mL HNO_3 65% (suprapur, Merck), sealed and placed in a larger Teflon bottle (60mL). This apparatus was left 5-6 hours in an oven at 150°C, after which bottles and flasks were brought to room temperature and left open under laminar flow hood until a brown dry residue remained. 2) 500µL HNO_3 65% and 500µL HF 40% were added to the remainder. The flasks and bottles were closed and put in an oven 5-6 hours at

150°C, prior to open evaporation at room temperature under laminar flow hood, until a white dry residue was obtained. This residue was ultrasonically dissolved in 5mL HNO_3 0.1N. The samples were diluted with HNO_3 0.1N to 15mL.

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

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

2.4. Data treatment and statistical analysis

To our knowledge no certified reference material for sediment trap material exists today and complete procedural blanks are hard if not impossible to realize. We carefully examined the raw data in order to investigate for possible artifacts and contamination. To do so we used enrichment factors (EFs) to trace the anthropogenic component of samples, either from anthropogenic inputs or contamination during sampling. We chose EFs standardized to Al, which is the most commonly used soil dust reference. These ratios are usually defined for a given element as (e.g. (Herut et al., 2001; Heimbürger et al., 2010b):

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

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

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

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

where X_i is a given value of a variable in a sample, X_{avg} is the average of that variable and X_{std} is its standard deviation. Z-scores allow keeping the relative variation of the original data while reducing all variables to a similar range of variation avoiding scaling effects. The best solution was obtained with a Varimax rotation, which is more restrictive with the variables associated to the principal

components (i.e. maximizes the proportion of variance of the variables in the principal components). The square of the factor loadings was used as an estimation of the proportion of variance of each variable for each principal component. Statistical computations were performed with XLSTAT® software from Addinsoft.

3. Results and Discussion

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

Metal mean concentrations and vertical metal export fluxes at the DYFAMED site and various other moorings in the Mediterranean and Black Sea are shown in Table 2. The variability of metal and OC concentrations is relatively low (RSD = 21-46 %) compared to the variability of vertical export flux (RSD = 147 %). This implies that the temporal variability of TM and OC fluxes (calculated as the product of TM or OC and vertical export flux) is almost entirely governed by the variability of the vertical export flux. This is also the case for other Mediterranean sediment moorings, suggesting that this is a general feature. Vertical export fluxes, OC and metal concentrations are roughly in the same ranges as values presented by Migon (2002) and Heimbürger et al. (2012), and also comparable to finding in other basins of the Mediterranean Sea (Theodosi et al., 2010; Roussiez et al., 2012; Theodosi et al., 2012) and the Black Sea (Theodosi et al., 2013). Miquel et al. (2011) suggested that under a one-dimensional scenario, ~38% of OC leaving the 200m-depth horizon is remineralized before reaching the 1000m-depth horizon. OC concentrations during the selected sampling period were with values between 2 and 19%, not different from the typical range of the complete 20-year DYFAMED time-series (Miquel et al., 2011).

The vertical export flux at DYFAMED follows a well-known seasonal pattern (Miquel et al., 1994; Migon et al., 2002; Ternon et al., 2010; Miquel et al., 2011; Heimbürger et al., 2013). This pattern was repeated over the duration of the sampling period and characterized by the following known sequence:

In winter (December to February), the cooling and evaporation of surface waters lead to the formation of dense water. The vertical convection of dense water leads to rapid downward transport of dissolved (Copin-Montégut and Avril, 1993; Avril, 2002)

and particulate matter (flush-down effect), including metals (Béthoux and Gentili, 1999; Heimbürger et al., 2013). The vertical export flux during dense water convection contains a higher portion of atmospherically-deposited mineral material, that has been accumulated in the mixed layer during the preceding stratified period (Migon et al., 2002; Heimbürger et al., 2010a). As a result, the OC concentration is the lowest. The seasonal pattern of vertical export flux shows reproducible peaks in January-February (e.g., 2004 and 2005; Fig. 2). During the mesotrophic period (March to May), the vertical export flux is driven by primary production. Nutrients brought to surface waters by the previous dense water convection trigger phytoplanktonic blooms in spring, and generate moderate vertical export fluxes e.g., 2003 and 2004; Fig.2). The spring vertical export flux is characterized by moderate OC concentrations, as a result of the combination of biogenic material and mineral material. The intensity of the vertical export flux under mesotrophic conditions directly depends on the intensity of the spring bloom conditioned by the dense water convection in winter (Marty and Chiavérini, 2010).

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

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

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

2.) Small increases in the vertical export flux were recorded between October and December. For example, a peak was observed in fall 2005 (Fig. 2), while vertical

export fluxes were negligible in 2003 and 2004 during the same period. Strong easterly winds were observed early October 2005 and yielded a decrease of sea surface temperature of 3.6°C (from 20.9 to 17.3°C) within 5 days at the Météo-France buoy ODAS located nearby the mooring line. Such a rapid temperature decrease suggests wave-induced mixing below the surface mixed layer. The mixing with nutrient-rich from below the thermocline may have supplied nutrients to the depleted surface layer and triggered a fall bloom. This fall bloom was probably dominated by nano- and picophytoplankton (Heimbürger et al., 2010a) and resulted consequently only in a small increase in the vertical export flux (Marty et al., 2009).

This seasonal pattern suggests that, apart from dense water convection episodes associated in spatially restricted Mediterranean areas (among which is the Ligurian Sea), the vertical export of atmospherically-deposited material is almost entirely driven by the magnitude and variability of primary production. This statement is in agreement with many studies that pointed out the prominent role of primary production in the removal of mineral material (e.g. (Fowler et al., 1987; Buat-Menard et al., 1989; Jickells et al., 1998; Grotti et al., 2001; Hamm, 2002; Migon et al., 2002). Marty and Chiavérini (2010) stated that the efficiency of the vertical transfer under mesotrophic conditions directly depends on the intensity of the water column mixing and the subsequent diatom bloom. However, several recent papers (e.g. (Armstrong et al., 2002; Francois et al., 2002; Klaas and Archer, 2002; Armstrong et al., 2009; Lee et al., 2009; Ternon et al., 2010) have postulated that mineral particles, originating mainly from atmospheric dust deposition, control the sedimentation rate of biogenic material by ballasting biogenic matter, particularly when zooplankton fecal pellet production is low (Lee et al., 2009). This process presumably increases the density of OC aggregates and, therefore, their sinking rates. It was also suggested that mineral particles protect OC from oxidation and remineralization (De La Rocha and Passow, 2007).

The present paper contributes to the ongoing debate of whether atmospheric deposition or primary production/dense water convection controls the marine vertical export flux. We examined sediment trap samples from the DYFAMED site, that have been analyzed previously for OC and Al, but not for the anthropogenic and natural metals presented here (Ternon et al., 2010). The authors concluded that atmospheric deposition events drive the marine vertical export flux. The outstanding feature of the present dataset is that nearly all metals, whether of crustal or

anthropogenic origin, are highly correlated (Table 3). This suggests that all metals are exported to depth at the same time, independently of their different depositional seasonal pattern. However, this does not hold true for Cd, Zn and Cu, which suggests that these metals are less efficiently associated with sinking particles. Metal solubility can be proposed as an explanation: Despite possible adsorption onto lithogenic material such as metal oxide surfaces at seawater pH (Fu and Allen, 1992), Cd is among the most soluble metals studied here (Migon, 2005). This also applies to Zn (Kersten et al., 1991). The ability of Cu to complex with dissolved organic ligands (Muller, 1996) might also lead to lower contribution to the pool of sinking particles. The solubility of those three metals might explain losses in sediment traps.

An alternative explanation could be related to the processing of the sediment trap samples. Rinsing the particles by deionized water may have led to osmotic bursting of planktonic cells, thereby releasing metals within the cytoplasm of algal cells. Zinc, Cu, and Cd reside in phytoplankton cytoplasm to a significantly greater extent than most of the other metals that were assessed (these other metals are typically bound to cell walls and membranes), thus bursting of planktonic cells could lead to an enrichment of Zn, Xu and Cd.

However, despite its high solubility, Pb is actually significantly correlated with Al, V, Cr, Mn, Fe, and Ni. This is presumably due to its strong affinity for suspended particulate matter, principally Al, Fe and Mn oxides, organic matter, carbonates and clay (Kersten et al., 1991). Among the seven highly correlated metals (Al, V, Cr, Mn, Fe, Ni, and Pb), one can find crustal (Al, Fe), intermediate (Cr, Mn), and anthropogenic elements (V, Ni, and Pb). Natural and anthropogenic metals depict distinct seasonal deposition patterns related to their different emission sources (Heimbürger et al., 2010b). For example, it is well known that the deposition of crustal metals is strongly associated with Saharan dust episodes (Bonnet and Guieu, 2006; Heimbürger et al., 2010b; Ternon et al., 2010). Saharan dust events are generally observed in spring and summer in the western Mediterranean (Moulin et al., 1997; Heimbürger et al., 2010b). Atmospheric deposition of anthropogenic metals does not exhibit this pulsed character, and most of the anthropogenic inputs occur in winter, when polluted air masses from Northern Europe influence the Ligurian Sea (Barnaba and Gobbi, 2004; Duncan and Bey, 2004; Heimbürger et al., 2010b). Anthropogenic metals have various emission sources which are temporally

338 variable. This may also lead to different seasonal patterns of their atmospheric
339 deposition. For example, V and Ni emissions result mainly from oil combustion,
340 whereas major Pb emissions results from steel metallurgy plants, mining complexes
341 in Eastern Europe or Kazakhstan, leaded petrol carried by long-range atmospheric
342 transport from North Africa, Middle East or Eastern Europe (Bollhöfer and Rosman,
343 2001; Migon et al., 2008). Individual metal deposition to the Northwestern
344 Mediterranean Sea surface is temporally variable, according to the nature and the
345 individual seasonal patterns of their emission sources (Heimbürger et al., 2010b).
346 Different seasonal variations in the supply of atmospheric deposition to surface
347 waters and the rate of particle removal from surface waters result in a rather
348 constant vertical export flux of metal through the year. Similar observation was made
349 for dust deposition at the BATS time-series (Jickells et al., 1998). As mentioned
350 above, the Northwestern Mediterranean Sea receives much higher loads of
351 atmospheric metal deposition and the water column is mixed every winter by dense
352 water convection. Vertical export flux in the Mediterranean Sea is driven by dense
353 water convection in winter (flush-down effect) and by primary production in spring
354 (Miquel et al., 1994; Migon et al., 2002; Miquel et al., 2011).
355 We hypothesized that atmospheric metal deposition accumulates in the marine
356 surface layer in the absence of dense water convection and low biological activity
357 (under stratified oligotrophic conditions). Indeed, individual dust particles have,
358 based upon Stokesian calculations (Stokes, 1901), a negligible settling velocity
359 (<5 $m.d^{-1}$; (Buat-Menard et al., 1989)). Therefore, the transfer of particulate metals
360 from the sea surface to 1000m-depth without the driving force of hydrology or biology
361 would require at least 200 days. This is consistent with particulate metal residence
362 times calculated at the BATS time-series site (Jickells et al., 1984). This time being
363 longer than the oligotrophic period (on average, ~ 5 months in the Northwestern
364 Mediterranean Sea), atmospheric deposition (dissolved matter and particles that do
365 not dissolve) cannot be removed from surface waters without packaging onto large
366 organic particles or aggregates, incorporation into fecal pellets (Fowler and Knauer,
367 1986; Wang and Fisher, 1998), or adsorption onto planktonic debris and fecal pellets
368 during their sinking (Fisher et al., 1991).
369 In spite of Stokesian considerations, we investigated if field observations could
370 suggest that atmospheric deposition of mineral loads is capable of causing vertical

export fluxes, either by direct sinking of mineral particles, or indirectly by atmospheric fertilization of surface waters.

Ternon et al. (2010) concluded that atmospheric deposition events drive the marine vertical export flux at the DYFAMED time-series site. Their interpretation is based on the fact that "…for this 4-years time-series, high OC fluxes were related to high marine lithogenic fluxes (their Fig. 8), forming high export events…". Both variables, OC flux and the marine lithogenic flux, are calculated as the product of the marine vertical export flux and the concentration of OC and Al, respectively. That means that both flux variables contain a similar variable, and are therefore not independent.

If we examine the atmospheric data closely we can identify 4 Saharan dust events (atmospheric flux of >1000mg.m^{-2}.d^{-1}). Only one single Saharan dust event actually resulted in significant marine vertical export flux, taking the same threshold value. This exceptionally strong input of mineral dust observed over the Ligurian Sea occurred in February 2004, when 22,210 mg.m^{-2} were deposited during a single event (Bonnet and Guieu, 2006). Marine vertical export fluxes increased during this period (Ternon et al., 2010). This Saharan dust event occurred during the dense water convection period and the marine vertical export fluxes remained elevated for the entire dense water convection period (Heimbürger et al., 2013). It is thus difficult to clearly determine what was the driving force (hydrology or atmospheric deposition) for this vertical export flux event. None of the 3 other Saharan dust events that occurred during our sampling period (Ternon et al., 2010) actually resulted in significant marine vertical export flux. For instance, a significant atmospheric dust episode that occurred during oligotrophic stratified conditions, in summer 2006 over the Ligurian Sea (Heimbürger et al., 2010b; Ternon et al., 2010) did not yield increased marine vertical export fluxes.

To further investigate the relationship of atmospherically-deposited particles and the marine vertical export flux we chose to study their chemical composition using EFs. Anthropogenic sources can be distinguished from natural ones using EFs. We calculated EFs for each metal relative to the Al concentration (M_{sample} / Al_{sample}) and normalized to the ratio ($M_{background}$ / $Al_{background}$) of Earth's continental crust (Wedepohl, 1995). Summary statistics of EFs and EF of Mediterranean aerosols are given in Table 4. EFs of all metal of the marine vertical export flux (1.23 to 8.93) are much lower compared to those of Mediterranean aerosols (2.59-597) (Heimbürger et al., 2010b). This, and the fact that vertical export flux EFs show only very low

variability, suggests again a common transport mechanism for all studied metals and that intense deposition events are smoothed out.

We applied principal component analysis after z-score transformation and Varimax rotation to extract the geochemical signatures of the chemical composition of the vertical export flux and to get insights into the underlying factors accounting for them. The square of the factor loadings was used as an estimation of the proportion of variance of each variable for each principal component (Table 5). Factor 1 explains 58 % of the variation with the main contribution of OC and all metals except Cu, Zn and Cd. The negative OC value explains the relative dilution effect of the OC contribution to metal concentrations of the vertical export flux. Factor 2 explains 21 % of the variation and is principally determined by OC, Cu and Zn. This confirms once more that all metals (except Cu, Zn and Cd, see discussion above) are accumulated in the surface waters, homogenized and exported to depth at the same time.

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

4. Conclusions

Our results suggest that the marine vertical export flux of metals is controlled by hydrology and biology, and not by atmospheric deposition. This statement is in agreement with studies by (Deuser et al. (1983); Jickells et al. (1984); Buat-Menard et al., 1989; 1998; Passow (2004)) and De La Rocha and Passow (2007). For instance, Deuser et al. (1983) noticed early on the decoupling of atmospheric

deposition and marine vertical export flux at the BATS time-series site. At the BATS time-series site, the removal of mineral particles from the surface ocean was controlled by biology. We show that the vertical export flux at the DYFAMED time-series site is controlled by both, hydrology and biology. The hydrology of the Northwestern Mediterranean Sea is strongly constrained by meteorological conditions (winter temperature, wind events, rain events) and it conditions biology (Marty and Chiavérini, 2010). As a consequence, the marine vertical export flux in the Northwestern Mediterranean Sea is strongly dependent on climatic and meteorological conditions as well. Therefore, the understanding of the interannual/decadal variability of vertical export fluxes of elements in relation with climatic and meteorological changes requires i) reliable measurements of vertical export fluxes, including the use of proxies such as ^{234}Th and ^{230}Th to minimize possible bias in the measurements (Rutten et al., 2000; Roy-Barman et al., 2009), and ii) good knowledge of physical (climatic and meteorological) parameters that determine the magnitude of dense water formation, as well as their interannual/decadal variability (Stabholz et al., 2013). This is important in terms of ongoing global change, because any alteration of the climatic/meteorological conditions would significantly impact the marine vertical export flux, and this would ultimately determine the evolution of metal cycling in the Northwestern Mediterranean, independently from changes in the atmospheric (metal) deposition. Furthermore, we recommend comparing elemental concentrations rather than elemental fluxes in marine vertical export studies.

463 Acknowledgements
464 This work was supported by the LEFE program COMET (COnstructing
465 MEditerranean Time-series). We also wish to thank the crew of the *RV Tethys II* for
466 their valuable assistance at sea, the team of the DYFAMED time-series station
467 (Observatoire Océanologique de Villefranche-sur-Mer, CNRS-INSU) and METEO-
468 FRANCE for wind data. The International Atomic Energy Agency is grateful for the
469 support provided to its Environment Laboratories by the Government of the
470 Principality of Monaco.

Tables

Table 1 Certified reference material (CRM) validation results, expressed in $\mu g.g^{-1}$. The median relative standard deviation (RSD, in %) is calculated from full replicates including the mineralization step, 10 for GBW, 5 for BCSS-1 and PACS. The median recovery observed between certified and measured values is expressed in %. Values noted * are close to the detection limit. Mean RSD values can be used to determine the uncertainty of the analytical method.

Table 2. Mean metal concentrations and fluxes at the DYFAMED site and various other moorings in the Mediterranean and Black Sea. Variability of metal concentrations is relatively low compared to the variability of vertical export flux. *values have been estimated from the available data

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

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

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

497 **Figure captions**

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

500

501 **Figure 2** Seasonal and interannual variability of vertical export flux and particulate
502 metal concentrations of a sediment trap moored at the DYFAMED site during 2003-
503 2007. Vertical export flux (column, right axis) and metal concentrations (black line
504 with dots) are expressed in $mg.m^{-2}.d^{-1}$ and $\mu g.m^{-2}.d^{-1}$, respectively.

505

References

Andersen, V., Prieur, L., 2000. One-month study in the open NW Mediterranean Sea (DYNAPROC experiment, May 1995): overview of the hydrobiogeochemical structures and effects of wind events. Deep Sea Research Part I: Oceanographic Research Papers, 47(3): 397-422.

Angelidis, M.O., Radakovitch, O., Veron, A., Aloupi, M., Heussner, S., Price, B., 2011. Anthropogenic metal contamination and sapropel imprints in deep Mediterranean sediments. Marine Pollution Bulletin, 62(5): 1041-1052.

Armstrong, R.A., Lee, C., Hedges, J.I., Honjo, S., Wakeham, S.G., 2002. A new, mechanistic model for organic carbon fluxes in the ocean based on the quantitative association of POC with ballast minerals. Deep Sea Research Part II: Topical Studies in Oceanography, 49(1–3): 219-236.

Armstrong, R.A., Peterson, M.L., Lee, C., Wakeham, S.G., 2009. Settling velocity spectra and the ballast ratio hypothesis. Deep Sea Research II, 56(18): 1470-1478.

Avril, B., 2002. DOC dynamics in the northwestern Mediterranean Sea (DYFAMED site). Deep Sea Research Part II: Topical Studies in Oceanography, 49(11): 2163-2182.

Baker, E.T., Milburn, H.B., Tennant, D.A., 1988. Field assessment of sediment trap efficiency under varying flow conditions. Journal of Marine Research, 46(3): 573-592.

Barnaba, F., Gobbi, G.P., 2004. Aerosol seasonal variability over the Mediterranean region and relative impact of maritime, continental and Saharan dust particles over the basin from MODIS data in the year 2001. Atmos. Chem. Phys. Discuss., 4(4): 4285-4337.

Béthoux, J.P., Courau, P., Nicolas, E., Ruiz-Pino, D., 1990. Trace metal pollution in the Mediterranean Sea. Oceanologica acta, 13(4): 481-488.

Béthoux, J.P., Gentili, B., 1999. Functioning of the Mediterranean Sea: past and present changes related to freshwater input and climate changes. Journal of Marine Systems, 20(1-4): 33-47.

Bollhöfer, A., Rosman, K.J.R., 2001. Isotopic source signatures for atmospheric lead: the Northern Hemisphere. Geochimica et Cosmochimica Acta, 65(11): 1727-1740.

Bonnet, S., Guieu, C., 2006. Atmospheric forcing on the annual iron cycle in the western Mediterranean Sea: A 1-year survey. Journal of Geophysical Research-Oceans, 111(C9).

Buat-Menard, P., Davies, J., Remoudaki, E., Miquel, J.C., Bergametti, G., Lambert, C.E., Ezat, U., Quetel, C., La Rosa, J., Fowler, S.W., 1989. Non-steady-state biological removal of atmospheric particles from Mediterranean surface waters. Nature, 340(6229): 131-134.

Buesseler, K.O., Antia, A.N., Chen, M., Fowler, S.W., Gardner, W.D., Gustafsson, O., Harada, K., Michaels, A.F., Rutgers van der Loeff, M., Sarin, M., Steinberg, D.K., Trull, T., 2007. An assessment of the use of sediment traps for estimating upper ocean particle fluxes. Journal of Marine Research, 65(3): 345-416.

Burd, A.B., Jackson, G.a., 2009. Particle Aggregation. Annual Review of Marine Science, 1(1): 65-90.

Carroll, M.L., Miquel, J.-C., Fowler, S.W., 1998. Seasonal patterns and depth-specific trends of zooplankton fecal pellet fluxes in the Northwestern Mediterranean Sea. Deep Sea Research Part I: Oceanographic Research Papers, 45(8): 1303-1318.

Chester, R., Nimmo, M., Corcoran, P.A., 1997. Rain water aerosol trace metal relationships at Cap Ferrat: A coastal site in the western Mediterranean. Marine Chemistry, 58(3-4): 293-312.

555 Copin-Montégut, G., Avril, B., 1993. Vertical distribution and temporal variation of
556 dissolved organic carbon in the North-Western Mediterranean Sea. Deep Sea
557 Research Part I: Oceanographic Research Papers, 40(10): 1963-1972.
558 De La Rocha, C.L., Passow, U., 2007. Factors influencing the sinking of POC and the
559 efficiency of the biological carbon pump. Deep Sea Research II, 54(5-7): 639-658.
560 Desboeufs, K.V., Losno, R., Colin, J., 2003. Figures of merit of pneumatic and ultrasonic
561 sample introduction systems in inductively coupled plasma-multichannel-based
562 emission spectrometry in an ultra-clean environment. Anal Bioanal Chem, 375(4):
563 567-573.
564 Desboeufs, K.V., Losno, R., Colin, J.L., 2001. Factors influencing aerosol solubility during
565 cloud processes. Atmospheric Environment, 35(20): 3529-3537.
566 Deuser, W.G., Brewer, P.G., Jickells, T.D., Commeau, R.F., 1983. Biological Control of the
567 Removal of Abiogenic Particles from the Surface Ocean. Science, 219(4583): 388-
568 391.
569 Duarte, C.M., Agusti, S., Kennedy, H., Vaque, D., 1999. The Mediterranean climate as a
570 template for Mediterranean marine ecosystems: the example of the northeast Spanish
571 littoral. Progress In Oceanography, 44(1-3): 245-270.
572 Duncan, B.N., Bey, I., 2004. A modeling study of the export pathways of pollution from
573 Europe: Seasonal and interannual variations (1987–1997). J. Geophys. Res.,
574 109(D8): D08301.
575 Durrieu de Madron, X., Guieu, C., Sempéré, R., Conan, P., Cossa, D., D'Ortenzio, F.,
576 Estournel, C., Gazeau, F., Rabouille, C., Stemmann, L., Bonnet, S., Diaz, F., Koubbi,
577 P., Radakovitch, O., Babin, M., Baklouti, M., Bancon-Montigny, C., Belviso, S.,
578 Bensoussan, N., Bonsang, B., Bouloubassi, I., Brunet, C., Cadiou, J.F., Carlotti, F.,
579 Chami, M., Charmasson, S., Charrière, B., Dachs, J., Doxaran, D., Dutay, J.C., Elbaz-
580 Poulichet, F., Eléaume, M., Eyrolles, F., Fernandez, C., Fowler, S., Francour, P.,
581 Gaertner, J.C., Galzin, R., Gasparini, S., Ghiglione, J.F., Gonzalez, J.L., Goyet, C.,
582 Guidi, L., Guizien, K., Heimbürger, L.E., Jacquet, S.H.M., Jeffrey, W.H., Joux, F., Le
583 Hir, P., Leblanc, K., Lefèvre, D., Lejeusne, C., Lemé, R., Loÿe-Pilot, M.D., Mallet,
584 M., Méjanelle, L., Mélin, F., Mellon, C., Mérigot, B., Merle, P.L., Migon, C., Miller,
585 W.L., Mortier, L., Mostajir, B., Mousseau, L., Moutin, T., Para, J., Pérez, T.,
586 Petrenko, A., Poggiale, J.C., Prieur, L., Pujo-Pay, M., Pulido, V., Raimbault, P., Rees,
587 A.P., Ridame, C., Rontani, J.F., Ruiz Pino, D., Sicre, M.A., Taillandier, V.,
588 Tamburini, C., Tanaka, T., Taupier-Letage, I., Tedetti, M., Testor, P., Thébault, H.,
589 Thouvenin, B., Touratier, F., Tronczynski, J., Ulses, C., Van Wambeke, F.,
590 Vantrepotte, V., Vaz, S., Verney, R., 2011. Marine ecosystems' responses to climatic
591 and anthropogenic forcings in the Mediterranean. Progress In Oceanography, 91(2):
592 97-166.
593 Fisher, N.S., Nolan, C.V., Fowler, S.W., 1991. Scavenging and retention of metals by
594 zooplankton fecal pellets and marine snow. Deep Sea Research Part A.
595 Oceanographic Research Papers, 38(10): 1261-1275.
596 Fowler, S.W., Buat-Ménard, P., Yokoyama, Y., Ballestra, S., Holm, E., Nguyen, H.V., 1987.
597 Rapid removal of Chernobyl fallout from the Mediterranean surface waters by
598 biological activity. Nature, 329(6134): 56-58.
599 Fowler, S.W., Knauer, G.A., 1986. Role of large particles in the transport of elements and
600 organic compounds through the oceanic water column. Progress In Oceanography,
601 16(3): 147-194.
602 Francois, R., Honjo, S., Krishfield, R., Manganini, S., 2002. Factors controlling the flux of
603 organic carbon to the bathypelagic zone of the ocean. Global Biogeochem. Cycles,
604 16(4): 1087.

605 Fu, G., Allen, H.E., 1992. Cadmium adsorption by oxic sediment. Water Research, 26(2):
606 225-233.
607 Grotti, M., Soggia, F., Abelmoschi, M.L., Rivaro, P., Magi, E., Frache, R., 2001. Temporal
608 distribution of trace metals in Antarctic coastal waters. Marine Chemistry, 76(3): 189-
609 209.
610 Guerzoni, S., Molinaroli, E., Rossini, P., Rampazzo, G., Quarantotto, G., De Falco, G.,
611 Cristini, S., 1999. Role of desert aerosol in metal fluxes in the Mediterranean area.
612 Chemosphere, 39(2): 229-246.
613 Guidi, L., Stemmann, L., Jackson, G.A., Ibanez, F., Claustre, H., Legendre, L., Picheral, M.,
614 Gorsky, G., 2009. Effects of phytoplankton community on production, size and export
615 of large aggregates: A world-ocean analysis. Limnology and Oceanography, 54(6):
616 1951-1963.
617 Hamm, C.E., 2002. Interactive aggregation and sedimentation of diatoms and clay-sized
618 lithogenic material. Limnol. Oceanogr., 47(6): 1790-1795.
619 Heimbürger, L.E., Cossa, D., Marty, J.-C., Migon, C., Averty, B., Dufour, A., Ras, J., 2010a.
620 Methylmercury distributions in relation to the presence of nano- and
621 picophytoplankton in an oceanic water column (Ligurian Sea, North-western
622 Mediterranean). Geochimica Et Cosmochimica Acta, 74(19): 5549-5559.
623 Heimbürger, L.E., Cossa, D., Thibodeau, B., Khripounoff, A., Mas, V., Chiffoleau, J.-F.,
624 Schmidt, S., Migon, C., 2012. Natural and anthropogenic trace metals in sediments of
625 the Ligurian Sea (Northwestern Mediterranean). Chemical Geology, 291(0): 141-151.
626 Heimbürger, L.E., Lavigne, H., Migon, C., D'Ortenzio, F., Estournel, C., Coppola, L.,
627 Miquel, J.-C., 2013. Temporal variability of vertical export flux at the DYFAMED
628 time-series station (Northwestern Mediterranean Sea). Progress in Oceanography,
629 119(0): 59-67.
630 Heimbürger, L.E., Migon, C., Cossa, D., 2011. Impact of atmospheric deposition of
631 anthropogenic and natural trace metals on Northwestern Mediterranean surface
632 waters: A box model assessment. Environmental Pollution, 159(6): 1629-1634.
633 Heimbürger, L.E., Migon, C., Dufour, A., Chiffoleau, J.F., Cossa, D., 2010b. Trace metal
634 concentrations in the North-western Mediterranean atmospheric aerosol between 1986
635 and 2008: Seasonal patterns and decadal trends. Science of The Total Environment,
636 408(13): 2629-2638.
637 Herut, B., Nimmo, M., Medway, A., Chester, R., Krom, M.D., 2001. Dry atmospheric inputs
638 of trace metals at the Mediterranean coast of Israel (SE Mediterranean): sources and
639 fluxes. Atmospheric Environment, 35(4): 803-813.
640 JGOFS, 1996. Protocols for the Joint Global Ocean Flux Study (JGOFS) core measurements.
641 Jickells, T.D., Deuser, W.G., Knap, A.H., 1984. The sedimentation rates of trace elements in
642 the Sargasso Sea measured by sediment trap. Deep Sea Research Part A.
643 Oceanographic Research Papers, 31(10): 1169-1178.
644 Jickells, T.D., Dorling, S., Deuser, W.G., Church, T.M., Arimoto, R., Prospero, J.M., 1998.
645 Air-borne dust fluxes to a deep water sediment trap in the Sargasso Sea. Global
646 Biogeochemical Cycles, 12(2): 311-320.
647 Kersten, M., Kriews, M., Förstner, U., 1991. Partitioning of trace metals released from
648 polluted marine aerosols in coastal seawater. Marine Chemistry, 36(1–4): 165-182.
649 Klaas, C., Archer, D.E., 2002. Association of sinking organic matter with various types of
650 mineral ballast in the deep sea: Implications for the rain ratio. Global Biogeochem.
651 Cycles, 16(4): 1116.
652 Krahmann, G., Schott, F., 1998. Longterm increases in Western Mediterranean salinities and
653 temperatures: anthropogenic and climatic sources. Geophysical Research Letters,
654 25(22): 4209-4212.

655 Laubier, L., 2005. Mediterranean Sea and humans: Improving a conflictual partnership.,
656 Handbook of Environmental Chemistry, pp. 3-27.
657 Lee, C., Armstrong, R.A., Cochran, J.K., Engel, A., Fowler, S.W., Goutx, M., Masqué, P.,
658 Miquel, J.C., Peterson, M., Tamburini, C., Wakeham, S., 2009. MedFlux:
659 Investigations of particle flux in the Twilight Zone. Deep Sea Research II, 56(18):
660 1363-1368.
661 Lévy, M., Memery, L., Andre, J.M., 1998. Simulation of primary production and export
662 fluxes in the Northwestern Mediterranean Sea. Journal of Marine Research, 56(1):
663 197-238.
664 Martín, J., Sanchez-Cabeza, J.A., Eriksson, M., Levy, I., Miquel, J.C., 2009. Recent
665 accumulation of trace metals in sediments at the DYFAMED site (Northwestern
666 Mediterranean Sea). Marine Pollution Bulletin, 59(4-7): 146-153.
667 Martin, J.H., Knauer, G.A., Karl, D.M., Broenkow, W.W., 1987. VERTEX: carbon cycling in
668 the northeast Pacific. Deep Sea Research I, 34(2): 267-285.
669 Martin, J.M., Milliman, J.D., 1997. EROS 2000 (European River Ocean System). The
670 western Mediterranean: An introduction. Deep Sea Research II, 44(3-4): 521-529.
671 Marty, J.-C., 2002. The DYFAMED time-series program (French-JGOFS). Deep Sea
672 Research II, 49(11): 1963-1964.
673 Marty, J.-C., Garcia, N., Raimbault, P., 2008. Phytoplankton dynamics and primary
674 production under late summer conditions in the NW Mediterranean Sea. Deep Sea
675 Research Part I: Oceanographic Research Papers, 55(9): 1131-1149.
676 Marty, J.C., Chiavérini, J., 2010. Hydrological changes in the Ligurian Sea (NW
677 Mediterranean, DYFAMED site) during 1995–2007 and biogeochemical
678 consequences. Biogeosciences, 7: 2117-2128.
679 Marty, J.C., Chiavérini, J., Pizay, M.D., Avril, B., 2002. Seasonal and interannual dynamics
680 of nutrients and phytoplankton pigments in the western Mediterranean Sea at the
681 DYFAMED time-series station (1991-1999). Deep Sea Research II, 49(11): 1965-
682 1985.
683 Marty, J.C., Goutx, M., Guigue, C., Leblond, N., Raimbault, P., 2009. Short-term changes in
684 particulate fluxes measured by drifting sediment traps during end summer
685 oligotrophic regime in the NW Mediterranean Sea. Biogeosciences, 6(5): 887-899.
686 Marty, J.C., Nicolas, E., J.C., M., Fowler, S.W., 1994. Particulate fluxes of organic
687 compounds and their relationship to zooplankton fecal pellets in the northwestern
688 Mediterranean Sea. Marine Chemistry, 46: 387 - 405.
689 Migon, C., 2005. Trace Metals in the Mediterranean Sea. In: Saliot, A. (Ed.), The
690 Mediterranean Sea. Springer, Berlin, Heidelberg, New York.
691 Migon, C., Robin, T., Dufour, A., Gentili, B., 2008. Decrease of lead concentrations in the
692 Western Mediterranean atmosphere during the last 20 years. Atmospheric
693 Environment, 42(4): 815-821.
694 Migon, C., Sandroni, V., Marty, J.-C., Gasser, B., Miquel, J.-C., 2002. Transfer of
695 atmospheric matter through the euphotic layer in the northwestern Mediterranean:
696 seasonal pattern and driving forces. Deep Sea Research II(49): 2125-2141.
697 Miquel, J.-C., Martín, J., Gasser, B., Rodriguez-y-Baena, A., Toubal, T., Fowler, S.W., 2011.
698 Dynamics of particle flux and carbon export in the northwestern Mediterranean Sea:
699 A two decade time-series study at the DYFAMED site. Progress In Oceanography,
700 91(4): 461-481.
701 Miquel, J.C., Fowler, S.W., La Rosa, J., Buat-Ménard, P., 1994. Dynamics of the Downward
702 Flux of Particles and Carbon in the Open Northwestern Mediterranean-Sea. Deep Sea
703 Research I, 41(2): 243-261.

Morley, N.H., Burton, J.D., Tankere, S.P.C., Martin, J.M., 1997. Distribution and behaviour of some dissolved trace metals in the western Mediterranean Sea. Deep Sea Research II, 44(3-4): 675-691.

Moulin, C., Guillard, F., Dulac, F., Lambert, C.E., 1997. Long-term daily monitoring of Saharan dust load over ocean using Meteosat ISCCP-B2 data: 1. Methodology and preliminary results for 1983–1994 in the Mediterranean. Journal of Geophysical Research: Atmospheres, 102(D14): 16947-16958.

Muller, F.L.L., 1996. Interactions of copper, lead and cadmium with the dissolved, colloidal and particulate components of estuarine and coastal waters. Marine Chemistry, 52(3–4): 245-268.

Niewiadomska, K., Claustre, H., Prieur, L., d'Ortenzio, F., 2008. Submesoscale physical-biogeochemical coupling across the Ligurian Current (northwestern Mediterranean) using a bio-optical glider. Limnology and Oceanography, 53(5): 2210-2225.

Passow, U., 2004. Switching perspectives: Do mineral fluxes determine particulate organic carbon fluxes or vice versa? Geochemistry Geophysics Geosystems, 5: 5.

Roussiez, V., Heussner, S., Ludwig, W., Radakovitch, O., Durrieu de Madron, X., Guieu, C., Probst, J.-L., Monaco, A., Delsaut, N., 2012. Impact of oceanic floods on particulate metal inputs to coastal and deep-sea environments: A case study in the NW Mediterranean Sea. Continental Shelf Research, 45(0): 15-26.

Roy-Barman, M., Lemaître, C., Ayrault, S., Jeandel, C., Souhaut, M., Miquel, J.C., 2009. The influence of particle composition on Thorium scavenging in the Mediterranean Sea. Earth and Planetary Science Letters, 286(3-4): 526-534.

Rutten, A., de Lange, G.J., Ziveri, P., Thomson, J., van Santvoort, P.J.M., Colley, S., Corselli, C., 2000. Recent terrestrial and carbonate fluxes in the pelagic eastern Mediterranean; a comparison between sediment trap and surface sediment. Palaeogeography, Palaeoclimatology, Palaeoecology, 158(3-4): 197-213.

Sarthou, G., Jeandel, C., 2001. Seasonal variations of iron concentrations in the Ligurian Sea and iron budget in the Western Mediterranean Sea. Marine Chemistry, 74(2-3): 115-129.

Scholten, J.C., Fietzke, J., Vogler, S., van der Loeff, M.M.R., Mangini, A., Koeve, W., Waniek, J., Stoffers, P., Antia, A., Kuss, J., 2001. Trapping efficiencies of sediment traps from the deep Eastern North Atlantic: the Th-230 calibration. Deep Sea Research II, 48(10): 2383-2408.

Stabholz, M., Durrieu de Madron, X., Canals, M., Khripounoff, A., Taupier-Letage, I., Testor, P., Heussner, S., Kerhervé, P., Delsaut, N., Houpert, L., Lastras, G., Dennielou, B., 2013. Impact of open-ocean convection on particle fluxes and sediment dynamics in the deep margin of the Gulf of Lions. Biogeosciences, 10(2): 1097-1116.

Sternberg, E., Jeandel, C., Miquel, J.-C., Gasser, B., Souhaut, M., Arraes-Mescoff, R., Francois, R., 2007. Particulate barium fluxes and export production in the northwestern Mediterranean. Marine Chemistry, 105(3–4): 281-295.

Stokes, G.G., 1901. Mathematical and Physical papers, Cambridge University Press, Cambridge, pp. 413.

Ternon, E., Guieu, C., Loÿe-Pilot, M.-D., Leblond, N., Bosc, E., Gasser, B., Miquel, J.-C., Martín, J., 2010. The impact of Saharan dust on the particulate export in the water column of the North Western Mediterranean Sea. Biogeosciences, 7: 809-826.

Theodosi, C., Markaki, Z., Tselepides, A., Mihalopoulos, N., 2010. The significance of atmospheric inputs of soluble and particulate major and trace metals to the eastern Mediterranean seawater. Marine Chemistry, 120(1-4): 154-163.

753 Theodosi, C., Parinos, C., Gogou, A., Kokotos, A., Stavrakakis, S., Lykousis, V.,
754 Hatzianestis, J., Mihalopoulos, N., 2012. Downward fluxes of elemental carbon,
755 metals and polycyclic aromatic hydrocarbons in settling particles from the deep
756 Ionian Sea (NESTOR site), Eastern Mediterranean. Biogeosciences Discuss., 9(12):
757 19165-19197.
758 Theodosi, C., Stavrakakis, S., Koulaki, F., Stavrakaki, I., Moncheva, S., Papathanasiou, E.,
759 Sanchez-Vidal, A., Koçak, M., Mihalopoulos, N., 2013. The significance of
760 atmospheric inputs of major and trace metals to the Black Sea. Journal of Marine
761 Systems, 109–110(0): 94-102.
762 UNEP/MEDPOL, 2004. United Nations Environment Program: Mediterranean Action Plan
763 MED POL Transboundary diagnostic analysis (TDA) for the Mediterranean Sea.,
764 Athens.
765 Wang, W.X., Fisher, N.S., 1998. Excretion of trace elements by marine copepods and their
766 bioavailability to diatoms. Journal of Marine Research, 56(3): 713-729.
767 Wedepohl, H.K., 1995. The composition of the continental crust. Geochimica Et
768 Cosmochimica Acta, 59(7): 1217-1232.
769
770