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Dynamics of particle flux and carbon export in the northwestern Mediterranean Sea: A two decade time-series study at the DYFAMED site

Juan-Carlos Miquel *, Jacobo Martín [1], Beat Gasser, Alessia Rodriguez-y-Baena [2], Tarik Toubal [3], Scott W. Fowler [4]

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

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ABSTRACT

The DYFAMED time-series station, located in the open Ligurian Sea, is one of the few pluriannual flux programs in the world and the longest in the Mediterranean Sea. The trap data series is one of only three multi-decadal data sets in existence, and it provides flux information for an environment that is distinct from the other long-term data sets. At DYFAMED, downward fluxes of particles, carbon and other major elements have been regularly measured with sediment traps since 1986 at fixed depths of 200 and 1000 m. An overview is presented of the main trends of particle and carbon fluxes observed during the period 1988–2005, period when the mooring was located on the northern side of the Ligurian Sea. In spite of considerable interannual variability, fluxes displayed a marked seasonal pattern with the highest fluxes occurring during winter and spring and lowest fluxes throughout the stratified season (summer–autumn). Organic carbon fluxes measured at both depths were highly variable over time, ranging from 0.3 to 59.9 (mean 6.8) mg C m^{-2} d^{-1} at 200 m, and from 0.2 to 37.1 (mean 4.3) mg C m^{-2} d^{-1} at 1000 m. Mass fluxes were maximal in winter, whereas carbon fluxes were maximal in late spring. Reasonably good agreement existed between particle fluxes at both depths over the years, indicating a relatively efficient and rapid transport of particles from the upper ocean to the deep sea. However, during certain periods mass flux increased with depth suggesting lateral inputs of particles that by-pass the upper trap. Since 1999, the system has apparently shifted towards an increasing occurrence of extreme flux events in response to more vigorous mixing of the water column during the winter months. Although annual mass fluxes have increased in the last years, mean POC fluxes have not substantially changed over time, due mainly to lower carbon contents of the sinking particles during maxima of mass flux.

1. Introduction

During the last decades, the pathways and dynamics of particles in the sea have been recognized as a crucial vector in the global cycling of elements and the functioning of marine ecosystems (Deuser and Ross, 1980; Fowler and Knauer, 1986; Asper et al., 1992; Waniek et al., 2005). The eventual sinking of part of the organic matter produced in the upper ocean transfers energy to the heterotrophic communities inhabiting the meso-pelagic and deep benthic realms, and constitutes a major pathway of atmospheric carbon (both natural and anthropogenic) to the deep sea. As more CO_2 is biologically fixed and exported to the deep ocean, the partial pressure of CO_2 in seawater at the ocean–atmosphere interface decreases, promoting further sequestration of atmospheric CO_2 in the sea. This transfer of carbon to the deep realm after assimilation by marine photosynthetic organisms is the basis of the "biological pump".

The capacity of the biological pump to sequester atmospheric carbon is not only a function of primary production. As long as the fixed carbon remains in the upper water column, it can be readily released back to the atmosphere via respiration. Only when carbon is transported beyond the depth of winter mixing does it become separated from exchange with the atmosphere for climatically significant periods of time (Lampitt and Antia, 1997). Sinking particles, although constituting a small pool of the total standing stock of biotic and abiotic matter in the water column, are a prime vector for the downward transport of carbon and labile organic compounds on which deep heterotrophic ecosystems depend for their nourishment.

* Corresponding author. Tel.: +377 97 97 72 59; fax: +377 97 97 72 73.
E-mail address: j.c.miquel@iaea.org (J.-C. Miquel).

[1] Present address: Instituto de Ciencias del Mar (CSIC), Paseo Marítimo de la Barceloneta 37-49, 08003 Barcelona, Spain.

[2] Present address: International Atomic Energy Agency, Wagramer Strasse 5, P.O. Box 100, A-1400 Vienna, Austria.

[3] Present address: Laboratoire de dynamique et de gestion intégrée des zones côtières, Université du Québec à Rimouski. 300, Allée des Ursulines, Rimouski (Québec), Canada G5L 3A1.

[4] Present address: Institute Bobby, 8 Allée des Orangers, 06320 Cap d'Ail, France.

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During the last three decades, sediment trap studies have provided crucial insights into the dynamics of the downward flux of marine particles, and its role in the global biogeochemical cycles and deep-sea ecology (see Honjo et al., 2008 for review). In spite of some intrinsic limitations that for the most part remain unresolved (see for reviews Thomas and Ridd, 2004; Buesseler et al., 2007), sediment traps are still the best presently available tool for studying the flux and composition of sinking particles in the sea over periods ranging from days to years.

Due to the high variability that oceanic biogeochemical processes undergo over different temporal scales, long-term observations have become necessary to correctly interpret the temporal variability of the particle flux, to discern anomalies from recurrent patterns, and eventually to document the response of pelagic ecosystems to human pressure and climatic changes. The permanent DYFAMED mooring in the Ligurian Sea stands as one of the few long-term studies of marine downward particle flux, the longest in the Mediterranean and third world-wide after the Hawaii Ocean Time-series program (Karl and Lukas, 1996) and the US JGOFS Bermuda Atlantic Time-series Study (Steinberg et al., 2001).

The DYFAMED program (DYnamique des Flux Atmosphériques en MEDiterranée et leur évolution dans la colonne d'eau; i.e. "DYnamics of Atmospheric Fluxes in the Mediterranean Sea") was initiated in 1986 with the study of the atmospheric fluxes along the coast of Corsica (Fig. 1). During spring 1986, a mooring line equipped with a sediment trap at 200 m depth was deployed 12.8 nautical miles NW off Calvi (northwest Corsican coast), at 42°44′N; 8°32′E. Soon after this pioneering trap deployment, the Chernobyl reactor disaster on April 26th delivered substantial quantities of artificial radionuclides to the atmosphere and the nuclear fallout reached the Mediterranean coastal waters in a matter of days. Fortuitously, the trap moored near Corsica became a privileged station to study the transit of the radionuclides derived from the Chernobyl accident through the water column (Fowler et al., 1987). The effort devoted to trace the Chernobyl aftermath also provided some of the first clues on atmospheric-ocean coupling in the region, namely the relatively fast response between surface production and the export of particles below the photic zone through biological processes (Fowler et al., 1987; Buat-Ménard et al., 1989). These unique results encouraged the development of the station into a time-series site and the installation of traps at several depths. As a result, in 1987 the French research community implemented the time-series program DYFAMED, within which IAEA-MEL was responsible for carrying out the time-series vertical particulate flux studies.

In February 1988, shortly before the Corsican mooring was discontinued (June 1988), a second mooring with traps at 200 m and 1000 m was deployed 28 nautical miles off continental France, at 43°25′N; 7°52′E (Fig. 1). In spite of some interruptions due to maintenance breaks and accidents, the geographical position and trap depths have been maintained for the last 22 years through more than 48 consecutive mooring deployments. The rationale for choosing permanent depth horizons at 200 and 1000 m was to obtain the best points of reference of downward flux and transformations of marine sinking particles with the aid of only two sampling depths. The organic carbon flux at 200 m depth was taken as an approximation of export flux from the overlying waters or new production (Avril, 2002; Eppley and Peterson, 1979). Since the transformations that sinking particles undergo during their descent through the water column take place mainly in the upper 1000 m, with little change at greater depths (Armstrong et al., 2002; Klaas and Archer, 2002), the combination of both depth horizons offers a realistic framework to study the dynamics of particles sinking through the "twilight zone" of the water column.

The DYFAMED time-series became part of France-JGOFS (Joint Global Ocean Flux Study) from 1991 to 1997 and from then on was incorporated in the French program PROOF (Processus Biogéochimiques dans l'Océan et Flux). Since 1995, the DYFAMED station also became an integrated Observation Site of the French CNRS/INSU. Within this framework, the DYFAMED site was the focal point for a number of both short and long-term multidisciplinary surveys (Marty, 2002), not restricted only to the mooring line, but encompassing many other complementary activities including the water column (Chiavérini et al., 1999), the ocean–atmosphere interface (Migon et al., 2002; Ternon et al., 2010) and the seafloor (Guidi-Guilvard, 2002; Martín et al., 2009). Several

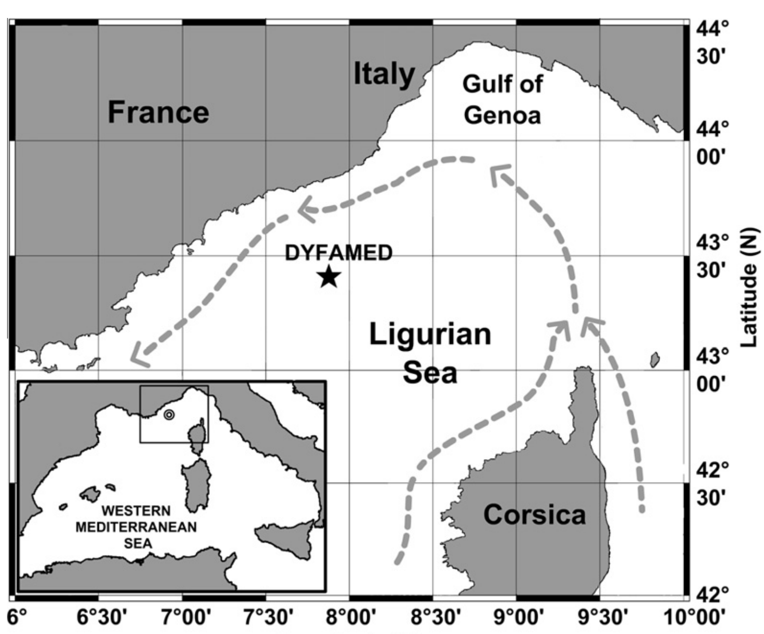

Fig. 1. Geographic map of the study area, showing the position of the DYFAMED mooring line. Dashed arrows indicate the dominant regional circulation.

international projects such as MEDFLUX (Lee et al., 2009a,b) and BARMED (van Beek et al., 2009) have also profited from the DYFAMED program. At the end of 2005, IAEA-MEL transferred the responsibility for overseeing the long term study to the Observatoire Océanologique of Villefranche-sur-Mer (OOV).

Here we present and discuss the historic (1988–2005) time-series of downward particle flux and composition collected by sediment traps at 200 and 1000 m depth at the DYFAMED site off continental France. The sediment trap time-series from the early deployments (1986–1988) NW of Corsica were reported earlier by Fowler et al. (1987) and Miquel et al. (1994) and will not be considered here.

2. Regional setting

The DYFAMED site is located in the open Ligurian Sea, 52 km off the nearest coastline over an average bottom depth of 2330 m (Fig. 1). The Ligurian Sea is one of the main sub-basins of the northwestern Mediterranean, limited to the north by the French coast, to the east by the Gulf of Genoa, to the south by the island of Corsica and to the west by the Gulf of Lions.

The main oceanographic feature of the Ligurian Sea is the Northern Current (NC) (Font et al., 1988; Millot, 1999), a large-scale current formed by the confluence of the Eastern Corsica Current and the Western Corsica Current (Astraldi and Gasparini, 1992). The NC flow is constrained by the topography in an approximate SW direction from the Gulf of Genoa to the eastern Spanish Mediterranean. Since it is a trans-regional entity, the NC is given different names as it crosses the different oceanographic (and political) domains. In the region of the DYFAMED site, it is usually referred to as the Liguro-Provençal Current. In close association with this current, a density front is established in the approximate location of the NC main core, which separates lighter waters on the continental side from the denser offshore waters (Sournia et al., 1990). The coupled effect of the NC and the density front hampers lateral inputs from the continent to the DYFAMED site (Andersen and Prieur, 2000), although recent work argues against a strict isolation (e.g. Roy-Barman et al., 2002; Lee et al., 2009b). In general, the NC is wider and shallower during summer with limited mesoscale variability, while during winter the NC tends to flow closer to the coast in a narrower and deeper jet (Albérola et al., 1995; Millot, 1999). The general cyclonic circulation of the Ligurian Sea produces in its central portion a zone of divergence (Nezlin et al., 2004) resulting in the fertilization of the upper mixed layer with nutrient-rich upwelled waters. Although this central divergence zone is a permanent feature, it is modulated by seasonal fluctuations of the regional circulation and by local wind-forcing (Warren et al., 2004).

The upper water column of the northwestern Mediterranean exhibits a well-defined thermal cycle consisting of marked stratification during summer and vertical mixing in winter due to dense water formation (van Haren and Millot, 2003). The maximum values of the mixed layer depth (MLD) are observed in February and March (D'Ortenzio et al., 2005) due to intermediate and deep water formation by open sea convection (Mertens and Schott, 1998; Martín et al., 2010).

The annual cycle of primary production is closely linked to the alternation of stratified and mixing periods in the surface water column. Consequently, in spite of certain interannual variability, the main biological processes follow a fairly seasonal sequence. An initial phytoplankton bloom is usually noted around February after the winter mixing, and is usually followed by a second bloom in April–May during the onset of stratification (Marty et al., 2002). Nutrients then become depleted in the upper water column as stratification consolidates during summer, and in this way primary production is limited until the next mixed season. However, it has been suggested that the summer period in the northwestern Mediterranean is far from being as oligotrophic as is often considered, since secondary blooms may occur as a consequence of regional or local upwelling and the weakening of the pycnocline in response to wind gusts (Estrada, 1996 and references therein). Estimations of annual primary production in the photic layer are in the range 77–232 g C m^{-2} $year^{-1}$ (Jacques, 1988; Minas et al., 1988; Marty et al., 2002).

Deposition of atmospheric dust is an important source of particles in the Ligurian Sea. In particular, Saharan dust can be transported far from its point of origin by the winds and produce massive depositions in the northwestern Mediterranean (Loÿe-Pilot et al., 1986; Moulin et al., 1997; Ternon et al., 2010).

3. Materials and methods

3.1. Experimental design

Since 1988, the DYFAMED mooring has included two permanent sequential sediment traps at 200 and 1000 m nominal depths. The timeline of available sediment trap data from the mooring is given in Fig. 2. The exact geographical locations and sampling dates for every mooring deployment are shown in Table 1, along with the sediment trap type used at each of the two depths. Accurate calculations and simulations with the software CALM (Girardot, 1992) were performed during the design and construction of the mooring line to ensure the proper buoyancy of the lines and vertical orientation of the instruments. Sampling periods for the traps varied between 7–15 days depending on logistical constraints and scientific objectives, but were identical at both depths during a same deployment. Turn-around cruises were conducted approximately every 3–4 months to check the mooring line, retrieve samples and current meter data, and install new sampling cups and batteries. Gaps in the time-series are due to technical issues and, in two cases, the loss (non-recovery) of the complete mooring.

Fig. 2. Time diagram of the available sediment trap data for each depth. From 1988 to 1991 several depths where sampled in addition to the permanent 200 and 1000 m nominal horizons. This period of high vertical resolution has been discussed by Miquel and La Rosa (1999). Only the long-term time-series of fluxes at 200 and 1000 m depth are considered in this study. PPS3 was the main trap used until 1991, and was replaced by the PPS5 model from 1993 to present.

Table 1
Geographical position, depth and dates of the mooring deployments during the time-series DYFAMED study.

Cruise ID	Deployment date	Recovery date	Latitude 43°N	Longitude 07°E	Bottom depth (m)	Sediment trap type	
						200 m	1000 m
DYF1	26/02/1988	07/06/1988	24.78′	52.13′	2300	PPS3	–
DYF2	14/06/1988	30/08/1988	24.80′	52.73′	2300	PPS3	PPS3
DYF3	30/08/1988	02/11/1988	24.80′	52.73′	2300	PPS3	PPS3
DYF4	12/12/1988	06/02/1989	24.60′	52.80′	2300	PPS3	PPS3
DYF5	08/02/1989	02/05/1989	24.63′	52.91′	2300	PPS3	PPS3
DYF6	04/05/1989	24/07/1989	24.31′	52.62′	2280	PPS3	PPS3
DYF7	27/07/1989	30/10/1989	24.17′	51.95′	2280	PPS3	PPS3
DYF8	02/11/1989	16/01/1990	25.65′	54.06′	2280	PPS3	PPS3
DYF9	18/01/1990	20/03/1990	25.65′	54.06′	2280	PPS3	PPS3
DYF10	30/03/1990	18/06/1990	25.67′	52.68′	2280	PPS5	PPS5
DYF11	31/07/1990	08/10/1990	25.60′	53.80′	2330	PPS3	PPS3
DYF12	11/10/1990	02/12/1990	25.60′	53.80′	2330	PPS3	PPS3
DYF13	20/12/1990	19/03/1991	25.60′	54.00′	2330	PPS5	PPS3
DYF14	22/04/1991	25/06/1991	25.60′	54.00′	2330	PPS5	PPS5
DYF15	01/07/1991	Lost					
DYF16	12/05/1993	04/12/1993	25.93′	54.14′	2350	PPS5	PPS5
DYF17	10/12/1993	28/03/1994	26.11′	53.39′	2323	PPS5	PPS5
DYF18	07/05/1994	07/12/1994	26.11′	53.13′	2370	PPS5	PPS5
DYF19	09/12/1994	03/05/1995	25.71′	52.49′	2330	PPS5	PPS5
DYF20	05/05/1995	02/06/1995	25.71′	52.49′	2330	PPS5	PPS5
DYF21	02/06/1995	02/10/1995	24.67′	50.23′	2304	PPS5	PPS5
DYF22	04/10/1995	Lost					
DYF23	16/10/1997	17/03/1998	24.28′	52.54′	2324	PPS5	PPS5
DYF24	18/03/1998	20/07/1998	24.28′	52.64′	2330	PPS5	PPS5
DYF25	22/07/1998	26/01/1999	24.27′	52.36′	2324	PPS5	PPS5
DYF26	04/02/1999	11/07/1999	24.27′	52.00′	2320	PPS5	PPS5
DYF27	14/07/1999	08/12/1999	24.24′	53.27′	2330	PPS5	PPS5
DYF28	10/12/1999	28/03/2000	24.06′	52.65′	2330	PPS5	PPS5
DYF29	01/04/2000	17/07/2000	24.01′	52.66′	2330	PPS5	PPS5
DYF30	19/07/2000	04/12/2000	24.53′	52.47′	2325	PPS5	PPS5
DYF31	05/12/2000	25/07/2001	23.90′	52.53′	2330	PPS5	PPS5
DYF32	27/07/2001	26/11/2001	23.59′	53.10′	2330	PPS5	PPS5
DYF33	28/11/2001	17/03/2002	22.44′	51.86′	2330	PPS5	PPS5
DYF34	20/03/2002	15/07/2002	22.67′	52.01′	2330	PPS5	PPS5
DYF35	17/07/2002	21/11/2002	22.38′	52.03′	2330	PPS5	PPS5
DYF36	23/11/2002	10/03/2003	22.50′	52.02′	2330	PPS5	PPS5
DYF37	12/03/2003	07/07/2003	22.22′	52.03′	2330	PPS5	PPS5
DYF38	08/07/2003	29/11/2003	22.51′	51.96′	2322	PPS5	PPS5
DYF39	13/12/2003	28/05/2004	24.53′	54.41′	2320	PPS5	PPS5
DYF40	30/05/2004	13/09/2004	25.20′	53.46′	2332	PPS5	PPS5
DYF41	17/09/2004	20/10/2004	25.55′	53.88′	2328	PPS5	PPS5
DYF42	22/10/2004	17/02/2005	24.54′	53.53′	2320	PPS5	PPS5
DYF43	19/02/2005	30/07/2005	23.43′	52.61′	2302	PPS5	PPS5
DYF44	01/08/2005	20/11/2005	25.22′	54.15′	2346	PPS5	PPS5

3.2. Deployed instruments

The sequential sediment traps used in this study were Technicap PPS3 and PPS5 models. From 1988 to 1991 the PPS3 was the main model used, whereas from 1993 onwards, only PPS5 traps were in operation. Both models have a programmable rotor coupled to a carrousel where 6 or 12 (PPS3), or 24 (PPS5) 260 ml sampling bottles are attached. The system allows placing the sampling bottles in reception position at pre-set intervals. The only important difference between both models is the geometry of the collectors. The PPS3 trap consists of a cylindro-conical collector with an aspect ratio (height/width) of 2.5 in the cylindrical section and an unbaffled aperture of 0.125 m^2 (Heussner et al., 1990). PPS5 traps are conical collectors (declivity = 36°) with an aperture of 1 m^2. Since hydrodynamic bias is a matter of concern particularly with conical shapes (Gardner, 1980a,b; Buesseler et al., 2007), the PPS5 traps are covered with baffled lids to reduce current shear at the mouth of the trap, but also to prevent large zooplankton and fish from entering the traps. In fact, certain vertically migrating fishes (*Notolepis* sp.) were a common nuisance in the trap samples before baffles were installed, contaminating samples and in some cases blocking the rotary mechanism (Miquel et al., 1994). These baffles consisted of a mesh of hexagonal honeycomb cells, with uniform aspect ratios of 6.3. (height 50 mm, width 8 mm). Both models of Technicap trap were used during an intercomparison exercise carried out in the field and no significant difference in data collected with these models was noticed (Miquel et al., 2001).

Decay and physical disruption of organic matter, as a consequence of microbial activity and zooplankton grazing, may affect sediment trap collections quantitatively and qualitatively if they are not properly poisoned (Gardner et al., 1983; Khripounoff and Crassous, 1994). Furthermore, particulate matter settled in the trap tends to dissolve unless a fixing agent is added (Gardner, 1995). To overcome these problems, sampling bottles were filled prior to deployment with a 2% (v/v) formaldehyde solution. From the several poison and preservative agents tested in past studies, formalin has proven to be the best suited (Knauer et al., 1984) with only one serious drawback: it significantly lowers pH and hence compromises the preservation of carbonates in the samples. To prevent this, the solution was buffered to saturation with analytical-grade sodium borate; pH was re-checked after every trap sample retrieval.

Following the recommendations of Knauer and Asper (1989) and UNESCO (1994), moorings were designed to maintain vertical trap orientation, and equipped with current meters to monitor hydrodynamics in the vicinity of the traps. The available time-series current data start in 1994 and consist of records from current meters Aanderaa RCM (series 5–8) attached 5 m below trap depths. These current meters record current speed by means of a rotor counter and current direction by means of a fixed vane coupled to an internal compass. The measurement interval of the current meters was set to 2 h in most cases, although other intervals (1–3 h) were used during early deployments. The complete current meter time series are available as online supporing material.

3.3. Laboratory work

3.3.1. Processing of sediment trap samples

Immediately after trap retrieval, samples were transported to the lab and stored at 4 °C in the dark until they were processed. Swimmers (those organisms deemed to have actively entered the traps) were extracted from the samples following a sorting procedure which involves several steps. First, the samples were wet-sieved through 1500 and 600 μm mesh size filters to remove any large organisms. The remaining smaller swimmers were then handpicked with forceps under a dissecting microscope (Michaels et al., 1990; Miquel et al., 1993). The swimmers were identified at least to the main representative taxa and their dry weight determined. Macroaggregates, zooplankton pellets, and other macroparticles retained in the sieves and considered part of the gravitational flux, were reincorporated into the bulk sample.

After extraction of swimmers and liquid subsampling for particular analysis (see for details Miquel and La Rosa, 1999), the remaining trap sample was rinsed with Milli-Q water to remove salt and then freeze-dried. Total downward particle flux in units of mg m^{-2} d^{-1} was calculated from the lyophilized samples. Whenever possible, fecal pellets present in the samples were counted under light microscopy and categorized according to their geometric shape (Miquel et al., 1994; Carroll et al., 1998).

3.3.2. Analytical methods

Total carbon and nitrogen were measured using an Heraeus CHN-O-Rapid and since 1988 with an Elementar Vario EL analyzer. Both analyzers are based on the oxidative combustion of dried samples at high temperature and analysis of the resulting gases by means of a thermal conductivity detector. Blanks and standards (Acetanilide Merck pro analyze C = 71.1%; N = 10.4%) were intercalated between samples for calibration purposes. To measure organic carbon, samples were pre-treated with 1 M H_3PO_4. Inorganic carbon was then calculated as the difference between total and organic carbon. Depending on mass availability and quality of the results, at least two replicates of each sample (2–4 mg) were run for both total and organic carbon in order to reduce the uncertainties linked to sample heterogeneity and laboratory processing. Mean standard deviations between consecutive replicates, expressed as percentage of the mean value, averaged 1.61 (1.45)% for total carbon, 2.39 (2.58)% for organic carbon, and 2.90 (3.16)% for nitrogen in samples from the 200 (1000) m depth for the entire dataset. An interlaboratory comparison carried out by King et al. (1998) has further validated the analytical method. Carbon in samples from deployments DYF18 through DYF21 was measured by coulometric titration using a CM5012 coulometer (UIC). An intercomparison conducted between the Elementar Vario EL and the coulometer yielded an excellent agreement between the two analytical methods (R^2 = 0.985; n = 30).

3.4. Additional data

Since 1991, the Observatoire Océanologique of Villefranche-sur-Mer (OOV) has conducted monthly surveys to monitor the oceanographic, biological and water column properties at the site (Marty, 2002). Hydrographical and pigment data used in this study were provided by the French Service d'Observation Dyfamed maintained by OOV. The methodologies used to acquire and process these data are described at www.obs-vlfr.fr/sodyf and by Chiavérini et al. (1999).

4. Results

4.1. 'Swimmers'

The term 'swimmers' encompasses all pelagic zooplankton species that enter the traps by their own means and thus are not part of the true settling particle flux. The total and relative abundance of swimmers varied greatly over time but on average they represented twice and one third of the passively sinking particle flux at 200 m and 1000 m respectively (all quantities given as dry weight). Temporal variability of swimmer abundance was also less at 1000 than at 200 m. At the deeper depth, maximum abundances were apparent in summer from July to September while seasonality in swimmer abundance was not so clearly evident at 200 m. At 1000 m, the swimmers were mainly represented by copepods and shelled pteropods, whereas at 200 m the swimmers were more diverse and included substantial numbers of amphipods (particularly the Hyperid *Phronima sedentaria*), euphausiids and ostracods. A detailed study on the zooplankton swimmers collected at the DYFAMED station is currently under way and the results will be published elsewhere.

4.2. Long-term sampling of downward particle fluxes at 200 and 1000 m depth

A total of 44 mooring deployments were conducted from 1988 to 2005 at the DYFAMED site. In spite of some interruptions due to maintenance operations and accidents, the time-series comprise 15 years of nearly-continuous data. A total of 362 (398) sediment trap samples were successfully retrieved and processed from the 200 (1000) m depth level.

The complete time-series of mass, organic carbon, inorganic carbon and nitrogen fluxes from 1988 to 2005 are presented in Fig. 3 (data is available as supporting online material). At 200 m depth, total downward mass flux varied within a factor of 410, from minimum values ~3 mg m^{-2} d^{-1} to a maximum of 1228 mg m^{-2} d^{-1} measured in February 2004. At 1000 m total fluxes varied similarly ranging from ~2 mg m^{-2} d^{-1} to 893 mg m^{-2} d^{-1}. The mean downward flux, averaged over the period 1988–2005 was 94.9 ± 145.1 mg m^{-2} d^{-1} and 87.4 ± 124.3 mg m^{-2} d^{-1} at 200 and 1000 m, respectively. Organic carbon fluxes (Fig. 3B) ranged from 0.3 to 59.9 mg m^{-2} d^{-1} (mean value = 6.8 ± 8.0 mg m^{-2} d^{-1}) at 200 m and from 0.2 to 37.1 mg m^{-2} d^{-1} (mean value = 4.3 ± 5.4 mg m^{-2} $d^{-1)}$ at 1000 m depth. Inorganic carbon fluxes (Fig. 3C) ranged from virtually zero to maximum values of 41.2 mg m^{-2} d^{-1} and 55.1 mg m^{-2} d^{-1} at 200 m and 1000 m depth, respectively. Mean values of PIC flux were 3.4 ± 5.3 mg m^{-2} d^{-1} at 200 m and 3.2 ± 5.4 mg m^{-2} d^{-1} at 1000 m. Nitrogen fluxes ranged from minimum values below 0.1 mg m^{-2} d^{-1} to maxima of 12.3 and 4.3 mg m^{-2} d^{-1} at 200 m and 1000 m depth, respectively. Mean nitrogen fluxes (Fig. 3D) for the whole sampling period 1988–2005 were 1.0 ± 1.2 mg m^{-2} d^{-1} at 200 m and 0.5 ± 0.6 mg m^{-2} d^{-1} at 1000 m.

The complete time-series suggest two distinct major periods in terms of the amplitude of flux variability. A first period from 1988 to 1998 was characterized by a lower variability of mass fluxes, with the only exception being a flux peak at both depths during late spring 1991. In contrast, from 1999 onwards pulses of extreme flux became more frequent (Fig. 3A). These differences are expressed by the coefficient of variation (CV = standard deviation/mean) of the mass flux. At 200 m depth, CV increased from 54.0% in the period 1988–1998 to 195.6% in the period 1999–2005. Similarly, at

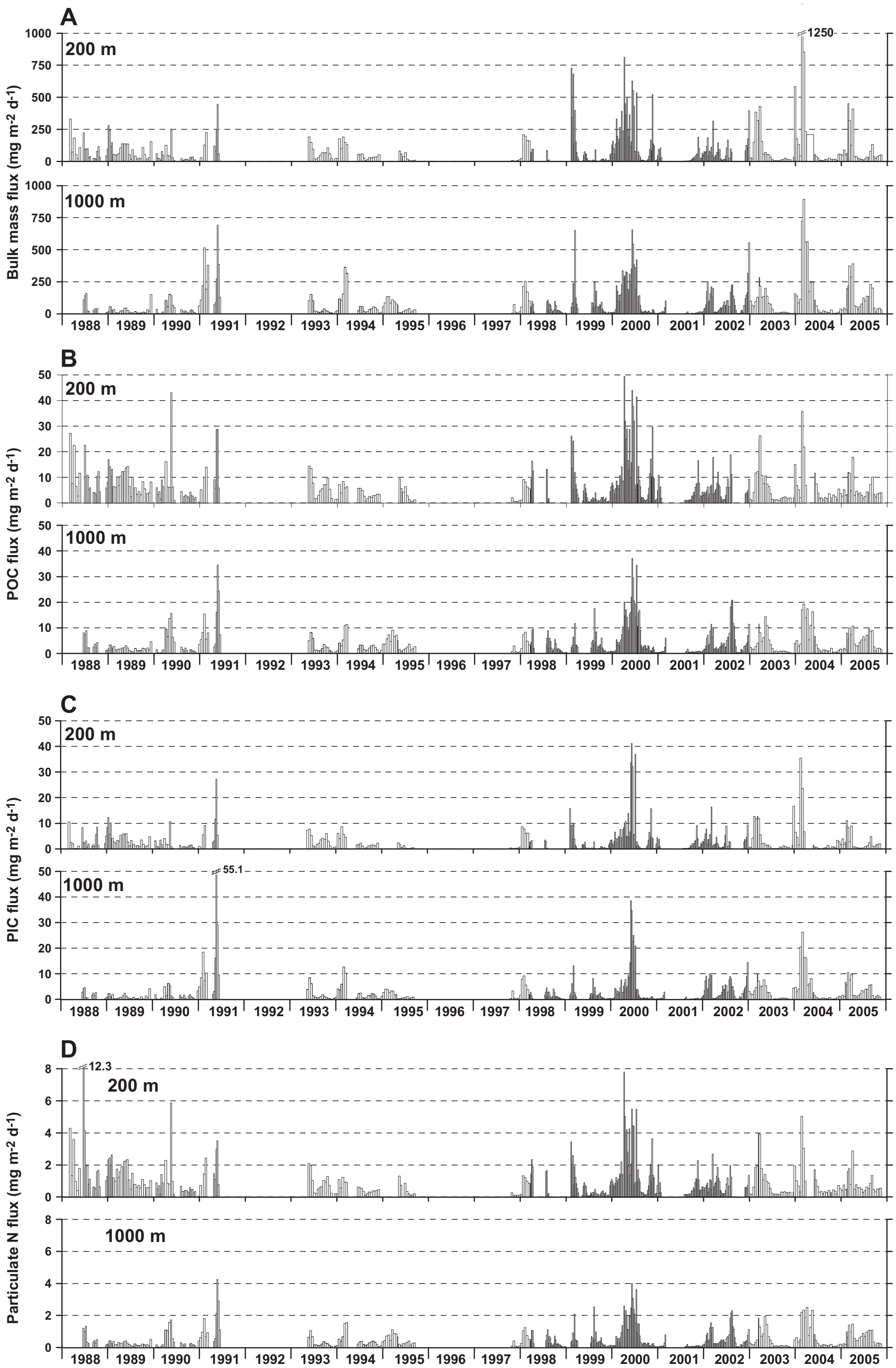

Fig. 3. Time-series of downward particle fluxes measured at 200 and 1000 m depth in the DYFAMED station from 1988 to 2005. (A): Bulk mass; (B): particulate organic carbon; (C): particulate inorganic carbon; (D): particulate nitrogen. The width of bars represents the sampling period integrated by each sample which varied from 7 to 15 days.

1000 m depth the CV increased from 61.3% to 141.4% between the two periods considered.

4.3. Seasonal trends

Figs. 4 and 5 integrate the historical dataset over biweekly intervals in order to visualize an average yearly cycle of particulate fluxes and composition at 200 and 1000 m depth. The seasonality of particle flux is depicted in Fig. 4, and the seasonal trends of particle composition in Fig. 5. In spite of the considerable interannual variability (expressed in Figs. 4 and 5 by the standard deviations of pluriannual means), some general seasonal patterns can be identified.

Most of the year-round mass flux at both depths is concentrated in the first half of the year, with the maximum flux centered in late

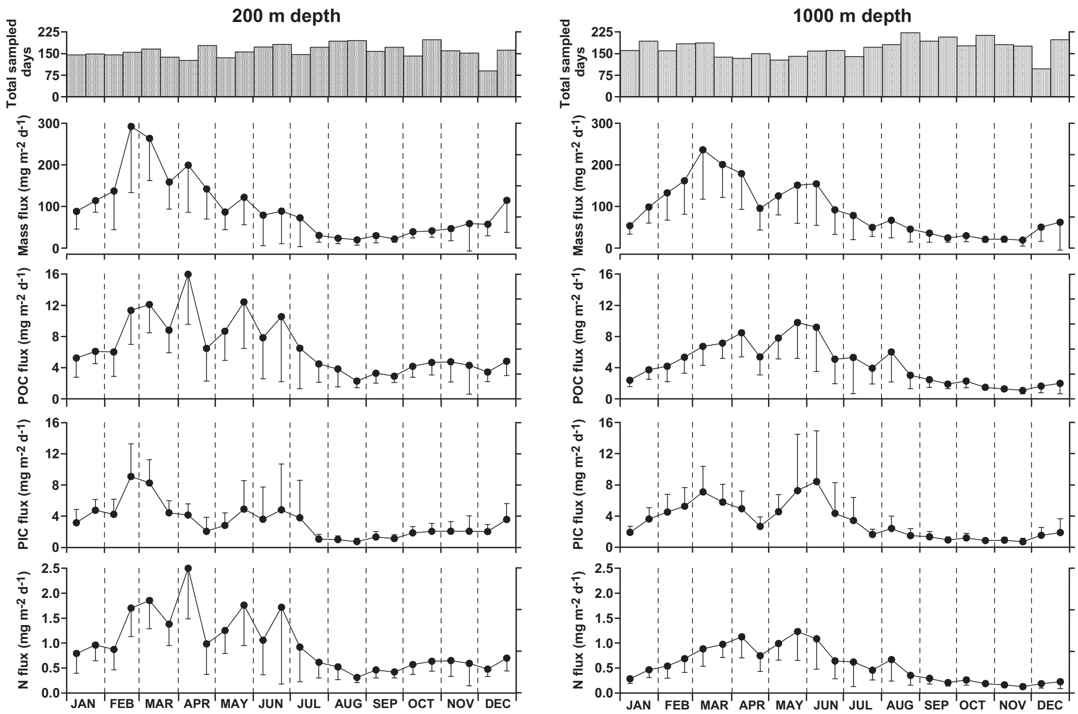

Fig. 4. Bi-weekly means (1988–2005) of particle flux parameters at the DYFAMED site. The upper bar graph indicates the number of days integrated in each bin.

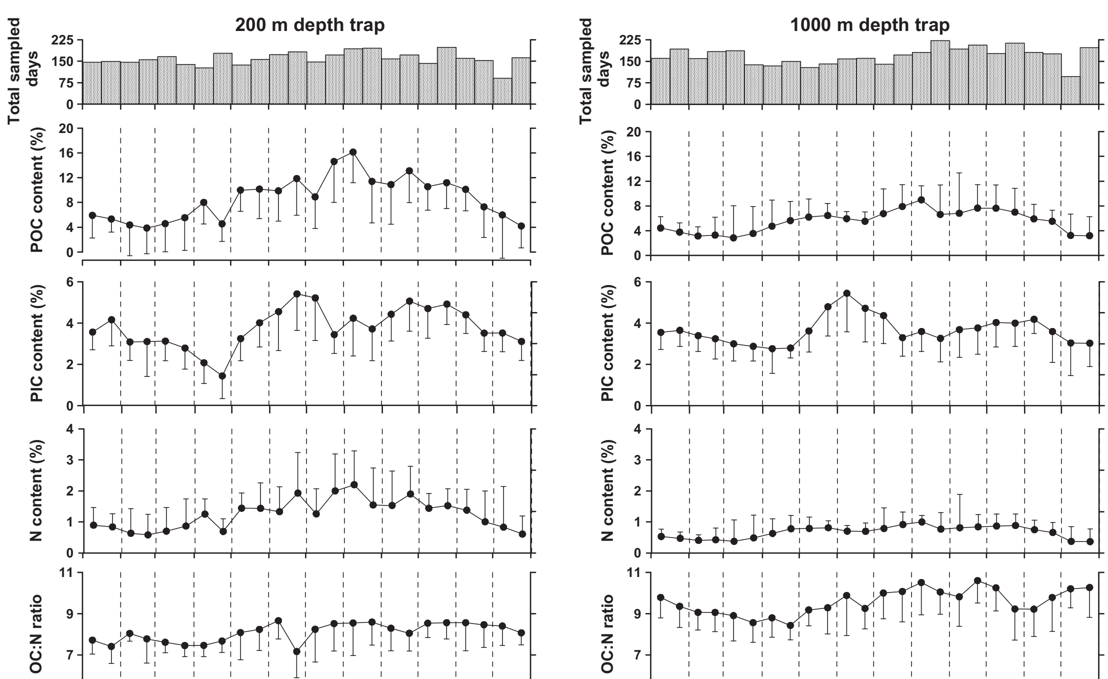

Fig. 5. Bi-weekly means (1988–2005) of particle composition at the DYFAMED site. Contents of organic and inorganic carbon and nitrogen are expressed as percentage of sample dry weight. Bi-weekly mean OC:N atomic ratios of settling particles are also shown. The upper bar graph indicates the number of days integrated in each bin.

winter, declining afterwards through spring and summer and reaching minimal values in late summer–autumn (Fig. 4). These seasonal maxima usually occur during the months of February and March, and are composed of a low proportion of organic matter in comparison with the following months. Also, the standard deviations associated to the biweekly means are particularly high during the months of higher particle sinking flux (late winter), indicating the strong interannual variability and event-driven nature of these maxima.

During spring, fluxes and organic carbon content gradually increase reaching a plateau between May and June. Fluxes are in general lower and richer in organic matter during summer. However, occasionally pulses of total mass and organic fluxes were noted giving rise to small maxima in summer. In contrast, both

Table 2
Time-weighted mean fluxes and flux-weighted mean concentrations of main constituents of settling particles at 200 and 1000 m depth. The data was integrated to obtain mean values representing a year-long time interval. The period and the total number of days used to compute each annual mean are indicated. In each case, these periods were chosen in order to include only one winter per period (given that winter fluxes are very variable from year to year) and to optimize the available data. For comparison purposes, we have only considered periods where data exists simultaneously at both depths.

Yearly period	Initial date	Final date	Sampled days	Total flux (g m^{-2} $year^{-1}$)	POC flux (g m^{-2} $year^{-1}$)	PIC flux (g m^{-2} $year^{-1}$)	N flux (g m^{-2} $year^{-1}$)	OC content % DW	IC content % DW	N content % DW
200 m										
1988–1989	15/06/1988	12/06/1989	273	36.1	4.3	1.6	0.8	11.8	4.4	2.1
1989–1990	25/06/1989	05/06/1990	297	20.6	2.6	0.8	0.4	12.5	3.9	1.8
1990–1991	01/08/1990	28/05/1991	221	28.4	2.5	1.4	0.4	8.9	4.8	1.3
1993–1994	13/05/1993	10/06/1994	315	31.0	2.1	1.4	0.3	6.9	4.5	1.0
1994–1995	25/06/1994	03/09/1995	295	11.6	1.2	0.4	0.2	10.1	3.4	1.3
1997–1998	18/10/1997	10/08/1998	200	27.0	1.8	1.0	0.3	6.6	3.8	1.0
1999–2000	15/07/1999	20/07/2000	358	60.2	3.8	2.1	0.5	6.3	3.5	0.9
2001–2002	06/08/2001	29/07/2002	352	21.8	1.8	1.0	0.3	8.3	4.4	1.2
2002–2003	05/08/2002	24/07/2003	258	48.2	2.6	1.5	0.4	5.5	3.1	0.8
2003–2004	07/08/2003	02/08/2004	294	60.6	2.3	1.8	0.3	3.8	3.0	0.5
2004–2005	16/08/2004	14/08/2005	362	24.7	1.6	0.7	0.2	6.5	3.0	1.0
Total	15/06/1988	14/08/2005	3225	33.9	2.4	1.3	0.4	7.1	3.7	1.1
1000 m										
1988–1989	15/06/1988	12/06/1989	273	14.1	1.1	0.6	0.1	7.5	4.0	1.0
1989–1990	25/06/1989	05/06/1990	297	14.9	1.3	0.5	0.1	8.6	3.7	1.0
1990–1991	01/08/1990	28/05/1991	221	52.1	2.4	2.8	0.3	4.6	5.4	0.6
1993–1994	13/05/1993	10/06/1994	315	28.9	1.3	1.1	0.2	4.5	4.0	0.6
1994–1995	25/06/1994	03/09/1995	295	10.9	0.8	0.4	0.1	6.9	3.6	0.9
1997–1998	18/10/1997	10/08/1998	200	31.2	1.4	1.1	0.2	4.5	3.6	0.6
1999–2000	15/07/1999	20/07/2000	358	56.0	3.0	2.1	0.4	5.4	3.7	0.6
2001–2002	06/08/2001	29/07/2002	352	19.7	1.2	0.9	0.1	5.8	4.4	0.7
2002–2003	05/08/2002	24/07/2003	258	47.4	2.0	1.6	0.2	4.1	3.4	0.5
2003–2004	07/08/2003	02/08/2004	294	51.2	1.5	1.5	0.2	2.8	3.0	0.4
2004–2005	16/08/2004	14/08/2005	362	34.6	1.5	1.0	0.2	4.2	2.8	0.6
Total	15/06/1988	14/08/2005	3225	32.6	1.6	1.2	0.2	4.9	3.7	0.6

mass and carbon averaged fluxes are remarkably low and stable from late summer through autumn (Fig. 4).

At 1000 m depth, mass and particulate organic carbon (POC) fluxes were lower than at 200 m, but a maximum of mass flux could still be seen in winter, with a lag time of about two weeks in relation to the upper trap. A secondary peak between May and June was apparent, in coincidence with the maximum of POC flux.

The biweekly integrated flux of particulate inorganic carbon (PIC) flux at 200 m (Fig. 4) showed a bimodal distribution with a maximum in winter that seems a consequence of the seasonal maximum mass flux during the same months, and a secondary, broader maximum between late spring and early summer. This secondary seasonal increase of PIC flux is not only broader but also undergoes much more seasonal variability than the maximum winter flux.

Regarding the seasonality of particle composition, at 200 m POC content increased steadily from winter to a maximum in mid-summer (Fig. 5). Inorganic carbon was also maximum in summer, between June and July. The content in organic carbon as well as its lability (approximated by the OC:N ratio) clearly decreased from 200 m to 1000 m depth. Seasonal variability of PIC content was less pronounced than in the case of POC content (Fig. 5). POC content was not only lower at 1000 m but also more stable than at 200 m. The summer maximum of POC content was also evident at 1000 m, but was not as marked as the maxima noted at 200 m.

4.4. Annual mean fluxes and particle composition

Mean annual particle fluxes and mean annual particle compositions were estimated as time-weighted mean fluxes and

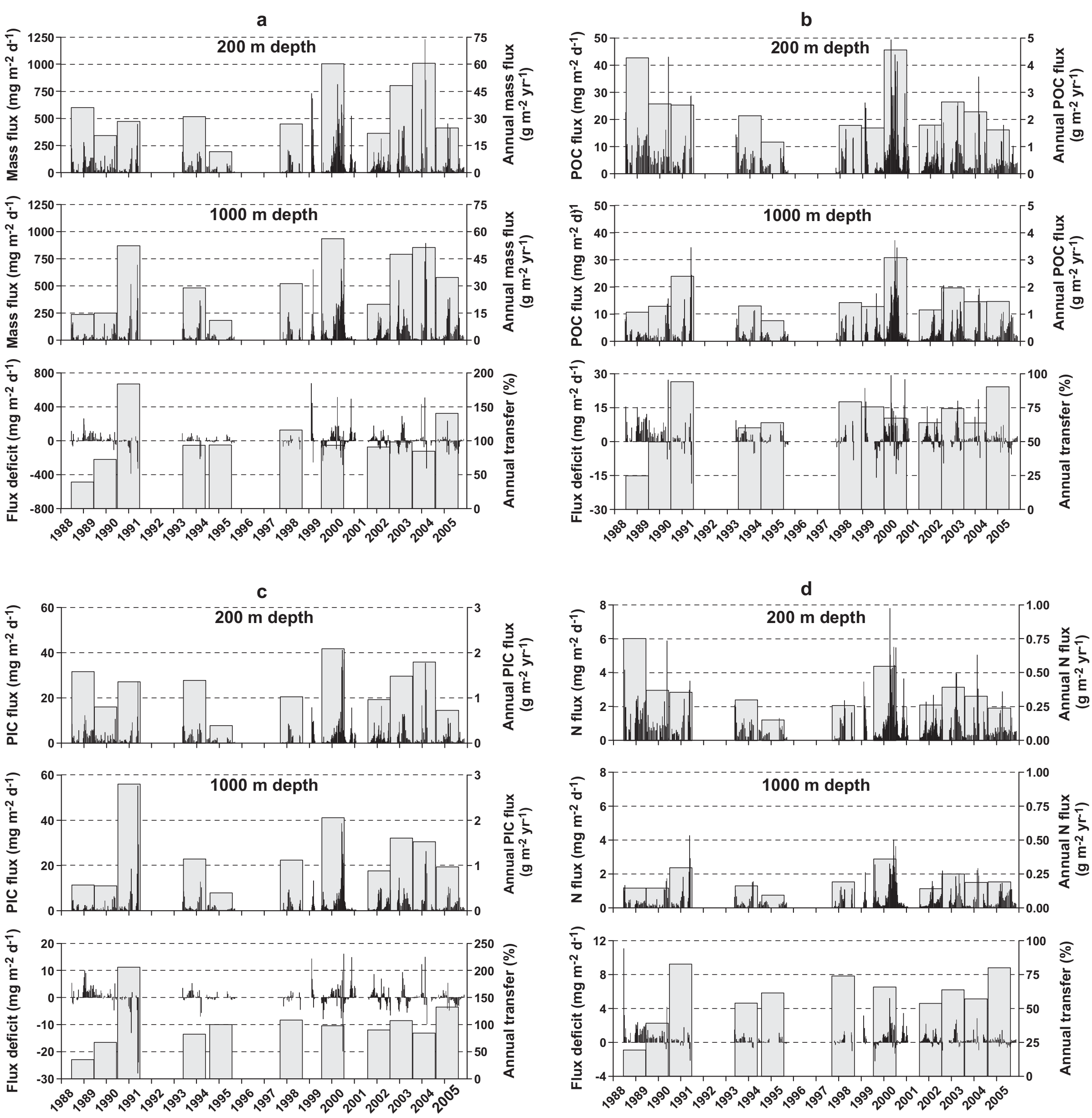

Fig. 6. Annual integration of particle fluxes at the DYFAMED site. (a) Bulk mass flux. (b) POC flux. (c) PIC flux. (d) Particulate nitrogen flux. For each parameter, the upper and middle panels show mean annual fluxes (wide bars) calculated from the original flux time-series (thin bars) at 200 and 1000 m depth respectively. Only periods when both traps were in operation simultaneously have been considered. Lower panels for each parameter show the difference of fluxes between 200 and 1000 m depth (thin bars) and computed annual percentage of total transfer from 200 m to 1000 m depth (wide bars). A transfer higher than 100% indicates an annual period where the mean flux was higher at 1000 m depth than at 200 m.

Table 3
Transfer of particulate mass and components (organic carbon, inorganic carbon and nitrogen) between 200 and 1000 m depth obtained as the difference between them over the period 1988–2004. Calculations are presented based on the entire dataset and also separated into four idealized seasons. Year 2005 was not included in the calculations due to suspected bias in the collection process (see text for details).

	Mass (%)	POC (%)	PIC (%)	PN (%)
All seasons	87.76	60.82	90.78	51.00
December–February	73.94	53.37	75.05	45.10
March–May	96.29	63.67	104.86	56.00
June–August	142.94	82.85	130.31	66.22
September–November	65.15	45.23	57.44	38.58

flux-weighted mean concentrations, which is equivalent to what had been collected by a single cup during a year-long time interval. Instead of integrating calendar years, we averaged the fluxes measured between two consecutive summers when available data made it possible or, in another case, between two consecutive periods of the year excluding winters. This criterion was chosen to include only one winter period in every mean value, provided that flux pulses occur most often during that season. In order to reliably compare the mean flux between both sampling depths, only periods when both traps were working simultaneously were considered to calculate the annual means. Furthermore, the strong interannual variability of particle fluxes discouraged filling missing values with extrapolations. A summary of the calculated mean annual fluxes and mean annual particle composition, along with the time intervals and number of days integrated for each mean value, are presented in Table 2.

Fig. 6 displays the mean annual fluxes of total mass, POC, PIC and particulate nitrogen, and also compares fluxes at 200 and 1000 m depth, expressed both as the difference of instantaneous flux between 200 and 1000 m and the computed percentage of transfer from 200 and 1000 m assuming that the transport of particles is one-dimensional.

During the first years of sampling (1988–1990), fluxes were consistently lower at 1000 m depth due to the attenuation of the settling flux routinely observed in open ocean settings. In the following years, the computed percentage of mass transfer from 200 to 1000 m was significantly higher than during 1988–1990, and in some cases (notably 1991 and 2005), it was above 100%, i.e., the annually integrated mass flux was higher at 1000 m.

The percentage of transfer from 200 m to 1000 m by sinking of particles and major elements is reported in Table 3. The total sampling period as well as idealized four seasons were considered. Excess flux at 1000 m with respect to 200 m is more apparent during summer, suggesting a delay in the sinking of the particles produced in the upper ocean during spring.

5. Discussion

5.1. Assessment of sediment trap efficiency

The fact that, in many subaquatic environments, horizontal current speeds can surpass by several orders of magnitude the sinking velocities of suspended particles, has raised attention to the impact that water flow relative to a sediment trap can cause on trapping efficiency (see for reviews Knauer and Asper, 1989; Gardner, 1995; Buesseler et al., 2007). Under the flow conditions prevalent in many marine environments, most particles are not collected by sediment traps as a result of passive sinking, but by means of a turbulent water-exchange process in the mouth of the trap. Therefore, changes in approach velocity and trap geometry can affect the process of particle collection (Gardner, 1980a; Butman, 1986). Laboratory and field experiments conducted by Gardner (1980a,b) demonstrated that above certain speed limits, which depend mainly on the geometry of the collector, the traps underestimate the downward flux with increasing current speed. In Gardner's calibration experiments, cylinders proved to be better suited than cones in providing a good estimation of downward particle flux. Although the conical PPS5 was the trap model most used, it should be noted that the trap openings were covered with baffled lids, and that the velocities experienced by the traps were low.

Under laboratory conditions, the collecting efficiency of cylinders tends to improve with increasing aspect (height/diameter) ratio. Gardner (1980b) reported that cylindrical collector with aspect ratios between 2 and 3 appear to yield accurate measurements of vertical fluxes in flows up to 15 cm s^{-1}. In the field Gardner et al. (1997) found that collecting efficiencies of cylinders with an aspect ratio of 3 were not affected at current speeds up to 22 cm s^{-1}.

The available time-series of current speed at the DYFAMED station are presented graphically in Fig. 7 and summarized in Table 4 including, for each trap depth and deployment, the percentages of current speed data above 12 cm s^{-1}, a threshold level which has been used as a performance limit in trap studies (e.g., Fabrés et al., 2002; Martín et al., 2006). It must be taken into account that the effective aspect ratio of baffled PPS5 ($\sim$6) makes that threshold very conservative in the present case. Current speeds above 12 cm s^{-1} were relatively rare (Table 4), with the exception of the survey DYF43 (spring 2005), when a significant enhancement of the currents was observed at both depths, resulting in current maxima up to 34 cm s^{-1} and percentages of the current measurements above 12 cm s^{-1} of 41.6% and 27.0% for the 200 m and 1000 m depth trap respectively. For the remainder of the deployment periods, current speeds above 12 cm s^{-1} were in all cases below 8.5% and in most cases below 1% (Table 4).

Strong currents may pose another problem to sediment trap performance by tilting the mooring line or the trap itself. In this case, the relationship between current intensity and trap collection efficiency is the opposite of the case of strict hydrodynamic bias; i.e., as the trap body deviates from the vertical position, the collecting section increases resulting in overestimated fluxes (Gardner, 1985). In order to monitor the tilting of sediment traps, inclinometers were attached directly to the trap hull at both depths from October 1997 (Dyfamed deployment 23) to July 2003 (Dyfamed deployment 37). During all this recorded period there was no significant change in the tilting of the traps (<5°) indicating that the mooring line was very stable in the water and was not affected by hydrology. Although there was no tilt sensor installed during 2005, significant tilting of the traps is presumed for the winter-spring 2005 (Dyfamed deployment 43), judging from the fact that the pressure transducers installed in the RCM units recorded depth oscillations up to 100 m in coincidence with high current speeds.

We conclude that in spite of the implicit limitations and uncertainties of sediment traps in quantifying particle fluxes, which has been and still is a matter of controversy (see Thomas and Ridd, 2004 for a review), the consecutive sediment trap deployments used in this study have operated under similar, and rather weak, hydrodynamic conditions and thus have provided a coherent dataset, the only exception being spring 2005 in which case downward particle fluxes for that period must be regarded with caution. In any case it is noteworthy that a recent work by Roy-Barman et al. (2009) evaluated trapping efficiency at the DYFAMED site using the $^{230}Th/^{234}U$ disequilibria method, and concluded that the settling flux measured by traps was reliable, at least for the period considered in that study (1999–2000).

5.2. Seasonality of the particle flux

In spite of the high interannual variability of the downward flux at both depths, Fig. 4 defines some general seasonal features which

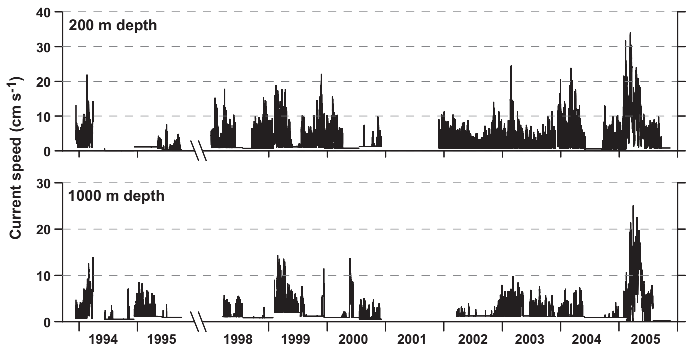

Fig. 7. Time-series of current speed from current meters deployed 5 m below trap depths (200 and 1000 m) at the DYFAMED site.

Table 4
Summary of current meter data at the DYFAMED site. Statistics relevant for assessing sediment trap performance are also included. 12 cm s^{-1} is used as a reference threshold beyond which sediment trap measurements are considered biased (see text for details). The period where high currents may have significantly biased the trap collections is highlighted.

Survey #	Start date	End date	Nominal depth (m)	Min (cm s^{-1})	Max (cm s^{-1})	Mean (cm s^{-1})	>12 cm s^{-1} (%)
17	11/12/1993	29/03/1994	200	1.0	21.8	4.9	3.3
			1000	0.8	13.9	3.5	1.0
18	09/06/1994	09/12/1994	200	0.1	0.6	0.1	0.0
			1000	0.6	7.1	0.6	0.0
19	11/12/1994	05/05/1995	200	1.1	1.1	1.1	0.0
			1000	1.2	8.5	2.3	0.0
20	06/05/1995	03/06/1995	200	0.8	4.3	1.0	0.0
			1000	1.1	1.1	1.1	0.0
21	03/06/1995	03/10/1995	200	0.3	7.6	0.6	0.0
			1000	0.9	3.7	0.9	0.0
23	17/10/1997	16/03/1998	200	0.9	15.2	3.4	0.7
			1000	–	–	–	–
24	18/03/1998	20/07/1998	200	0.9	17.7	2.7	0.8
			1000	1.1	5.7	1.6	0.0
25	22/07/1998	26/01/1999	200	0.7	15.4	3.1	0.8
			1000	0.9	3.1	0.9	0.0
26	04/02/1999	11/07/1999	200	1.1	18.8	4.1	5.0
			1000	2.0	14.3	4.4	1.9
27	14/07/1999	08/12/1999	200	1.1	22.0	4.3	3.4
			1000	1.2	7.6	1.6	0.0
28	10/12/1999	28/03/2000	200	0.8	15.5	3.7	1.8
			1000	0.9	11.4	1.0	0.0
29	01/04/2000	16/07/2000	200	0.8	6.4	0.9	0.0
			1000	0.9	13.7	2.3	0.9
30	19/07/2000	04/12/2000	200	1.2	9.8	1.5	0.0
			1000	0.6	5.0	1.0	0.0
33	28/11/2001	17/03/2002	200	0.8	11.2	3.7	0.0
			1000	–	–	–	–
34	20/03/2002	15/07/2002	200	0.8	8.7	2.8	0.0
			1000	1.3	4.0	1.3	0.0
35	17/07/2002	21/11/2002	200	0.8	13.9	2.9	0.6
			1000	1.3	3.1	1.3	0.0
36	23/11/2002	10/03/2003	200	0.7	24.4	3.6	4.4
			1000	1.3	9.7	2.7	0.0
37	12/03/2003	07/07/2003	200	0.7	11.2	3.0	0.0
			1000	1.3	8.4	2.7	0.0
38	08/07/2003	29/11/2003	200	0.7	11.3	2.6	0.0
			1000	1.1	7.6	1.7	0.0
39	13/12/2003	28/05/2004	200	0.7	23.8	5.9	8.5
			1000	1.1	7.3	1.7	0.0
40	30/05/2004	13/09/2004	200	0.5	4.1	0.5	0.0
			1000	0.9	0.9	0.9	0.0
41	17/09/2004	20/10/2004	200	0.5	12.9	2.9	0.5
			1000	0.9	1.5	0.9	0.0
42	22/10/2004	17/02/2005	200	0.5	31.7	3.9	6.9
			1000	0.9	10.6	1.2	0.0
43	**22/02/2005**	**23/06/2005**	**200**	**0.8**	**34.0**	**11.2**	**41.6**
			1000	**0.3**	**25.0**	**7.9**	**27.0**
44	01/08/2005	20/11/2005	200	0.8	9.7	1.8	0.0
			1000	0.3	0.3	0.3	0.0

are similar to those already depicted for the first years (1987–1990) of sampling at the DYFAMED stations (Miquel et al., 1993, 1994). Maximum mass fluxes take place during the winter months in conjunction with minimum organic contents of the sinking particles, indicating export of mainly mineral and/or refractory particles. This transference of organic-poor particles is coincident with the period of intense winter vertical mixing characteristic of the northwestern Mediterranean basin (van Haren and Millot, 2003). The maximum values of the mixed layer depth (MLD) are observed between February and March (D'Ortenzio et al., 2005) due to deep water formation through deep convection processes (Mertens and Schott, 1998). Although dense water formation in the northwestern Mediterranean occurs with greatest intensity off the Gulf of Lions (MEDOC area), this process can also be of importance in the central Ligurian Sea (van Haren and Millot, 2003; Martín et al., 2010).

Following the seasonal mixing of the water column in late winter, the illuminated upper water column is fertilized with nutrients and biological productivity attains a maximum in the following weeks. This event generally coincides with the onset of the thermal stratification which limits the sinking of phytoplankton cells thereby allowing them to spend more time in well-illuminated waters.

The peak of organic carbon flux, which followed by approximately 2 months the mass flux maximum, is due to the spring production in upper waters of fresh organic material with higher organic carbon content than earlier in the year. Also, this could be partially related to differential ballasting, given that carbonates also increase in the samples from winter to summer. It has been claimed that carbonates ballast and protect more efficiently organic matter from remineralization than does biogenic silica (François et al., 2002; Klaas and Archer, 2002; Lee et al., 2009b).

Low mass and organic particle fluxes characterized the period from late summer to early winter. Such low autumn values contrast with the measurements and assumptions of previous authors concerning the contribution of autumn phytoplankton blooms to the annual production and export of organic matter (Estrada, 1996 and references therein). The increase in length of the stratified season in the last few decades as suggested by Bosc et al. (2004) may partly account for the decreased importance of the fall bloom.

5.3. Composition of the downward particle flux and changes with depth

5.3.1. Mean annual values for POC, PIC and nitrogen

Mean contents of POC and PIC and particulate nitrogen averaged on a yearly basis are presented in Fig. 8. It is evident the decrease of organic carbon content with depth as well as the decrease of its variability. In comparison, inorganic carbon had a lower variability both over the years and between both sampling depths.

5.3.2. Relationships between particulate matter constituents

Potential relationships between mass flux and components of sinking particles are examined in Figs. 9 and 10. A power function gave the best fit for organic carbon versus mass flux (Figs. 9 and 10). A hyperbolic dependence exists between organic carbon and the mass flux at both depths (R^2 = 0.52, 0.44 at 200, 1000 m depth respectively). Visual observations of the fresh particulate material collected by traps reflect that dependence between organic matter and total downward flux: at both depths, a general tendency for less cohesive and light aggregates was associated with lower mass fluxes. Low mass fluxes often corresponded to mixtures of greenish fluffy aggregates and zooplankton fecal pellets with high carbon content. During episodes of high flux, the material acquired a more compacted, muddy appearance, likely reflecting a stronger contribution of mineral (clayish) particles. This was particularly true for the mass flux maximum from the time-series in February 2004 that was likely associated to higher terrigenous inputs from the Arno River and dust deposition (Ternon et al., 2010).

The relationship between organic carbon and nitrogen was linear and highly correlated at both depths (R^2 = 0.93 and 0.88 at 200 and 1000 m depth, respectively) but a greater slope of the fit at

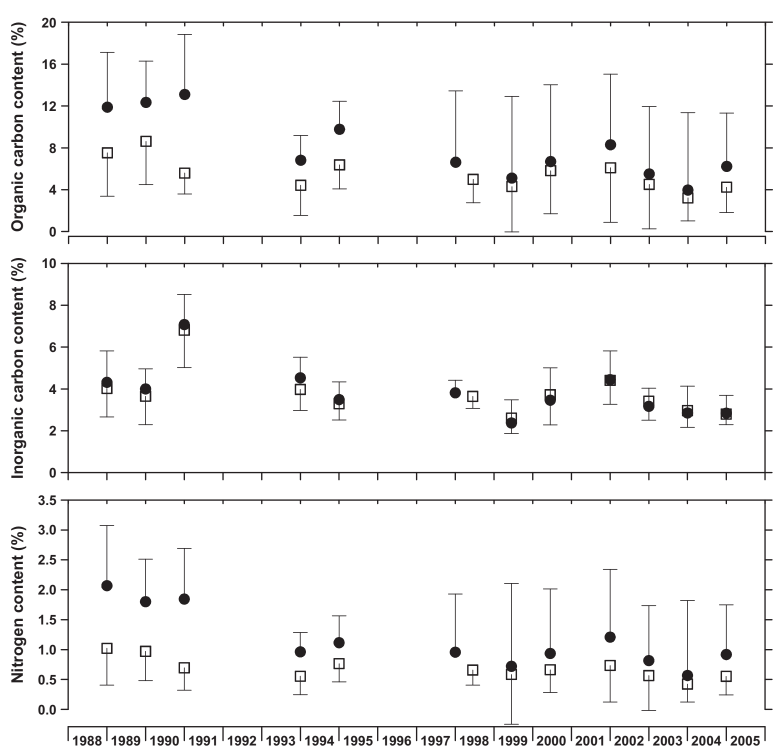

Fig. 8. Annual means of organic carbon, inorganic carbon and nitrogen content of sinking particles at 200 m (circles) and 1000 m (squares) depth at the DYFAMED station. Contents are expressed as percentage of the total dry weight. Standard deviations of the mean values are represented with vertical bars, oriented in the positive direction for 200 m and negative for 1000 m depth.

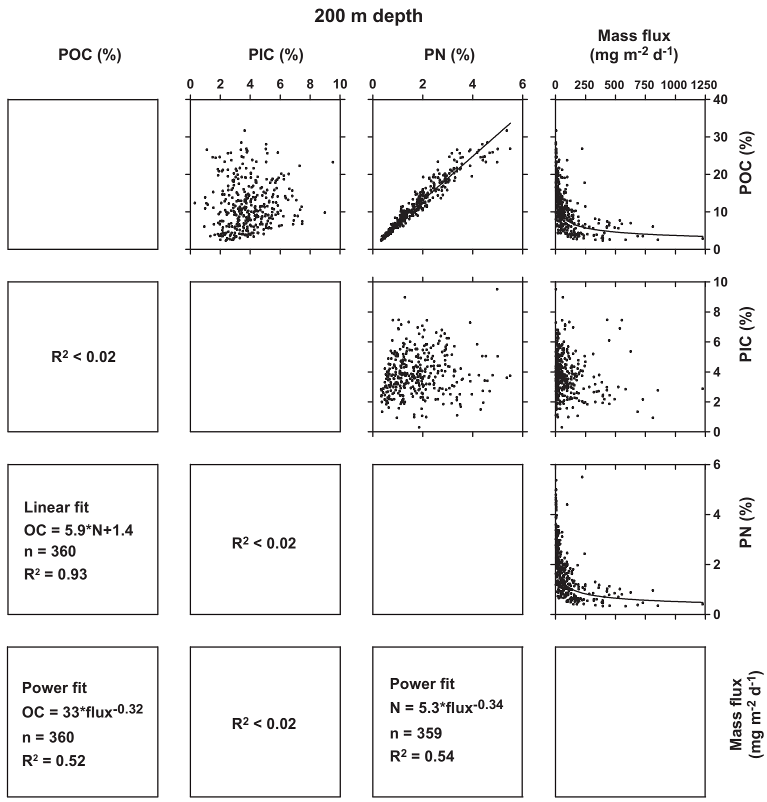

Fig. 9. Relationships between the main constituents in particulate matter and mass flux at 200 m depth. Where appropriate, equations of fits between pairs of variables are shown in the corresponding lower left panels, along with correlation coefficients (R^2) and number of data points fitted (n).

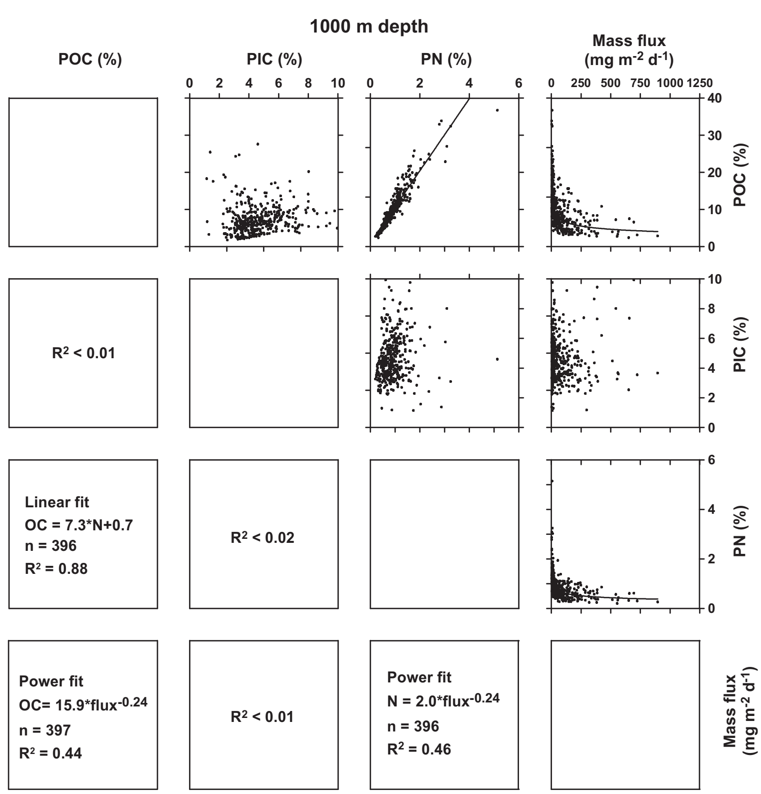

Fig. 10. Relationships between the main constituents in particulate matter and mass flux at 1000 m depth. Where appropriate, equations of fits between pairs of variables are shown in the corresponding lower left panels, along with correlation coefficients (R^2) and number of data points fitted (n).

1000 m depth relative to 200 m depth (Figs. 9 and 10) indicates preferential consumption of the labile fresh fractions of the organic matter. OC:N ratios were equal to the Redfield ratio at 200 m (5.9 ± 0.3) but, at 1000 m (7.3 ± 0.4) were systematically above the Redfield ratio suggesting selective remineralization of nitrogen-rich organic matter as particles settled from 200 to 1000 m, and/or lateral input of nitrogen-poor organic matter at depth. Also, this indicates that even freshly produced biodetritus undergoes some degree of mineralization before it is aggregated into fast sinking particles and/or has scavenged refractory organic matter while sinking. As shown in previous studies (Hedges et al., 2001; Lee et al., 2009b; Liu et al., 2009), particles tend towards a constant composition with depth suggesting that all hydrolysable organic matter is rapidly consumed, and the remainder is much more stable due to its refractory nature or its complexation with mineral matrices that protect organic matter from degradation.

Inorganic carbon was not correlated with any other particle constituents or the bulk flux (Figs. 9 and 10), a recurrent feature observed in other studies conducted in the northwestern Mediterranean (e.g., Monaco et al., 1990; Heussner et al., 1996). Although PIC content exhibits seasonal variability with maxima in summer (Fig. 5), coherent with the presence of calcareous phytoplankton in the oligotrophic summer season, it is noteworthy that mean biweekly PIC content was in all seasons above 2%. Converting this value into $CaCO_3$ (factor 8.33), a background concentration of nearly 20% dry weight of carbonates year-round is difficult to justify merely by phytoplankton calcification. Martín et al. (2006) interpreted this apparent background of inorganic carbon as a standing stock of particulate carbonate with long residence times, fed by continental inputs and residual calcareous biogenic debris. In other words, unlike the organic carbon measured in the traps, much of which can be interpreted as directly derived from primary production, only a fraction of the biogenic carbonate flux would have been recently produced. Regarding non-biogenic carbonates, they can enter the sea from river discharge (Ravaioli et al., 2003); however, assuming that no significant fluvial inputs of particulate matter reach the DYFAMED site, Saharan dust could be invoked instead as a primary source of non-biogenic carbonates.

The samples collected at 1000 m have a lower organic carbon content (Fig. 5) and a higher OC:N ratio (Figs. 9 and 10) compared to those at 200 m. The usual explanation to describe these changes involves the degradation of particles as they sink through the water column, a process mainly driven by bacterial respiration. Peterson et al. (2005) have estimated that ~50% of particulate mass in the northwestern Mediterranean Sea sinks with velocities in the range 200–500 m d^{-1}. Therefore a decrease of organic carbon content with depth could also be explained by enrichment of the flux with refractory particles at depth via lateral transport or also scavenging of suspended refractory particles as biogenic aggregates settle through the water column. These two additional particle sources, aside from explaining the vertical decreasing profile of organic carbon, could also explain the puzzling increase of total fluxes with depth that was apparent during certain periods.

5.3.3. POC:PIC ratio

The OC:IC ratio in sinking particles has been used to estimate the effectiveness of the biological pump to decrease CO_2 partial pressure in the ocean–atmosphere interface and hence to effectively sequester atmospheric CO_2 (Wefer, 1993; Honda et al., 1997; Wong et al., 1999). While carbon fixation by photosynthesis implies a decrease in CO_2 partial pressure and hence the dissolution of atmospheric carbon into the ocean, carbon fixation by calcification has a rather opposite effect. The calcification process shifts the inorganic carbon equilibrium in the sea water towards the dissolved gas.

Although organic particles reaching the 200 m depth trap may have already undergone remineralization, nonetheless they have been used to estimate the relative importance of photosynthesis or calcification in the fixation of CO_2 (e.g., Wong et al., 1999). Crawford and Purdie (1997) estimated a threshold POC:PIC ratio of 0.7, below which the CO_2 pump is expected to reverse (i.e., the net effect of carbon fixation is an increase in pCO_2). Changes in the POC:PIC ratio may also document ecological shifts from a diatom-based ecosystem to a higher proportion of carbonate producers (Wefer, 1993).

Fig. 11 presents the time-series of the POC:PIC ratio at the DYFAMED station. Some extreme values have been removed from the dataset, since zooplankton contamination or other methodological bias was suspected as the cause of these outliers. The ratio in DYFAMED trap samples was always superior to 0.7. Flux-weighted mean POC:PIC ratios of 2.0 and 1.4 were calculated at 200 m and 1000 m respectively. In general, a lower POC:PIC ratio was observed at 1000 m as expected due to the preferential degradation of organic carbon. However, on some occasions the ratio rapidly increased in the deeper trap. Reasons for this could be *in situ* production/repackaging of organic matter or lateral inputs of organic material. Over time, an increase of the amplitude of the POC:PIC ratio oscillations was apparent, especially at 200 m depth. During the 1980s and 1990s, the dataset shows rather stable values of the ratio, but from 1999 onwards a notable increase of the ratio occurred in summer, usually preceded by low values. This tendency was only absent from year 2002, due to the fact that the 200 m trap was clogged following an unusually high POC flux during summer (Martín and Miquel, 2010).

5.4. Coupling between upper water processes and POC flux at 200 m depth

It has been repeatedly argued that surface ocean processes are the key to understanding organic particle fluxes and hence the carbon cycle in the oceans (e.g. Smith et al., 2008). In order to explore

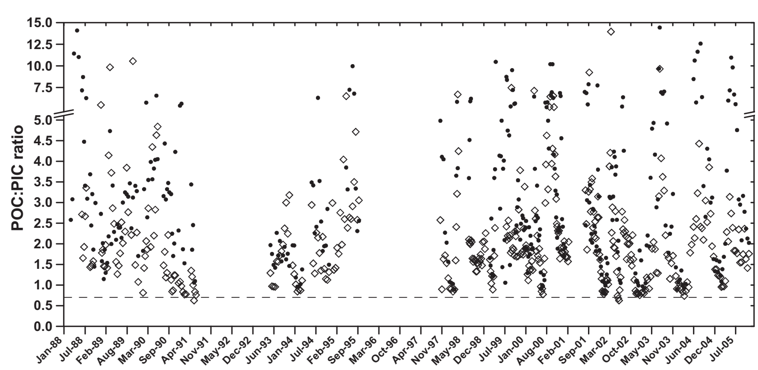

Fig. 11. Time-series of the POC:PIC ratio of sinking particles at 200 m depth (dots) and 1000 m depth (diamonds). The threshold ratio of 0.7 is also shown (see the text for details).

the degree of coupling between upper-water physical and biological processes and the export of particulate mass and carbon, in Fig. 12 we compare the POC flux at 200 m with *in situ* measurements of chlorophyll *a* in the upper water column and the calculated mixed layer depth (MLD). Chlorophyll *a* is used here as a proxy for phytoplankton biomass (Marty et al., 2002; Ras et al., 2008). MLD has been calculated from monthly hydrographical data as the distance from the surface (5 m depth) to the depth where the vertical density increase equals 0.05 kg m^{-3} (Levy et al., 1998).

Fig. 12 suggests that phytoplankton biomass has increased throughout the years, a trend already observed by Marty et al. (2002) for the period 1991–1999 and later confirmed for subsequent years (Marty and Chiavérini, 2010). Chl *a*, MLD and POC flux at 200 m seem related to some extent (Fig. 12). However, some years with very high POC fluxes like 2000 were not accompanied by elevated phytoplankton biomass and the opposite was also observed in other years. Overall, this may indicate that the pelagic ecosystem at the site is far from being in steady state, unless substantial downward export of organic carbon takes place in dissolved form. It has been claimed in the past that much of the POC losses with depth are due to dissolution, so that vertical transit of sinking particles redistributes carbon in depth, transporting more carbon below the mixing depths than would be estimated from POC profiles alone (Noji et al., 1999; Avril, 2002). Dissolved organic carbon (DOC) accounts for the majority of the total standing stock of carbon in the oceans (e.g., Wangersky, 1993; Lefèvre et al., 1996), and has been signaled before as a probable 'missing sink' in the carbon budget in the pelagic northwestern Mediterranean (Miquel et al., 1994). A recent study by Marty et al. (2009) in the DYFAMED area has revealed a very strong spatio-temporal patchiness of the biological processes that could partly explain the disagreements mentioned above.

The depth of the mixed layer was more connected to downward fluxes of POC than phytoplankton biomass (Fig. 12). A notable exception was 2005, when a remarkable winter mixing episode was followed by particularly high Chl *a* concentrations and by a downward flux not higher than in previous years with weaker mixing. An explanation for this could be related to the high currents recorded in winter–spring 2005 (Fig. 7 and Table 4) that may have affected the collecting efficiency of the traps.

5.5. Coupling of particle fluxes between 200 m and 1000 m depth

In Fig. 13 we explore the correlation between time-series of particle fluxes at 200 and 1000 m depth by means of the cross-covariance function (Xcov function, MATLAB 6.0). The cross-covariance is the cross-correlation function of two time-series after removing their means (Box and Jenkins, 1976; Conte et al., 2001). Given that the time-series are not continuous, and the high interannual variability of the flux discouraged filling major gaps by interpolation, we considered instead several periods of variable length, linearly interpolating only the smallest gaps (<7 days) to obtain a total of 7 continuous periods (see upper panel in Fig. 13). These subsets of data were re-sampled to a common time interval equivalent to the longest sampling period used in the sediment trap study (15 days).

In most cases, a remarkable coherence in phasing was observed between downward flux time-series at both depths (Fig. 13). In all the periods analyzed, maximum cross-covariance is found for zero lag, implying that particles exported from the 200 m depth horizon reach the 1000 m trap in a period ⩽15 d, or at least that the three-dimensional transport of particles is coherent at both depths within a time frame of two weeks.

Since settling trajectories of particles have a horizontal component and may be subject to variable currents, the paths followed by the particles that end up in a sediment trap moored at hundreds or thousands of meters below the surface can be very complex. For an efficient coupling between the upper and the deep ocean to occur,

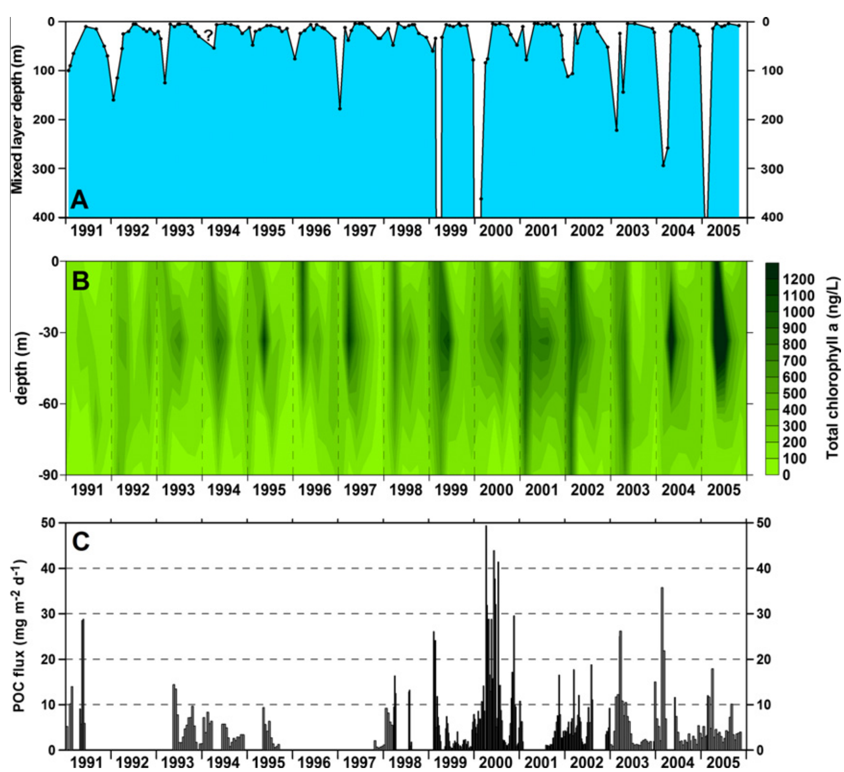

Fig. 12. Comparison between biological and physical parameters in the upper ocean at the DYFAMED site and the downward POC flux at 200 m depth. Contour plots integrate time-series data of: (A) mixed layer depth (calculated using the <0.05 kg m^{-3} criterion; see text for details); (B) chlorophyll *a* (used as a proxy for phytoplankton total biomass); (C) POC flux at 200 m depth.

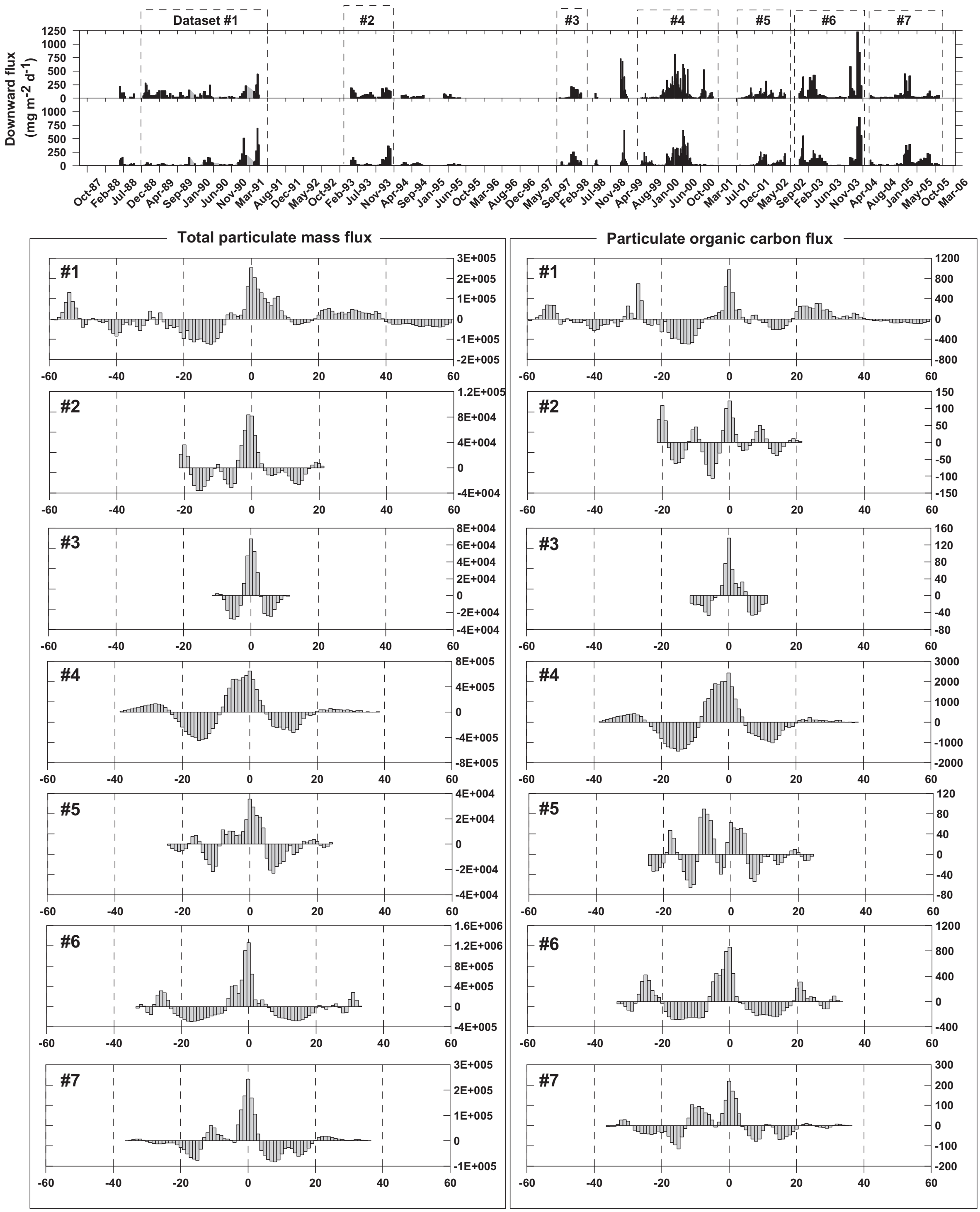

Fig. 13. Cross-covariance between total mass fluxes (left graphs) and organic carbon fluxes (right graphs) at 200 and 1000 m depths for seven selected periods (see upper panel and the text for details). The vertical scales express the covariance between both depth time-series against the temporal lag. Each bar corresponds to a uniform 15 days time interval. Temporal lag at 1000 m depth relative to 200 m is expressed as negative values in the horizontal axis.

one of two things is needed; i.e. fast sinking velocities of most particles making up the bulk of the measured flux, and/or homogeneity of the oceanographic and ecological conditions over a broad surrounding (catchment) area. In open ocean settings, the second condition is easier to obtain than in an enclosed sea such as the Mediterranean with heterogeneous physical boundaries and particle sources over relatively short spatial scales.

In spite of the relatively good coherence of fluxes at both depths when periods of several months or years are considered, it should be noted that in particular cases there was a total lack of correspondence between fluxes at the two depths, and also that on certain occasions the mass flux was higher at the greater depth. To account for these particular differences, several possibilities can be considered:

(a) Repackaging of zooplankton pellets and other macroparticles by zooplankton at intermediate depths (Carroll et al., 1998).

(b) Scavenging of refractory suspended particulate material. This standing stock of fine particles, unable to settle without the interplay of ballasting/scavenging/aggregation processes, constitutes a far more abundant part of the total standing stock of marine particulate matter than sinking aggregates. Since the residence time of this suspended pool of particles is longer, the organic content is depleted in comparison to freshly produced, settling biogenic particles. Hence, scavenging of suspended refractory particles by the rain of sinking biogenic debris could at least partly explain the decreased organic content of the sinking flux at depth.

(c) Different catchment areas. As pointed out by Deuser et al. (1988) and Siegel and Deuser (1997), the horizontal component of sinking particle trajectories results in sediment traps sampling a wide three-dimensional area termed the ''statistical funnel''. The deeper the trap the farther the particles can travel and the larger the catchment area integrated by a sediment trap. Hence, unless oceanographic and biological conditions are very homogeneous over large geographic areas, it is not surprising that catchment areas of sediment traps separated by hundreds of meters may differ to a large degree.

(d) Lateral advection of particles from the continental margin. This effect has been noted in many sediment trap studies; however, the DYFAMED site has long been regarded as an almost isolated area, protected from continental inputs by the natural barrier imposed by the density current along the coast and its associated baroclinic jet.

5.6. How ''open'' is the sea at the DYFAMED site?

In the open ocean, the rain of particles derived from surface production is generally the main contributor to fluxes of total and organic matter to the deep sea. In this respect, DYFAMED has been historically considered an open ocean site, isolated from continental inputs by the barrier effect imposed by a hydrographic front (Sournia et al., 1990) and an associated along-shore current located between the mooring site and the coast inhibiting exchanges with coastal and shelf waters. However, on continental margins and their vicinity, lateral advection from the continental masses must be taken into account as a major source of particles (Honjo et al., 1982; Heussner et al., 1996; Martín et al., 2007).

In spite of relatively good agreement between the flux at 200 and 1000 m depth at the DYFAMED site (Fig. 13), there were certain periods that clearly deviated from that pattern. Continental influence was visually noted in December 2003 and winter 2005 by the presence of vegetal debris in the trap samples, along with sediment of a cohesive and clayish appearance. The increase of mass flux with depth is a common feature of continental margins (e.g., Walsh, 1991). Thus, the isolation of the DYFAMED site, and probably all the open Ligurian Sea, from lateral inputs of continental particulate matter may have been overestimated.

Andersen and Prieur (2000) documented a weak horizontal advection and the stability of water masses in the area during a physical survey in May 1995. However, that one-dimensional scheme may not be suitable outside the stratification period or under certain energetic conditions. Upon relaxation of along-shore currents or due to increased vorticity, this barrier effect can be overcome. It is well documented that the frontal structure and the Northern Current main jet experience intense seasonal and mesoscale activity (e.g., Flexas et al., 2002) that may facilitate the exchanges with offshore waters.

Based on a series of recent sediment trap deployments in the Ligurian Sea, the supposed isolation of the DYFAMED site from lateral or continental inputs has been questioned (Lee et al., 2009b). Furthermore, Roy-Barman et al. (2002) inferred a substantial continental influence from the $^{230}Th/^{232}Th$ ratio profiles in the water column. In addition, studies of sediment accumulation at the seafloor beneath the site (Alleman et al., 2000; Martín et al., 2009) have suggested the existence of important lateral inputs of particles to account for the sedimentary budgets of trace metals and bulk mass. In particular, Martín et al. (2009) estimated a sediment accumulation rate of 0.44 kg m^{-2} y^{-1}, which is an order of magnitude higher than the pelagic flux (~33 g m^{-2} y^{-1}) measured by the pelagic traps discussed in this work. It would appear from all the evidence that lateral transport from the continental margin can at times play a role in particle flux at the DYFAMED site.

5.7. Signs of change

5.7.1. Increasing frequency of high flux pulses

In contrast with the relatively moderate fluxes and clear seasonal signals measured during the first years of the DYFAMED trap sampling program (Miquel et al., 1994), the range of fluxes and the occurrence of flux extremes considerably increased in the following years. A demarcation line can tentatively be drawn between 1998 and 1999. The first period from 1988 to 1998 was characterized by a lower variability and lower absolute values of mass fluxes, discounting an episode of unusually high flux in spring-summer 1991. In contrast, from 1999 onwards, pulses of extreme flux became more frequent than in previous years. For example, coefficients of variation of the mass flux measured at 200 m changed from 54.0% for the period 1988–1998 to 195.6% in the period 1999–2005. Similarly, at 1000 m an increase of CV from 61.3% to 141.4% occurred during the same period.

It is noteworthy, however, that in spite of an increase in the extreme values (i.e. a wider range of fluxes), the mean POC annual fluxes have not markedly changed at both depths (Fig. 6b), due to the lower carbon content in particles during high mass flux episodes. This suggests that the same amount of annual biogenic material is settling with a different timing, concentrated in shorter flux pulses, but not affecting the annual means.

The recent increase in frequency of high flux pulses is most probably not a mere local feature but rather the imprint of large-scale processes affecting all the northwestern Mediterranean. A long-term deployment of near-bottom and midwater traps in the Gulf of Lions (Heussner et al., 2006) also revealed remarkably higher fluxes during the last three years of the experiment (1999–2001) with respect to the previous years (1991–1998). Furthermore, a combined analysis of the temporal series with data sets from other studies in the nearby Gulf of Lions (Heussner et al., 2006; Palanques et al., 2006, 2011) show a remarkable simultaneity of maximum mass fluxes measured at the DYFAMED station and in the continental shelf and submarine canyons of the Gulf of Lions. Such a concomitance of particle transport events, in spite of their different nature (across-margin transport near the bottom of the continental slope and canyons in the latter case, and enhanced particle transport through the water column in the DYFAMED area) and the distance between these areas, reveals a rapid and simultaneous response of the entire northwestern Mediterranean system on a trans-regional scale, to long-range external forcing. Rather than a casual relationship between these distant observations, major meteorological processes of a greater scale may control the biogeochemical particle processes. Enhanced winter convection from 1999 onwards was also evident from the evolution of the mixed layer depth (Fig. 12). Also noteworthy was the coincidence of the proposed shift (around 1999) with the arrival of the Eastern Mediterranean Transient (important changes in formation site and deep water mass characteristics; see CIESM, 2000 for details) effects in the western Mediterranean Basin (Schroeder et al., 2006).

Finally, the increased frequency of flux peaks and deep lateral transport is closely linked to the increased frequency of open sea convection events in the northwestern Mediterranean during the period 1999–2006 (Marty and Chiavérini, 2010; Martín et al., 2010). For 2001, the notable gaps in the sediment trap data time-series do not allow a detailed discussion, but the response of the system to vertical mixing in terms of POC and mass downward transport is clear in the case of 1999 and 2000 (Fig. 12). For the year 2000, it is noteworthy that relatively deep MLD was observed for a more prolonged period than in 1999, well into spring, which could explain the unusually high (and prolonged) POC maxima during that particular year (Figs. 3B and 12).

A notable episode of winter vertical mixing was also observed in 2005 (Fig. 12), in concordance with relatively high currents measured by current meters at both trap depths (Fig. 7). However, no obvious signal was detected in terms of downward export of carbon or total mass (Figs. 3A and B and 12) during the same period or during its aftermath. A probable explanation for this lies in the potential undertrapping of PPS5 traps during periods of intense hydrodynamic conditions (Table 4).

5.7.2. Changes in the seasonality of particle dynamics

Low fluxes throughout late summer and autumn are noteworthy in the averaged annual cycle of particle fluxes (Fig. 4). It has been argued that autumn blooms may constitute a relevant part of the annual primary production in the northwestern Mediterranean (Estrada, 1996). If this is true, such secondary blooms are not reflected in a secondary annual maximum of particle downward export. Instead, our results document very low fluxes during all autumn, sometimes even lower than in summer, which may be a consequence of enhanced respiration during the stratified months. Also, the hypothetical disappearance of the autumn blooms in the northwestern Mediterranean was addressed by Bosc et al. (2004) using historical satellite data. Marty et al. (2002) also commented on the prolongation of the stratification period in the northwestern Mediterranean as a source of changes in the structure of the phytoplankton communities. An increase of the vertical density gradient in the upper 50 m of the water column at the DYFAMED site from 1991 to 2002, with the potential to decouple production of organic particles from their export to the deep sea, has been reported by Martín and Miquel (2010).

5.7.3. Recent changes in the pelagic ecosystem?

Béthoux et al. (2002) observed considerable alterations of the natural nutrient ratios in the Mediterranean during the last decades, and predicted a plankton community shift from a diatom-dominated system to a non-siliceous one. These predictions have received support from pluriannual studies of pigment and phytoplankton distribution (Marty et al., 2002). Integrated chl. *a* (0–200 m) at the DYFAMED site showed a pronounced peak in 1999 (Marty et al., 2002), in agreement with the mass and POC increases measured at both sediment trap depths. However, the same chl. *a* data do not reflect a significant increase in chl. *a* during 2000 in relation to the previous year, whereas POC flux were particularly important. This fits with the fact that the maximum flux in 2000 was not recorded in winter-spring like during 1999, but during late spring and early summer when phytoplankton rich in pigments other than chl. *a* usually dominate.

The shift foreseen by Béthoux et al. (2002) should be reflected by a decrease over time of the POC:PIC ratio, if coccolithophorids and other calcified phytoplankton were to occupy the voids left behind by diatoms. Such a decrease was not observed in the present study. However, it must be considered that particles collected at 200 m depth (and even more at 1000 m depth) may have already undergone dissolution and remineralization and hence may not be very representative of the actual balance between calcification and photosynthesis in the euphotic zone.

Increased occurrence of large salp fecal pellets in the DYFAMED sediment trap samples (data not shown, work in progress) from 1999 onwards, seems to point in the same direction. Salps are non-selective filter feeders, able to prey on a very wide range of particle sizes, and therefore a community shift like that predicted by Béthoux et al. (2002) could confer ecological advantage to salps relative to more selective feeders such as copepods. Furthermore, the fact that mean organic carbon fluxes have not increased from 1988 to 2005 while the mass flux did, suggests enhanced remineralization of organic particles, possibly mediated by enhanced regenerated production and smaller phytoplankton sizes with lower sinking rates.

6. Conclusions

Sinking particle fluxes have been studied at the DYFAMED site off continental France since 1988, constituting today the longest sediment trap time-series in the Mediterranean. Organic carbon fluxes measured at 200 and 1000 m depth were highly variable over time, ranging from 0.3 to 59.9 mg C m^{-2} d^{-1} at 200 m, and from 0.2 to 17.1 mg C m^{-2} d^{-1} at 1000 m. Maximum carbon fluxes were usually measured in spring–summer while total mass fluxes were highest in winter. Mean annual POC flux did not change significantly over the study period, however, from 1999 onwards the system has apparently shifted towards an increasing occurrence of pulsed extreme fluxes, in comparison to the lower and more constant fluxes in previous years. The organic carbon content of sinking particles was lower and also less variable with depth. This is attributed to several interlaced processes such as *in situ* respiration, lateral inputs of degraded material and scavenging of refractory suspended particles.

The highest fluxes occurred in late winter and spring, and lowest fluxes in late summer and autumn. Mass fluxes were generally maximal in winter, whereas carbon fluxes were maximal in late spring. In winter, vertical physical mixing leads to a rapid downward transfer of particles of the lithogenic matter accumulated in the surface layer. Phytoplankton blooms occur in spring in response to nutrient inputs brought into the upper waters by winter physical mixing. From summer through autumn, vertical particle flux tends to decrease as a consequence of density stratification in the upper waters which hampers both the upward flux of dissolved nutrients and the downward export of aggregates. During the stratified season, sinking fluxes were lower but the organic carbon content of the particles was maximal.

Under a one-dimensional scenario, ~38% of the POC leaving the 200 m depth horizon is remineralized before reaching the 1000 m horizon. However, the probable existence of lateral inputs and different source/catchment areas of particles makes it difficult to accurately estimate the downward export or to derive it from the total tri-dimensional transport.

A reasonably good agreement was apparent between the temporal evolution of the particle flux at 200 m and 1000 m depth, suggesting an efficient and rapid transport of particles from the upper ocean to the deep sea. However, this pattern is reversed during certain periods suggesting that under certain conditions sources other than vertical transport contribute to the fluxes measured at the 1000 m depth trap. Apparently, the frequency of these inversions has increased during the two-decade period studied. Lateral particle transport from the continental masses and drifting along with the mean circulation is suggested as a possible origin of the advected excess material.

From 1999, events of high mass flux have become more frequent. Most of these maxima occurred in winter and hence are not explainable on a simple biological basis. Instead, physical processes with high interannual variability, namely winter convection, are invoked to explain the recent trend. In spite of these increased flux events, annual POC flux was rather stable over time due to the lower organic content of the particles during maxima of total mass flux. Annual mass fluxes at 1000 m suggest an increase through the 1990s, while that trend was much less clear at 200 m depth. Changes in the nature of the flux were also observed in recent years, with increasing abundance of salp fecal pellets and gelatinous material (probably TEP).

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.pocean.2011.07.018.

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