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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 North-western 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 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.

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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; 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; Krahnemann and

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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., 2010a). 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., 2010a; 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 presumably reflects the evolution of anthropogenic metal emissions along the densely populated Mediterranean coast (~300 inhabitants per km² (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 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, 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 1000 m-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 (2350 m-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). Therefore, atmospheric metal inputs are believed to be by far the most significant source to the open Ligurian Sea (Migon et al., 2002). 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 Marty, 2002 and Lee et al. 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 2.3 m, collection area 1 m²) were equipped with a programmable 24-cup collector. The sampling cups contained a solution of 2% buffered formaldehyde in filtered seawater (0.22 µm) 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 600 µm and followed by hand-picking under the binocular microscope. The remaining samples were then desalted by rinsing on a Nuclepore filter (porosity 1 µm) with buffered (pH 7) deionized Milli-Q[®] Millipore water (resistivity: 18 MΩ cm) three times (JGOFS, 1996) and freeze-dried prior to analysis (Miquel et al., 1994, 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 (HNO₃) while the mineral aluminosilicate matrices were destroyed with HF. Every freeze-dried sample was weighed in 7 mL Teflon flasks, and dissolved as follows: (1) each flask was filled with 1 mL HNO₃ 65% (suprapur, Merck), sealed and placed in a larger Teflon bottle (60 mL). This apparatus was left 6 h 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) 500 µL HNO₃ 65% and 500 µL HF 40% were added to the remainder. The flasks and bottles were closed and put in an oven 6 h 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 5 mL HNO₃ 0.1 N and then diluted with HNO₃ 0.1 N to 15 mL.

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 1250 W and a sample flow of 1 mL min⁻¹ were used. An external calibration was performed with multi-elemental standard solutions made by mixing 1 g 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 > 12 cm 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.

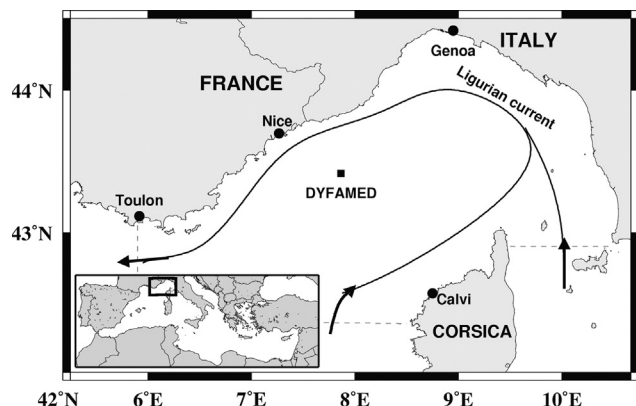


Fig. 1. Map of the Northwestern Mediterranean Sea and the location of the time-series sampling station DYFAMED.

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