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Temporal variability of vertical export flux at the DYFAMED time-series station (Northwestern Mediterranean Sea)

Lars-Eric Heimbürger^{a,b,c,*}, Héloïse Lavigne^{a,b}, Christophe Migon^{a,b}, Fabrizio D’Ortenzio^{a,b}, Claude Estournel^d, Laurent Coppola^{a,b}, Juan-Carlos Miquel^e

^a Université Pierre et Marie Curie, UMR 7093, Laboratoire d’Océanographie de Villefranche, F-06230 Villefranche-sur-Mer, France

^b Centre National de la Recherche Scientifique (CNRS), UMR 7093, Laboratoire d’Océanographie de Villefranche, Villefranche-sur-Mer, France

^c Geosciences Environment Toulouse (GET), Midi-Pyrenees Observatory (OMP), 14 Avenue Edouard Belin, 31400 Toulouse, France

^d Centre National de la Recherche Scientifique (CNRS), Laboratoire d’Aérodologie, 14 Avenue Edouard Belin, 31400 Toulouse, France

^e International Atomic Energy Agency, Environment Laboratories, 4 Quai Antoine 1er, MC 98000, Monaco

The temporal evolution of the vertical export flux at the DYFAMED time-series station (Ligurian Sea) over the last 20 years reveals a strong interannual variability. Winter convection allows particulate (and dissolved) matter to be vertically exported (“flush-down” effect). The efficiency of this process determines also the concentration of nutrients brought to surface waters and, therefore, the intensity of the subsequent phytoplankton bloom. The sequence “convection-bloom” is the main driving force of vertical export flux in this region. The present work attempts to better identify the parameters that control vertical export flux dynamics by observing a 20 year time-series in relation with the temporal variability of mixed layer depth and surface primary production. The consequences of a more stratified water column in the future on biological productivity and vertical export flux are pointed out.

1. Introduction

The Mediterranean Sea is a semi-enclosed basin where evaporation outweighs the sum of freshwater inputs (precipitations and rivers) with a negative balance of approximately 10% (Béthoux, 1979). In this concentration basin, prevailing winds in winter lead through cooling and evaporation to an increase in the density of the surface waters inducing vertical convection (Millot and Taupier-Letage, 2005; Stabholz et al. 2013). This is a key process for the Mediterranean biogeochemistry because vertical convection brings amounts of nutrient from depths to surface layers and enables early spring phytoplankton blooms (Migon et al., 2002). Besides, the relatively reduced dimensions of the Mediterranean Sea (2.51×10^6 km²) enhance the influence of continental emission sources, in particular atmospheric inputs, on the biogeochemistry of its open waters. Land masses are not only in proximity, but they are also heavily populated, subject to intense touristic, agricultural and industrial activities. As a result, atmospheric inputs enrich offshore surface waters in a variety of macro- and micronutrients (Guerzoni et al., 1999; Béthoux et al., 2002; Heimbürger et al., 2010b, 2011). Increased metal concentrations due to

anthropogenic emissions have been detected in marine sediment records (Martín et al., 2009; Heimbürger et al., 2012).

Due to the above described features and the short water residence times of 15 and 50 years in the Western and the Eastern Basin, respectively (Béthoux, 1980), the Mediterranean Sea is particularly sensitive to both climatic and environmental changes (Krahmann and Schott, 1998; Béthoux and Gentili, 1999; Duarte et al., 1999). On the one hand, nutrient inputs to the euphotic layer through vertical convection rely on climatic and meteorological conditions; on the other hand, atmospheric inputs of nutrients that affect Mediterranean surface waters are connected to environmental changes. Physical forcing (wind stress, temperature, and heat flux) seems to determine the timing and the magnitude of phytoplankton blooms in the Mediterranean Sea. Spring blooms are localized only in areas where strong meteorological features occur (D’Ortenzio and Ribera d’Alcalà, 2009), i.e. for the case of the Northwestern basin, the Ligurian Sea and the Gulf of Lions, under the action of prevailing northwesterly winds Mistral and Tramontane. Paleoclimatic studies have shown that the Mediterranean Sea is likely to drastically change its physical dynamics, owing to climatic changes affecting exchanges between the atmosphere and the sea surface, and this may have major biogeochemical consequences as a result of perturbations in the process of dense water formation, i.e. the availability of nutrients (Béthoux, 1984, 1993).

Production and mineralization of biogenic matter and deposition of atmospherically-transported inorganic nutrients both feed

* Corresponding author. Present address: Geosciences Environment Toulouse (GET), Midi-Pyrenees Observatory (OMP), 14 Avenue Edouard Belin, 31400 Toulouse, France. Tel.: +33 630266544.

E-mail addresses: larsheimbuenger@gmx.de, heimbuerger@get.obs-mip.fr (L.-E. Heimbürger).

surface waters, according to the seasonal occurrence of vertical mixing and atmospheric inputs, respectively. Therefore, the transfer of dissolved and particulate matter to depths also exhibits marked seasonal patterns (Copin-Montégut and Avril, 1993; Avril, 2002; Gačić et al., 2002; Migon et al., 2002; Sternberg et al., 2007; Heimbürger et al., 2010a). However, the debate is still open as to which process determines vertical export flux. Indeed, owing to the key role of vertical convection and atmospheric inputs in supplying nutrients to surface waters, it is still difficult to determine which processes control the temporal variability of vertical export flux to the seafloor. Armstrong et al. (2002) have postulated that fluxes of mineral material (biogenic silica, carbonate shells and atmospheric dust), rather than subsurface particulate organic carbon (POC) fluxes, determine deep POC fluxes. It is known that atmospheric Saharan lithogenic particles, biogenic silica and carbonate shells are likely to catalyze particle aggregation and ballast biogenic material, hence control their sinking rate (Lee et al., 2009b). Also, De La Rocha and Passow (2007) have suggested that lithogenic material may protect POC from oxidation and remineralization. To the contrary, numerous other studies have suggested that biological and biogeochemical processes occurring in the upper marine layer control the temporal variability of subsurface fluxes in the Northwestern Mediterranean (Fowler and Knauer, 1986; Fowler et al., 1987; Buat-Menard et al., 1989; Marty et al., 1994; Miquel et al., 1994, 2011; Migon et al., 2002; Passow, 2004; Passow and De La Rocha, 2006; Martín and Miquel, 2010). Migon et al. (2002) have shown that, besides the biological processes, the vertical mixing of the water column is an important factor determining the magnitude of the vertical export flux. Passow (2004) has pointed out that large aggregates (marine snow) exhibit high settling velocities ($50\text{--}200\text{ m d}^{-1}$) and presumably collect and scavenge amounts of mineral particles too small to sediment individually, according to Stokes' law (Stokes, 1901). It is difficult to state whether mineral fluxes determine POC fluxes or *vice versa*. With the present work we contribute to a better understanding of the relative importance of autochthonous physical and biological processes versus allochthonous atmospheric processes for marine vertical export fluxes. We present time-series data on vertical export flux collected by sediment traps together with the variability of mixed layer depth and primary production, from 1988 to 2008.

2. Experimental

2.1. Study site

The DYFAMED (Dynamique des Flux Atmosphériques en Méditerranée) time-series station (2350-m depth, $43^{\circ}25'N$, $7^{\circ}52'E$) is a long-term monitoring station in the open Ligurian Sea (Northwestern Mediterranean Sea) located 28 nautical miles off continental France, surrounded by the permanent geostrophic Ligurian frontal jet flow (Fig. 1) that results from the cyclonic circulation of the Northern Current (Millot, 1999). This front creates a band $\sim 30\text{-km}$ wide and to a depth of $>250\text{ m}$ that supposedly separates the sampling site from coastal lateral inputs by strong horizontal density gradient (Niewiadomska et al., 2008). The station is characterized by high salinity (>38), a shallow thermocline in summer and deep mixing events in winter. The productivity regime ranges from mesotrophy in spring to oligotrophy in summer and fall. After data averaged over the 1993–1999 period, the mean net primary production is $156\text{ g C m}^{-2}\text{ y}^{-1}$ (Marty and Chiavérini, 2002). Despite infrequent intrusions of waters coming from the Northern Current in winter (Millot, 1999), the DYFAMED station is probably minimally affected by lateral inputs. Acoustic Doppler Current Profiler (ADCP) measurements have shown that the site is sheltered from the Northern Current (Andersen and Prieur, 2000). Therefore, it is generally accepted as an open-ocean site.

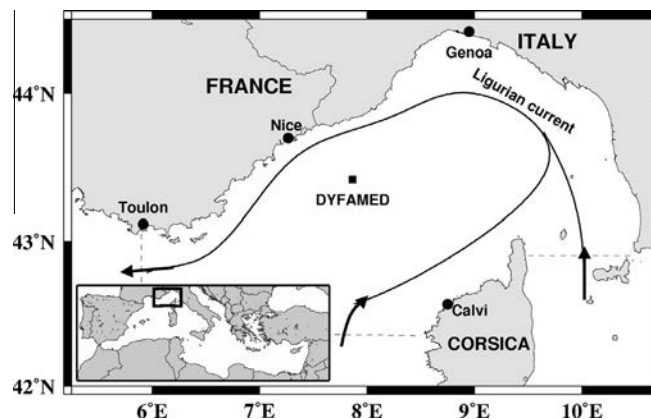


Fig. 1. Location of the DYFAMED time-series station.

Owing to the proximity and intensity of land-based emission sources, the Northwestern Mediterranean is strongly affected by atmospheric inputs of both natural lithogenic material, i.e. mainly Saharan dust (Moulin et al., 1998; Barnaba and Gobbi, 2004), and anthropogenic material (Duncan and Bey, 2004; Pey et al., 2010). In addition, the DYFAMED station is globally isolated from riverine inputs by the Northern Current, such inputs being particularly poor in the Ligurian Sea (Migon, 1993). Therefore, the atmosphere is considered the only significant external source of natural and anthropogenic matter to the open Ligurian Sea (Guerzoni et al., 1999). For this reason, the DYFAMED site has been used several times to study the interactions between atmospheric deposition and open-ocean surface waters (e.g., DYFAMED and MEDFLUX programs; see special issues Deep-Sea Research II 49, 11 (2002) and 56, 18 (2009a), respectively), and it is now viewed as a reference to monitor ongoing changes in the Northwestern Mediterranean Sea.

2.2. Methods

2.2.1. Sediment traps

Automated time-series sediment traps were moored at 200-m depth at the DYFAMED site. The conical sediment traps (Technicap PPS-5, height 2.3 m, collection area 1 m^2) were equipped with a programmable 24-cup collector. The sampling cups contained a solution of 5% buffered formaldehyde in filtered seawater ($0.22\text{ }\mu\text{m}$) to prevent *in situ* microbial degradation and grazing by swimmers. Formaldehyde has been widely used as preservative in trap time-series studies because its use reduces the loss of organic material from the trap (JGOFS, 1999). After recovery, the samples were stored in the dark at $4\text{ }^{\circ}\text{C}$. Swimmers were first removed by successive sieving through 1500 and 600 μm and further by hand-picking under a binocular microscope. The remaining samples after initial wet subsampling were then desalinated and freeze-dried for further analysis and the estimation of vertical export flux (Miquel et al., 1994, 2011). Vertical export fluxes were determined for samples from 1988 to 2008. Samples were missing for the following periods: 21 October to 13 December 1988, 5 June to 1 August 1990, 28 February to 22 April 1991, 7 June 1991 to 13 May 1993, 22 November 1994 to 6 May 1995, 18 September 1995 to 18 October 1997, 6 April to 23 July 1998, 10 August 1998 to 6 February 1999, 22 January 2001 to 28 July 2001, and 5 August 2002 to 24 November 2002.

2.2.2. Ocean color surface chlorophyll-a

From the daily Level 3 standard Mapped Images of SeaWiFS surface *Chl-a* at 9 km resolution downloaded from NASA web site (<http://oceancolor.gsfc.nasa.gov/>) for the period 1998–2009, the

DYFAMED ocean color chlorophyll-*a* time-series was obtained by averaging all pixels contained in a $\pm 0.1^\circ$ box centered on the DYFAMED geographical position. Although a bias in the ocean color surface *Chl-a* estimations obtained with the NASA standard algorithm (O'Reilly et al., 2000) was identified for the Mediterranean Sea (30% on the average, Bosc et al., 2004; Claustre et al., 2002; D'Ortenzio et al., 2002; Volpe et al., 2007), the NASA standard product was preferred to regional algorithms, because we focused more on the relative changes in phytoplankton dynamics than on the absolute values.

2.2.3. *In situ* chlorophyll

Monthly cruises were conducted on-board the *RV Téthys II*, except when meteorological conditions were too intense. On each cruise, two CTD casts were obtained, for the 0–200 m layer and the 0–2000 m layer, respectively. The CTD system was a SeaBird SBE 911 Plus unit mounted on a SeaBird rosette equipped with twelve 12-L Niskin bottles.

Vertical export fluxes may be *a priori* difficult to relate to concentrations of chlorophyll-*a* (*Chl-a*), because *Chl-a* concentrations do not give information on the relative abundances of phytoplankton populations. Different phytoplankton populations have different export potentials. Therefore, a decoupling between *Chl-a* and vertical export flux time-series is expected, as pointed out by Marty and Chiavérini (2002). The vertical export fluxes should also be compared with micro-, nano-, and pico-*Chl-a* concentrations to better show the causal relationships between phytoplankton biomass and vertical export flux, if any (Uitz et al., 2006). Specific diagnostic pigments are widely used as biomarkers of various phytoplankton species composition, and can be assigned, to a large extent, to different phytoplankton size classes (Goericke and Repeta, 1992; Claustre, 1994; Vidussi et al., 2001; Uitz et al., 2006). Therefore, the respective contribution of each class to the total standing algal stock (which means, in the present work, to vertical export fluxes) can be assigned as well. The chemotaxonomic correspondence of diagnostic pigments determined by High-Performance Liquid Chromatography (HPLC) is given in Table 1. Water samples for the determination of *Chl-a* concentrations were filtrated onto 25-mm Whatman GF/F glass fiber filters. The filters were frozen and analyzed by HPLC within 3 months. Filters were ground and sonicated in 3 mL methanol under dim light conditions. Protocols for HPLC pigment analysis, as well as the separation method used (RP-C8) to obtain a complete resolution between divinyl-*Chl-a* and *Chl-a* can be found in Vidussi et al. (1996a, 1996b). Pigment determination was performed using HPLC techniques (Ras et al., 2008). This method, initially proposed by Claustre (1994) and further improved by Vidussi et al. (2001) and Uitz et al. (2006), was used to estimate the contribution of three pigment-based size classes to the total phytoplankton biomass: micro- (>20 μm), nano- (2–20 μm), and picophytoplankton (<2 μm).

2.2.4. Mixed layer depth

The occurrence and intensity of mixing was assessed through the interannual variations of the MLD. For each CTD cast at the DYFAMED station, the profile of potential density was computed from profiles of potential temperature and salinity. Then, the MLD was assessed using a density criterion of 0.03 kg m^{-3} from a near-surface value at 10-m depth (de Boyer Montégut et al., 2004; D'Ortenzio et al., 2005). As shipboard CTD casts do not sufficiently resolve the temporal variability of the MLD, estimates of the MLD were also provided by an interannual run of the primitive-equation, free-surface, Symphonie model (Herrmann et al., 2008; Marsaleix et al., 2008) applied to the Northwestern Mediterranean. The Symphonie model was forced at the lateral boundaries by the interannual simulation of the Mediterranean Sea (Beuvier et al., 2010) and at the surface by the dynamic down-scaling of ECMWF named ARPERA (Herrmann and Somot, 2008). The horizontal resolution was $2.5 \times 2.5 \text{ km}^2$. MLD was computed from the daily averaged vertical diffusivities profiles using a threshold value of $4 \times 10^{-4} \text{ m}^2 \text{ s}^{-1}$ (Herrmann et al., 2008). Then, MLDs corresponding to the DYFAMED point were extracted and then daily averaged.

3. Results and discussion

The temporal variability of the vertical export flux is depicted in Fig. 2. The efficiency of moored sediment traps has been addressed by several studies (Honjo et al., 1992; Scholten et al., 2001; Yu et al., 2001; Buesseler et al., 2007, 2010). Scholten et al. (2001) found no relation between trapping efficiency, whereas Yu et al. (2001) and Buesseler et al. (2010) find lower trapping efficiencies for shallow moored traps. We cannot exclude the possibility such bias have affected our sediment trap moored at 200-m depth. Preliminary results on Thorium (Roy-Barman, pers. comm.) suggest that this sediment trap (200-m depth) captured the vertical export flux more efficiently than the lower trap of the same mooring line (1000 m-depth). Years 2005 and 2006 were affected by high current speeds (at both trapping depths). Current speeds $>10 \text{ cm s}^{-1}$ are likely to affect both quantitatively and qualitatively the trapping of sinking particles (Baker et al., 1988; Buesseler et al., 2007). This situation occurred from 22 February to 23 June 2005, and during most of the year 2006 due to strong episodes of deep water formation in the region (Martín and Miquel, 2010). Several studies have however used sediment traps in highly dynamic zones, such as the Gulf of Lions (Canals et al., 2006; Heussner et al., 2006; Stabholz et al., 2013). We preferred to discard such episodes of high current speeds in order to circumvent any bias. Samples from the above period of 2005 and the whole year 2006 are presented in Fig. 2, but they are not considered in the discussion.

3.1. Seasonal pattern

Vertical export flux time-series exhibit a reproducible seasonal pattern, as already observed in other marine regions (e.g. the

Table 1

Taxonomic significance and corresponding size class of diagnostic pigments measured by HPLC (from Vidussi et al., 2001, and references therein).

Pigments	Taxonomic significance	Size (μm)
Zeaxanthin	Cyanobacteria and prochlorophytes	<2
Divinyl-chlorophyll <i>a</i>	Prochlorophytes	<2
Chlorophyll <i>b</i> + divinyl-chlorophyll <i>b</i>	Green flagellates and prochlorophytes	<2
19' Hexanoyloxyfucoxanthin	Chromophytes nanoflagellates	2–20
19' Butanoyloxyfucoxanthin	Chromophytes nanoflagellates	2–20
Alloxanthin	Cryptophytes	2–20
Fucoxanthin	Diatoms	>20
Peridinin	Dinoflagellates	>20

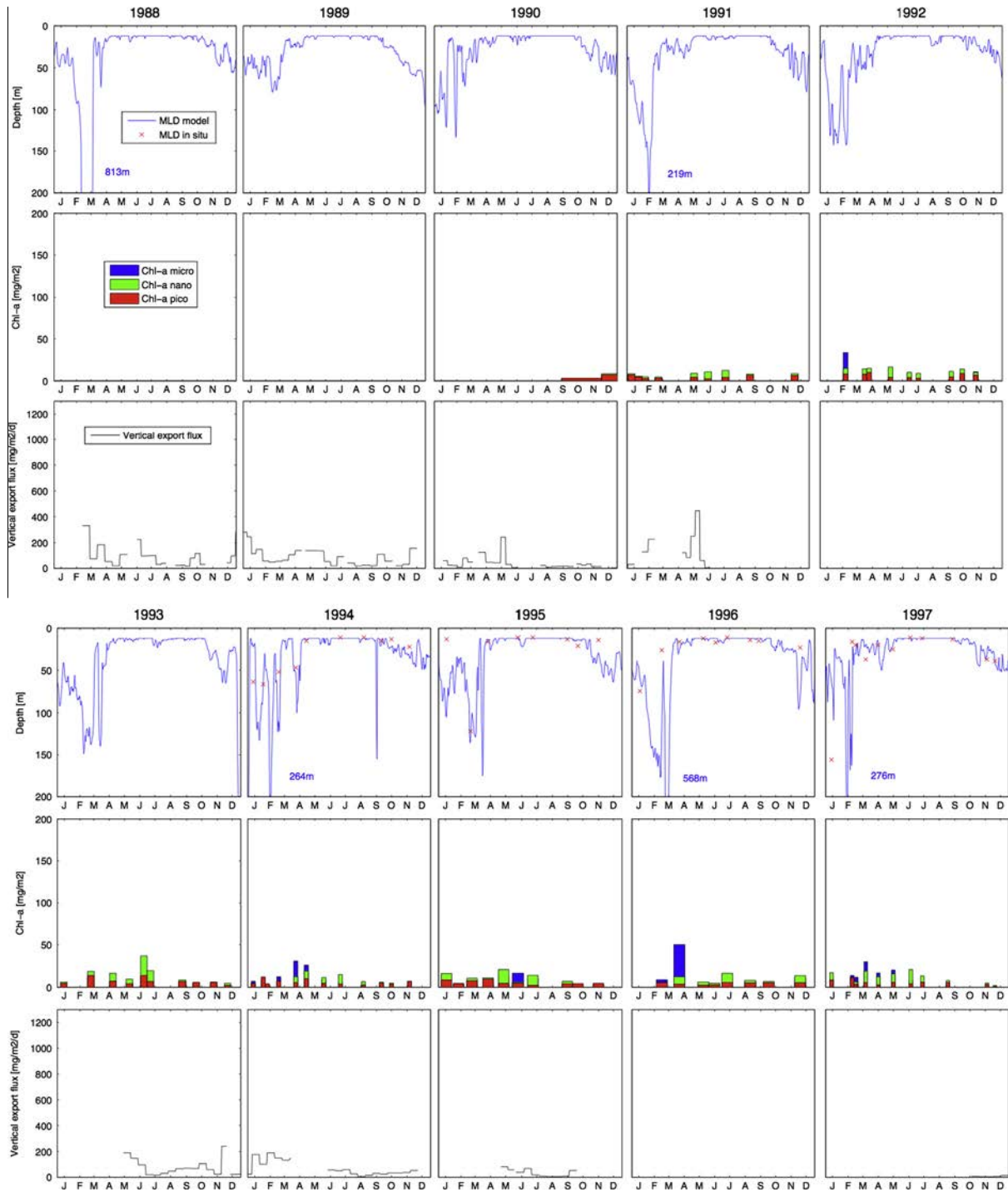


Fig. 2. Top panels: Yearly variations of discrete MLD calculated from the CTD profiles (crosses) and daily MLD from the Symphonie model (blue line). Middle panels: Daily ocean color surface *Chl-a* (line) and pigment derived micro-, nano- and pico-*Chl-a* concentrations integrated from surface to 200-m depth. Lower panels: Vertical export flux ($\text{mg m}^{-2} \text{d}^{-1}$) collected with the PPS-5 sediment traps deployed at the DYFAMED station from 1988 to 2007. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

northeast Atlantic; (Newton et al., 1994; Lampitt et al., 2001). Although the interannual reproducibility is not always marked, the vertical export flux time-series data Fig. 2 exhibit a seasonal pattern, of which interannual variations will be discussed in the following sub-section. Basically, this structure agrees with the three-step scenario proposed by Migon et al. (2002) at the same sampling station and same depth:

- (1) In winter, the cooling of surface water, combined with evaporation, increases its density and determines the vertical convection. This allows for a rapid downward transfer of dissolved and particulate matter, yielding high vertical export flux. This “flush-down effect” results from a combination of convection and gravitational flux, since the diving of dense surface waters breaks the stratification of the water

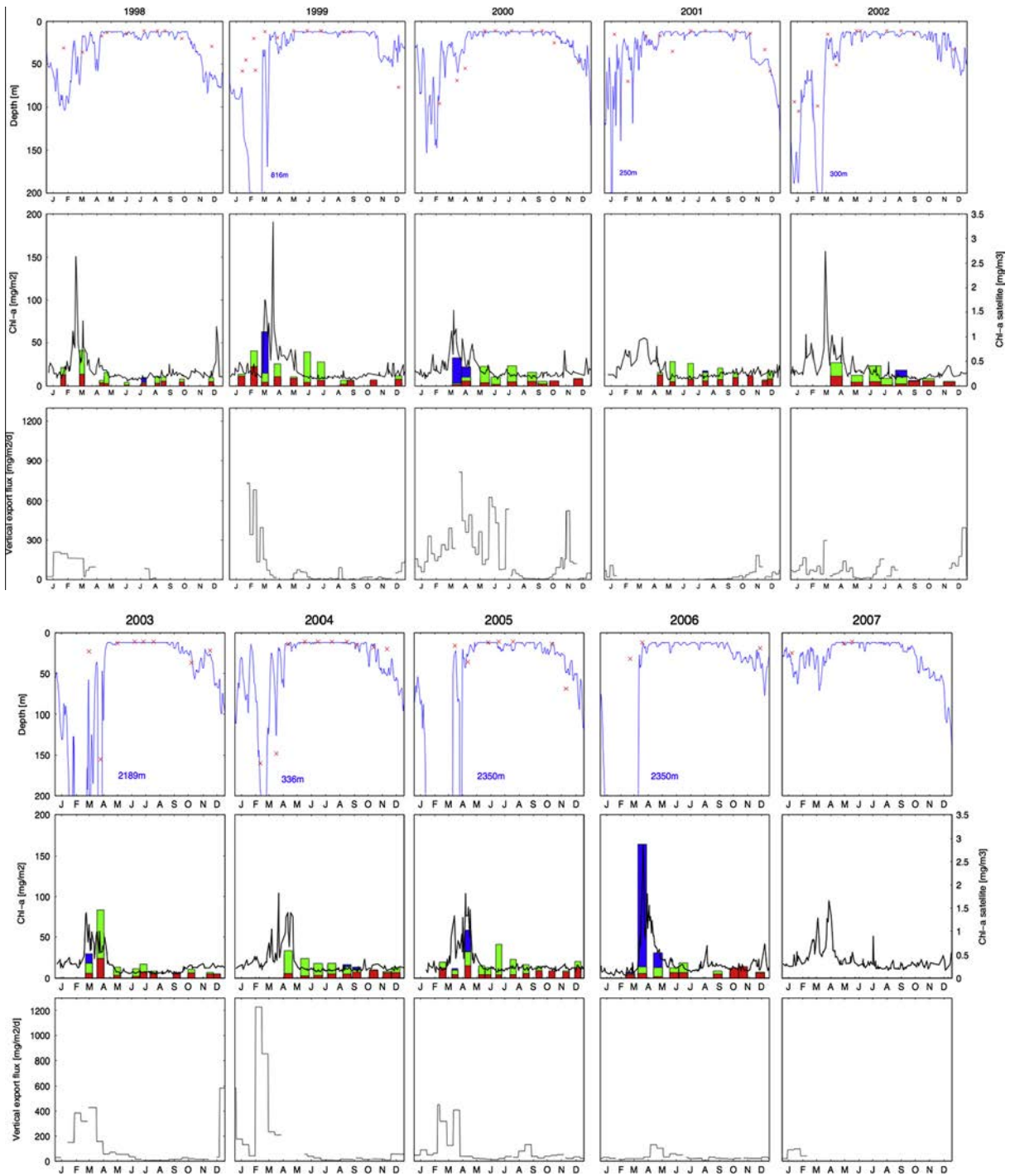


Fig. 2 (continued)

column and carries all material (particulate + dissolved) accumulated in the surface layer to depth. The rapid downward transfer of dissolved and particulate matter by this “flush-down effect” yields high vertical export fluxes. The magnitude of these fluxes may vary according to the amount of atmospheric material accumulated in surface waters during the preceding stratified period. In the present data set, highest vertical export fluxes were observed in 1999, 2003 and 2004. In those years, the MLD was greater (Fig. 2), suggesting a causal relationship between the efficiency of vertical mixing and the subsequent vertical export flux.

(2) In spring, nutrients brought to surface waters by the vertical mixing trigger phytoplankton blooms, which generate new material for the vertical transfer of dissolved and particulate matter. Maximum *Chl-a* occurs shortly after the MLD maximum. Gačić et al. (2002) observed a marked seasonal variability of POC fluxes in the Adriatic Sea. Spring maxima are associated with phytoplankton blooms. In spite of interannual variations in the intensity of the phytoplankton blooms, their seasonal distribution and biomass abundance are reproducible (Marty et al., 2002), with maximum values of carbon assimilation in March and April (Marty and

Chiviérini, 2002; Fig. 2). Indeed, high vertical export fluxes were observed within the present dataset in spring, as a result of biological productivity (e.g. 2000).

- (3) In summer and fall, the heating of the sea surface results in a stratified water column with a shallow ML which is rapidly exhausted of nutrients. During such oligotrophic conditions (June to November), the concentrations of biogenic matter in the photic layer are minimal. Therefore, owing to insignificant transfer of POC, atmospherically-transported individual particles presumably do not sink (or sink with negligible sinking velocity), according to Stokesian settling calculations (Stokes, 1901). In the absence of packaging into large biogenic material (adsorption onto phytoplanktonic debris or incorporation into fecal pellets), atmospheric particles thus accumulate in the surface ML. In addition, dissolved atmospheric matter (e.g., from atmospheric wet deposition) is not removed from surface waters *via* its assimilation by phytoplankton, and it accumulates in the surface ML (e.g. dissolved organic matter (DOM); (Copin-Montégut and Avril, 1993)). Consequently, the lowest vertical export fluxes are observed during this period of the year. For example, years 2003 and 2004 exhibited minimal vertical export fluxes during summer and fall (Fig. 2). However, summer 2002 was unusual, with relatively a high vertical export flux. This resulted from the combination of particularly strong summer stratification and the erosion of the thermocline by wind gales in late summer, with the subsequent release of the organic particulates accumulated above the pycnocline (Martín and Miquel, 2010).

3.2. Interannual variability

The present data set exhibits a marked interannual variability: for example, years 1989, 1990 and 2002 were characterized by low vertical export fluxes. In contrast, other years were characterized by much higher winter vertical export fluxes (e.g. by a factor of ~5 in 2004; Fig. 2).

In summer and fall, when no significant vertical export flux should be observed, some peaks appeared. Under oligotrophic conditions, wind-driven mixing episodes may break the vertical stratification, thus supplying nutrients from underlying layers to the surface layer, which triggers phytoplankton production (DiTullio and Laws, 1991; Andersen and Prieur, 2000). In general, this is particularly acute at the end of summer or in fall (Gačić et al., 2002; Marty et al., 2008). Andersen and Prieur (2000) have shown at DYFAMED an upward shift of the pycnocline of 10 m in three days, the nitracline being uplifted from 35 m to about 15-m depth. Moreover, such a vertical displacement (corresponding rather to a MLD thinning and a loss of heat content) should favor destratification during subsequent wind gusts. Relatively important vertical export fluxes during the summer/fall period were observed at the DYFAMED sampling station in 1988, 1989, 1993, 2000 and 2002. The occurrence of summer and/or fall blooms triggers the removal of material from the surface layer. Thus less material is available for vertical export flux during the following winter. In addition, the lack of DOM and organic aggregates afterwards will render the incorporation of atmospherically-deposited matter into organic aggregates more difficult, which is expected to prevent the scavenging of suspended minerals from surface waters (Passow and De La Rocha, 2006). In other words, whatever the hypothesis (i.e. POC is a carrier of mineral ballast or mineral material is a POC carrier), the amount of matter will be reduced and its export will be less efficient because aggregation processes will be less important. Among the examples cited above, the low vertical export fluxes observed in the winters 1990 and 2002 are likely a consequence of effective scavenging during fall.

Atmospheric inputs during the oligotrophic stratified period may also indirectly cause vertical export flux of matter accumulated in surface waters. Nutrient-rich atmospheric inputs have long been known to fertilize oligotrophic surface waters and to trigger enhanced primary production (Bergametti et al., 1992; Guerzoni et al., 1999; Migon and Sandroni, 1999; Bartoli et al., 2005). The present dataset shows several examples of vertical export fluxes observed during the oligotrophic period in the absence of concomitant changes of the MLD. These export events presumably resulted from atmospheric fertilization: 1988, 1989 and 1993, although we have no direct evidence of atmospheric deposition for those years. Vertical export fluxes are compared with micro-, nano-, and pico-*Chl-a* concentrations in Fig. 2. Microphytoplankton (essentially diatoms) are associated with the spring bloom period, whereas nano- and picophytoplankton (mostly cyanobacteria, chrysophytes and prymnesiophyte nanoflagellates) peak during the oligotrophic stratified period and fall (Claustre, 1994; Vidussi et al., 2001; Uitz et al., 2006; Heimbürger et al., 2010a).

Secondary phytoplankton blooms under oligotrophic conditions generate vertical export flux. For example, the high vertical export fluxes observed in July 2000 are related to micro- and nano-*Chl-a* peaks (i.e. secondary blooms of “large” phytoplankton populations, likely to result in a higher vertical export flux). This also applies to years 2002, 2005 and 1999, although it is much less clear for that latter case. The 1999 and 2005 export episodes may be chiefly attributed to nano-*Chl-a* concentrations, while that of 2002 may be due to an increase of micro-*chl a* concentration. Basically, it seems that such secondary blooms are more steadily related to nano-*Chl-a*, compared with micro-*Chl-a* or pico-*Chl-a*. This may be related to temperature and turbulence conditions associated with wind and atmospheric deposition in summer and fall, *a priori* not favorable to large organisms such as diatoms. The variability of pico-*Chl-a* during the oligotrophic period is much less meaningful. However, missing data in vertical export flux time-series do not permit a strengthening in the observations made above.

Data presented in Fig. 2 clearly shows that MLD is subject to large interannual variability. Very strong winter convection events were recorded in winters 1996–1997, 2004–2005 and 2007–2008, whereas shallower winter convection events occurred in winter 1990–1991, 1991–1992, 1992–1993, 1994–1995 and 2001–2002. Winter convection depths vary interannually by two orders of magnitude. Some winters were characterized by short, intense convection episodes (e.g. 1996–1997, 2005–2006), whereas others were defined by long-lasting winter convection (e.g. more than 3 months in 1998–1999). Well separated doublets were also observed (e.g. 1997–1998, 2006–2007, 2007–2008). The magnitude and duration of the winter mixing events presumably impacts the vertical export of matter accumulated in the surface layer to depth. Basically, it seems that deep MLDs generate high vertical export fluxes, either directly (i.e. *via* strong vertical mixing) or indirectly (i.e. *via* high biological productivity triggered by significant nutrient supply). The depth reached by convection may not be the only important factor to determine the efficiency of the vertical mixing. The duration of the winter convection may be a key factor. For example, the 1998–1999 winter convection was a long-lasting event characterized by several small convection episodes. Although it is difficult to estimate the resulting vertical export flux (recalling that the vertical export flux data was missing between 10 August 1998 and 6 February 1999), the high vertical export flux observed in February 1999 suggests that this long convection event yielded a significant export episode. The sharp and intense peaks of winter 2004–2005 and 2005–2006 MLDs probably yielded high vertical export fluxes, but the deep MLDs observed for these years cannot be discussed here, due to the occurrence of strong currents and possibly biased vertical export flux measurements. Nonetheless, micro-*Chl-a* concentrations clearly show that years 2006,

and 2005 to a much lesser extent, were characterized by high microphytoplankton concentrations. Apart from supposed strong hydrologically-driven downward transfer due to high “flush-down effect”, high concentrations of nutrients were brought to the surface layer, and possibly induced biologically-driven vertical export flux.

Since 1999, micro- and nanophytoplankton concentrations seem slightly higher than previous years. This is consistent with the statement of Marty and Chiavérini (2010) who observed in the early 2000s, at the same sampling station, an increase of mixing, nutrient concentration and microphytoplankton (mainly diatoms), presumably caused by deeper winter convection. As a result, vertical export flux capacity seems effectively higher since 1999, as suggested by Fig. 2. Marty and Chiavérini (2010) ascribed this increase to climatic and meteorological changes (droughts, in particular).

During the productive period, many changes in the intensity of the vertical export flux may occur, owing to changes in phytoplanktonic populations. However, the unusual duration of vertical export flux occurrence in spring 2000 elicits special attention. Indeed, many high transfers were observed between mid-March and mid-June, with two sharp peaks between the beginning of May and mid-June. It is likely that wind (and also, perhaps, atmospheric inputs of nutrients recorded during this period; Bartoli et al., 2005) renewed nutrient availability in the surface layer, and, therefore, yielded biologically driven vertical export fluxes. However, the complexity of vertical export flux variability during this period does not permit given flux episodes to be ascribed to given nutrient concentrations, and even less to given dominant organisms. Stemmann et al. (2002) observed high vertical export fluxes at DYFAMED related to phytoplankton changes, shortly after the spring bloom. According to Wangersky et al. (1986, 1989), when phytoplankton blooms crash, phytoplankton biogeochemistry changes as a result of nutrient stress and, in such conditions, the clumping of phytoplanktonic organisms may yield significant vertical export fluxes. This scheme may be affected (and renewed) by nutrient inputs, either wind-driven or by atmospheric nutrient inputs, which might explain the complex variability of vertical export flux in the productive/post-productive period in 2000. In addition, the shift from phytoplankton and zooplankton bloom maxima leads to changes in vertical export fluxes, in particular with efficient carriers such as fecal pellets (Alldredge and Silver, 1988; Fowler et al., 1991). Changes in the composition of zooplankton communities (e.g. salp blooms; Morris et al., 1988) may also drive changes in POC fluxes *via* changes in the size spectrum of fecal pellets, thus altering the vertical export flux.

3.3. Role of atmospheric inputs

The present data set suggests that winter vertical export fluxes are driven by the winter convection, yielding vertical mixing that efficiently exports particles from the surface layer (“flush-down effect”). However, atmospheric inputs can strongly impact vertical export flux, because scavenging of minerals by organic aggregates significantly increases the sinking velocity of aggregates (De La Rocha and Passow, 2007; Lee et al., 2009b). For example, Saharan dust episodes are likely to supply mineral matter to surface waters, which is gathered with organic material accumulated above the thermocline. This leads to a higher vertical export flux, according to Armstrong et al. (2002), Francois et al. (2002) and Lee et al. (2009a). The vertical export flux of winter 2004 is a striking example of this process: the winter vertical export flux recorded in 2004 was exceptionally high, while the MLD, although deep, was not exceptional (Fig. 2). During 2003–2004 winter convection, a very strong Saharan wet input reached Ligurian surface waters (14–26 February 2004), supplying up to 88% of total yearly atmospheric

deposited iron (Bonnet and Guieu, 2006; Ternon et al., 2010). Although the mere correlation between such a high atmospheric event and an exceptional vertical export flux supports no conclusion on whether ballast minerals determine POC sedimentation or *vice versa*, one can state that atmospheric minerals helped to accelerate the sinking of POC.

The question remains whether atmospheric inputs can trigger vertical export flux or not. Apart from the event cited above, other significant Saharan inputs have occurred (e.g. July 2004, June 2006) without yielding substantial increase in vertical export flux (Bonnet and Guieu, 2006; Ternon et al., 2010). Regarding the atmospheric event of June 2006, Pulido-Villena et al. (2008) observed bacterial response triggered by atmospheric dust deposition. Nevertheless, biomass data did not indicate a phytoplankton response, and no burst of vertical export flux was observed. This suggests that atmospheric inputs do not generally determine the occurrence of vertical export fluxes. Even when atmospheric minerals significantly increase the intensity of the vertical export flux (e.g. the exceptional event of February 2004), and, therefore, do play a key role in the transfer of organic aggregates to depth, their sinking requires the presence of POC. This statement is consistent with the hypothesis that biogenic material drives the settling of mineral material that would otherwise be too small to sink (Migon et al., 2002; Passow, 2004; Passow and De La Rocha, 2006). More generally, variability of winter mixing and the subsequently fuelled primary production is the ultimate driver of vertical export flux variability (Lampitt et al., 2010).

In summary, strong links between atmospheric inputs and vertical export flux may be observed under the following conditions: (i) atmospheric events occurring during the winter convection episode; (ii) atmospheric events occurring during the spring phytoplankton bloom; (iii) atmospheric events associated with wind-driven breakage of water-column stratification, thus supplying surface waters with nutrients from underlying waters; and (iv) atmospheric events that fertilize surface waters, triggering algal growth and significant POC production.

4. Conclusions

Our results suggest that the vertical export flux in the DYFAMED region is determined by winter convection and the subsequent phytoplankton bloom (*via* POC production and export for this latter case). Atmospheric inputs have a ballasting role but do not trigger episodes of enhanced vertical export flux. The variability of vertical export flux largely depends on MLD variability, which also determines the magnitude of the subsequent phytoplankton bloom. Sequestration of atmospheric CO₂ depends upon regional climatic and meteorological evolutions (temperature, rainfall amount, wind stress, solar radiation), which themselves determine the wintertime convection. Any perturbation or change in the parameters that control MLD variability and/or biological productivity is likely to impact vertical export fluxes and carbon sequestration, which, in return, is likely to impact regional climate and meteorology. Climatic, but also environmental changes, e.g. anthropogenic, silicon-depleted atmospheric inputs of nutrients that might lower the contribution of diatoms to carbon export flux (Buesseler, 1998; Béthoux et al., 2002; Bartoli et al., 2005), suggest that carbon sequestration might decrease in the following decades, which would result in an increase of sea surface temperatures and lead to a more stratified water-column. This is consistent with the trend hypothesized for the tropical and mid-latitude Global Ocean (Doney, 2006). However, the heating of Northwestern Mediterranean surface waters might also be counter-balanced by a concurrent increase of salinity, presumably driven by increased drought and wind frequencies, as suggested by Marty and

Chiavérini (2010). This might be specific to the Mediterranean Sea, which is strongly constrained by external conditions (Béthoux and Gentili, 1999; D'Ortenzio et al., 2003). The interannual variability of vertical export fluxes shown in the present work suggests that the strong physical forcing on the Northwestern Mediterranean may lead to antagonistic effects that make it difficult to predict at present whether stratification will increase or decrease in the future.

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