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DOC dynamics in the meso and bathypelagic layers of the Mediterranean Sea

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ABSTRACT

Seven years (2001–2008) of dissolved organic carbon (DOC) vertical profiles were examined in order to assess the main processes determining DOC concentration and distribution in the meso- and bathypelagic layers of the Mediterranean Sea. As expected, DOC showed high and highly variable concentrations in the surface layer of 57–68 μM (average values between 0 and 100 m), with a decrease to 44–53 μM between 200 and 500 m. Deep DOC distribution was strongly affected by deep-water formation, with a significant increase to values of 76 μM in recently ventilated deep waters, and low concentrations, comparable to those observed in the open oceanic waters (34–45 μM), where the oldest, deep waters occurred. In winter 2004/2005 a deep-water formation event was observed and the consequent DOC export at depth was estimated to range between 0.76–3.02 Tg C month^{-1}. In the intermediate layer, the main path of the Levantine Intermediate Water (LIW) was followed in order to estimate the DOC consumption rate in its core. Multiple regression between DOC, apparent oxygen utilization (AOU), and salinity indicated that 38% of the oxygen consumption was related to DOC mineralization when the effect of mixing was removed. In deep waters of the southern Adriatic Sea a DOC decrease of 6 μM, together with an AOU increase of 9 μM, was observed between the end of January 2008 and the end of June 2008 (5 months). These data indicate a rate of microbial utilization of DOC of about 1.2 μM C month^{-1}, with 92% of the oxygen consumption due to DOC mineralization. These values are surprisingly high for the deep sea and represent a peculiarity of the Mediterranean Sea.

1. Introduction

Dissolved organic carbon (DOC) in the ocean is a very large, dynamic reservoir of carbon. A percentage of the inorganic carbon, fixed by photosynthesis, is released as DOC in the water column, escaping the food web at various levels (phytoplankton, zooplankton, viruses, bacteria) through different processes (Carlson, 2002). This carbon has several possible fates: (1) if consumed by heterotrophic bacteria it can be: (i) transformed, through the microbial loop, into biomass and returned to the food web, (ii) respired to CO_2, (iii) transformed as newly released DOC; otherwise (2) it can be accumulated and exported by advection and/or convection. The DOC distribution in the sea depends, then, on its susceptibility to bacterial consumption and to its transport due to physical processes. Although the bulk of DOC represents a continuum of biological lability, three fractions have been defined (Carlson 2002, and references therein): (1) a labile fraction, with a turnover time of minutes to days; (2) a semi-labile fraction, with turnover time of months to years; and (3) a refractory fraction, with a turn over time of centuries to millennia. DOC concentrations in oceanic waters are mainly the result of biological activity, whereas its distribution is driven by water-mass circulation (Hansell, 2002), such as has been previously reported for the Mediterranean Sea (Santinelli et al., 2002, 2006, 2008; Seritti et al., 2003). As a consequence, circulation changes induced by climate change affect DOC distribution. Since DOC plays a central role in marine food web, a change in its distribution, in particular in the distribution of its semi-labile fraction, may have a strong impact on both the global carbon cycle and the whole marine ecosystem. Although many studies have been carried out in the last 25 years, DOC remains the most complex and least understood reservoir of carbon on the Earth. The difficulty to describe and quantify marine DOC dynamics is due to the very scarce information on its numerous sources and sinks and to its variable and unknown composition. So, today, we deal with more questions than answers.

The Mediterranean Sea is an oligotrophic basin in which primary production by autotrophs is generally weak and chlorophyll concentrations in the open sea rarely exceeds 2–3 mg m^{-3} (Sournia, 1973). A basin-scale chlorophyll east-west gradient has been observed. In the eastern basin the phytoplankton community was observed to be N and P co-limited, while bacteria and micrograzers were P-limited (Krom et al., 2005; Zohary et al., 2005; Pinhassi et al., 2006). The basin is also characterized by anomalous values in nutrient ratios, with a decreasing east-west gradient (N:P$>$25 and Si:N$>$1.3 in the Eastern Mediterranean; N:P$\sim$20 and Si:N$\leq$1.0 in the Western Mediterranean) (Ribera

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d'Alcalà et al., 2003; Krom et al., 2005). Recently, the biogeography of the Mediterranean Sea and the seasonal cycle of the surface biomass was characterized in different areas of the basin by analyzing ten years of SeaWiFS satellite surface chlorophyll concentrations (D'Ortenzio and Ribera d'Alcalà, 2009). These authors concluded that the Mediterranean Sea is characterized by "non-blooming" areas, exhibiting a sub-tropical regime, as well as by areas where, under particular conditions (both atmospheric and hydrographic), North Atlantic bloom-like events take place.

Some peculiar observations for the Mediterranean Sea have been reported in the literature, and their explanations are often connected to DOC dynamics: (1) In the deep waters of the Western Mediterranean Sea, Christensen et al. (1989) observed higher respiration rates than in open oceanic waters and they proposed that this behavior could be supported by the DOC exported at depth during deep water formation. (2) La Ferla and Azzaro (2004), in a synthesis of CO_2 production rates (CDPR), reported a decrease in CDPR in the Levantine Intermediate Water (LIW) from east to west, as well as higher CDPR in deep waters than in the LIW. (3) La Ferla et al. (2003) reported peculiar profiles of Mediterranean CDPR, with low respiration rates in the upper layer (due to oligotrophy) and with values similar to those reported in more productive sites in the deep layers. (4) Klein et al. (2003) observed a significant increase of the oxygen consumption rate in the Eastern Mediterranean Deep Waters (EMDW), as a consequence of the Eastern Mediterranean Transient (EMT); they explained this finding with a massive input of labile DOC to depth due to deep water formation in the Aegean Sea. (5) Lefévre et al. (1996) reported that in the aphotic layer (200–1000 m) in the northwestern Mediterranean Sea, particulate organic carbon (POC) can support only 20% of the overall organic matter remineralization and they emphasized the importance of DOC in maintaining deep-water metabolism. Finally, (6) in a study on the viral abundance and distribution in meso and bathypelagic waters of the Mediterranean Sea, Magagnini et al. (2007) observed the highest viral abundance so far reported for worldwide deep waters.

The main goal of this paper is to understand the DOC dynamics in the meso and bathypelagic layers of the Mediterranean Sea, in order to assess the main processes determining its concentration and distribution.

2. Material and methods

2.1. Data collection

DOC data were collected from 2001 to 2008 in various areas of the Mediterranean Sea (Fig.1, Table 1). Most of the data are from the Western Mediterranean (WM) and the Ionian Sea, whereas only a few stations were located close to the Levantine Basin. The period of each cruise and the area investigated are indicated in Table 1, together with the symbol that identifies each survey on the map (Fig. 1). Eight of the cruises were carried out between the beginning of spring and summer seasons, three data-sets refer to fall season, while no data were collected in summer or winter seasons (Table 1). At all stations, pressure, salinity and temperature were measured by a SBE 911 plus CTD, equipped with a rosette sampler with 24 × 10-L Niskin bottles. Physical data (salinity (S), potential temperature (θ), and potential density (σ_θ)) were kindly provided by the "*Istituto di Scienze Marine*" of the "*Consiglio Nazionale delle Ricerche*" (CNR-ISMAR), La Spezia and by the "*Istituto Nazionale di Oceanografia e Geofisica Sperimentale*“ (OGS), Trieste. Dissolved oxygen (DO) was measured with a SBE-13 sensor and data were continuously checked against Winkler titration. DO data were kindly provided by the CNR-ISMAR, La Spezia, Trieste and by the "*Stazione Zoologica Anton Dohrn*" (SZN), Napoli. Most of the physical data have been published previously (Table 1). Apparent oxygen utilization (AOU) was calculated by subtracting the concentration of DO from the oxygen at saturation.

2.2. Data selection

All the data-sets indicated in Fig. 1 and Table 1 were used for the horizontal map reported in Section 3.2 "DOC horizontal maps". Some of these data-sets (Fig. 2) were selected in order to show the most representative DOC vertical profiles for the whole Mediterranean Sea. The chosen areas were also characterized by particular features; the selections are justified in Section 3.1 "DOC and AOU vertical profiles". In Section 3.2.2 "DOC consumption at long temporal scale: the LIW case", only the samples collected in the core of the LIW, characterized by a S >38.70, were chosen

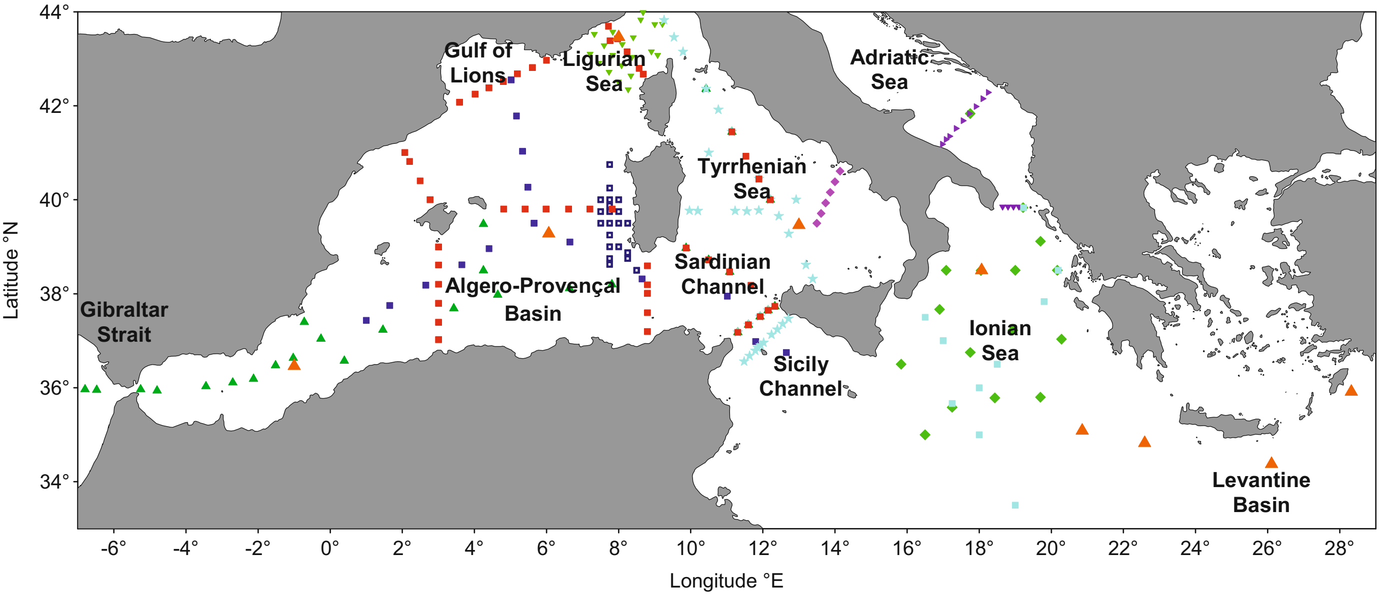

Fig. 1. Position of DOC sampling stations visited during different cruises. The symbols used are explained in Table 1 together with the sampling period of each cruise.

Table 1
Sampling periods and study areas of the cruises in which DOC data were collected. The symbols of each cruise, as employed in the map of Fig. 1, are reported.

Study Area	Period	Symbol in the Map	*N* samples	References
Sardinian Sea	March 2001	▣	239	Santinelli et al. (2008), Santinelli et al. (2006)
Southern Adriatic Sea and Ionian Sea	April 2002	◆	180	Manca et al. (2006), La Ferla et al. (2005)
Ligurian Sea	May 2003	▼	375	–
Tyrrhenian Sea	June 2004	★	374	–
Western Med	October 2004	▲	287	Schroeder et al. (2008a)
Western Med	May 2005	■	556	Schroeder et al. (2006), Santinelli et al. (2007) Schroeder et al. (2008a, 2008b)
Eastern-Western Med	June 2007	▲	164	–
Southern Adriatic Sea	November 2006	▼	166	–
Southern Tyrrhenian Sea	November 2006	◆	84	–
Ionian Sea	March 2008	■	192	–
Western Med	April 2008	■	262	–

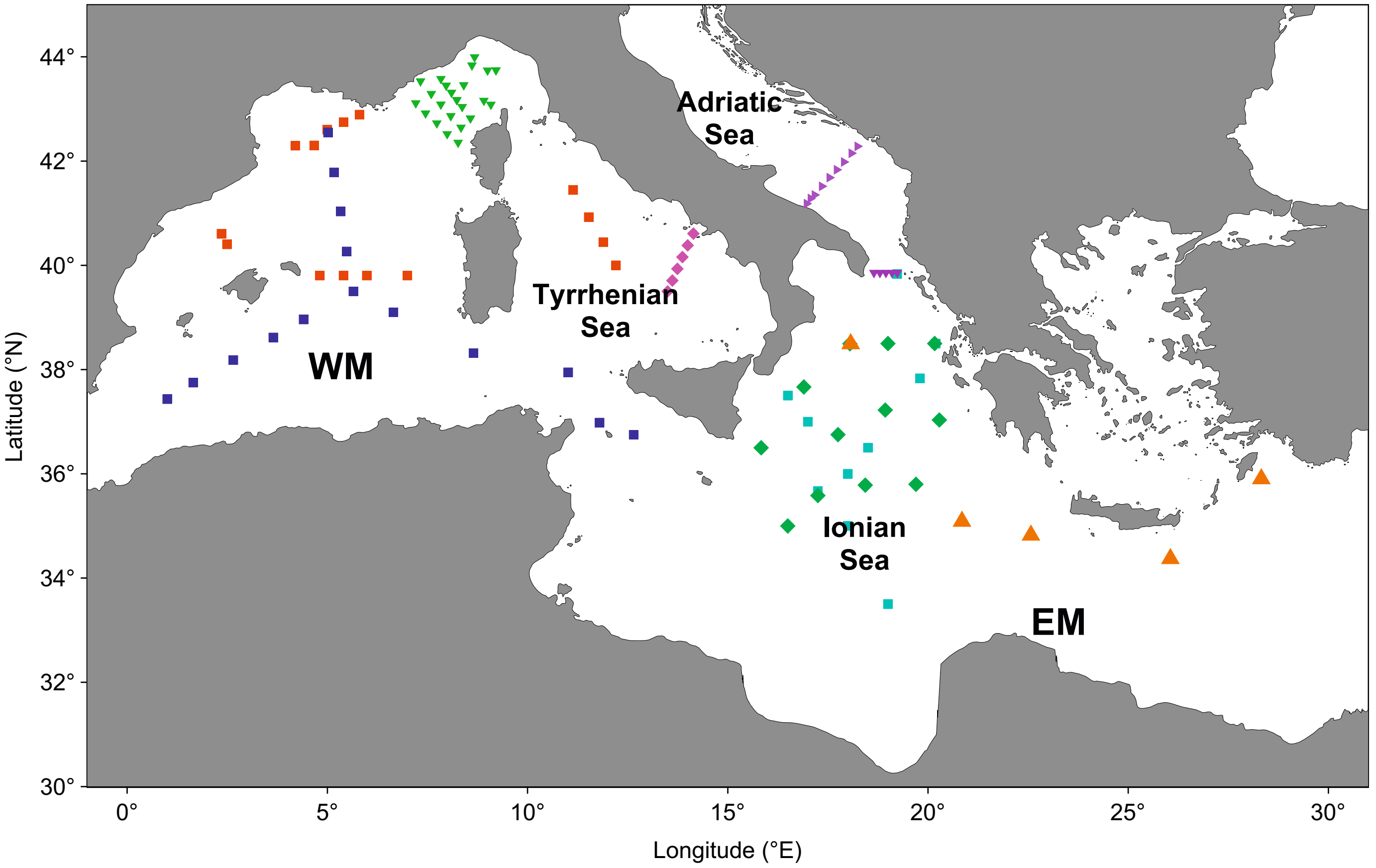

Fig. 2. Map of the stations for which the vertical profiles of mean DOC and AOU are reported in Fig. 3. Symbols refer to different cruises.

from the whole data set. Finally, in Section 3.2.4 "DOC export during WMDW formation" and Section 3.2.5 "DOC consumption at short temporal scale: the Adriatic Sea case", additional data were used in order to show DOC trends at the same locations sampled in different periods, both in the WM and in the Adriatic Sea.

2.3. DOC measurements

Seawater for DOC measurements was sampled with Niskin bottles, when the system CTD/rosette was going up. Samples were collected in dark glass bottles, preconditioned with filtered, open-sea water and rinsed 3–5 times with the sample before its collection. Samples were filtered on board through sterile 0.2 μm cellulose acetate membrane filters (Sartorius, Minisart, SM 16534 K) under low pressure of high-purity N_2. They were filtered quickly in order to avoid alteration by microbial activity. The type of filter was chosen after repeated testing for contamination, as it did not change DOC concentration, either in carbon-free water or in seawater. Before filtration, the filter was washed with ~50 ml of the sample to be filtered, in order to avoid contamination. Filtered samples were stored in amber glass bottles at 4 °C in the dark until the analysis. A check of DOC variation with time, in the storage conditions above reported, demonstrated the absence of significant differences within ten months from the collection.

DOC measurements were carried out in the shore laboratory with a Shimadzu 5000 TOC Analyzer, equipped with quartz combustion column filled with 1.2% Pt on silica pillows of approximately 2 mm diameter. Ten ml of sample were acidified with 50 µl of 50% H_3PO_4 and sparged for 10 min with CO_2-free pure air, in order to remove inorganic carbon, before the high temperature catalytic oxidation (Williams et al., 1993). One hundred µl of the sample were injected in the furnace after a fourfold rinsing with the sample to be analyzed. From 3 to 5 replicate injections were performed until the analytical precision was within 2% (± 1 µM). A four-point calibration curve was done by injection standard solutions of potassium hydrogen phthalate in the same concentration range of the samples. The system blank was measured every day at the beginning and the end of analysis using low-carbon water (2–3 µM) produced by a Milli-Q system. This low-carbon water was the same used to prepare the standard solutions and was acidified with 50% H_3PO_4 and sparged for 10 min with CO_2-free pure air, in the same way as the samples. DOC concentrations were calculated, according to Thomas et al. (1995), by the equation:

$$\mathrm{DOC}(\mu\mathrm{M}) = \frac{(\text{sample area} - \text{system blank area})}{(\text{slope of standard curve})}$$

The reliability of measurements was controlled twice daily by comparison of data with a DOC reference seawater sample kindly provided by Prof. D.A. Hansell of the University of Miami (measured value = nominal value ± 0.5 µM). This procedure also assures the goodness of the calibration curve (Sharp et al., 2002).

3. Results and discussion

3.1. DOC and AOU vertical profiles

Vertical profiles of mean DOC and AOU are reported in Fig. 3 in order to describe the main DOC dynamics in the Mediterranean Sea. They were computed by using all the data collected at selected stations in both the Western (WM, Fig. 3A, the four graphs on the left) and the Eastern Mediterranean Sea (EM, Fig. 3B, the four graphs on the right).

These stations were chosen as representative of the typical DOC and AOU vertical profiles observed in the whole Mediterranean Sea. In addition, these areas were characterized by unique physical characteristics, in particular: (i) deep-water formation (the Adriatic Sea and the Gulf of Lions) (Theocharis et al., 1998); (ii) high vertical stability (the Tyrrhenian Sea) (Hopkins, 1988; Astraldi et al., 2002); and (iii) a substantial change in the thermohaline circulation (the Ionian Sea) (Roether et al., 1996; Malanotte-Rizzoli et al., 1999). They are indicated in Fig. 2 with different symbols for each survey (Table 1). The DOC and AOU

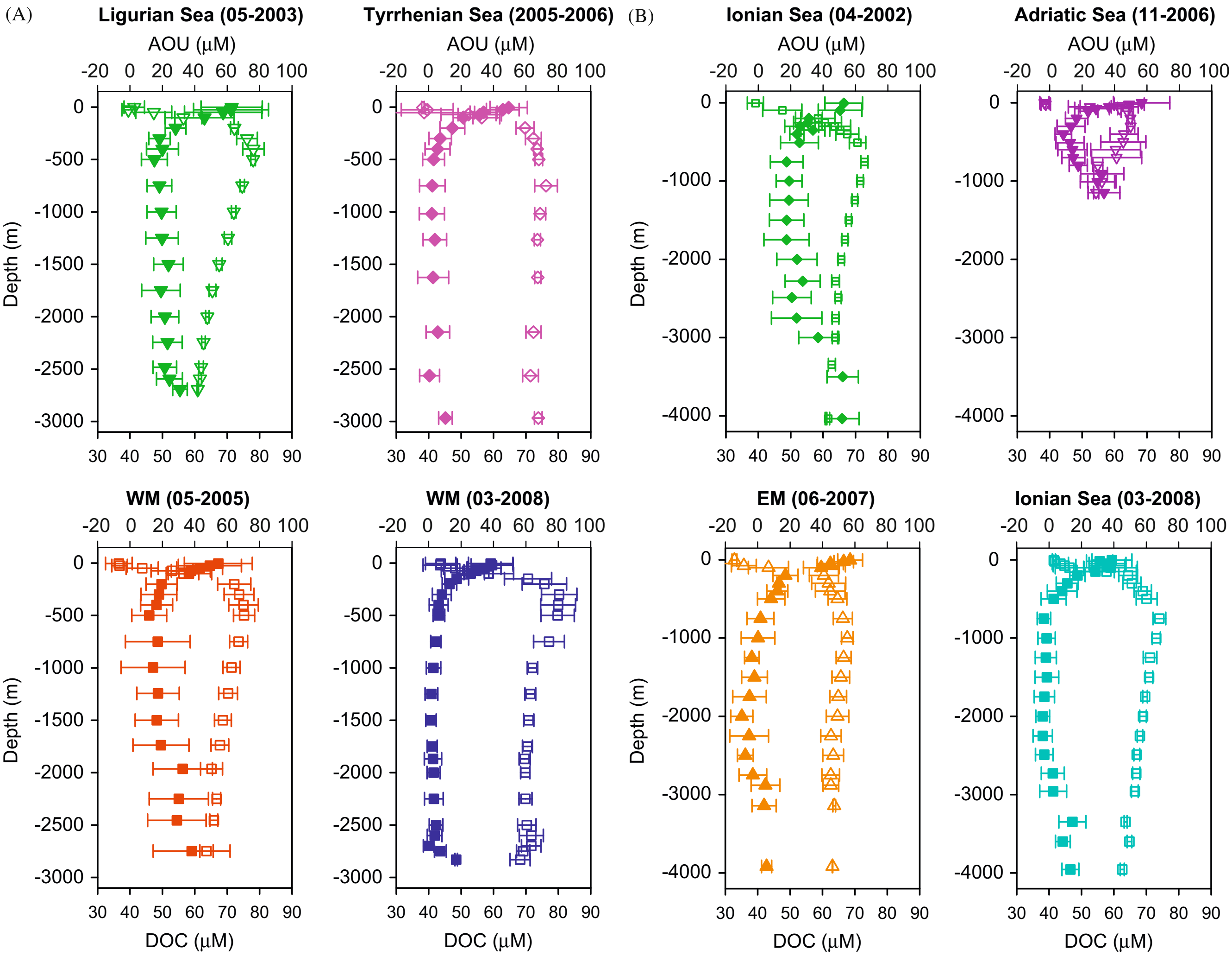

Fig. 3. Vertical profiles of mean DOC (filled symbols) and AOU (empty symbols), referring to different areas of both western (A) and eastern (B) Mediterranean Sea. The vertical profiles were computed from all the data collected at the different stations during a single cruise. The only exception is the Tyrrhenian Sea for which data collected in May 2005 and November 2006 were combined. WM, Western Mediterranean; EM, Eastern Mediterranean.

Table 2
Average concentrations and standard deviations of DOC and AOU data collected in the different depth layers of the stations indicated in Fig. 2.

Study Area (Sampling period)	Depth (m)	DOC (μM)	AOU (μM)	Sample N
Ligurian Sea *(May 2003)*	Surface (0-100)	68 ± 10 (50–100)		76
	Intermediate (200–500)	50 ± 4 (40–58)	73 ± 6 (54–81)	58
	Deep water (2000-bottom)	52 ± 4 (44–60)	45 ± 2 (41–49)	38
Tyrrhenian Sea (*May 2005, November 2006*)	Surface (0–100)	58 ± 7 (47–73)		42
	Intermediate (200–500)	44 ± 4 (39–54)	64 ± 5 (49–71)	34
	Deep water (2000-bottom)	42 ± 3 (37–48)	64 ± 4 (57–71)	18
WM (*May* 2005)	Surface (0–100)	62 ± 9 (48–95)		112
	Intermediate (200–500)	48 ± 5 (35–58)	68 ± 9 (45–85)	125
	Deep water (2000-bottom)	56 ± 9 (45–76)	52 ± 4 (43–56)	38
WM (*March* 2008)	Surface (0–100)	57 ± 7 (46–84)		62
	Intermediate (200–500)	44 ± 3 (38–49)	77 ± 12 (54–89)	51
	Deep water (2000-bottom)	42 ± 3 (38–49)	60 ± 5 (52–73)	44
Ionian Sea (*April* 2002)	Surface (0–100)	66 ± 6 (54–82)		24
	Intermediate (200–500)	53 ± 4 (47–63)	49 ± 11 (24–69)	47
	Deep water (3000-bottom)	63 ± 5 (52–72)	46 ± 2 (42–51)	13
Adriatic Sea (*November* 2006)	Surface (0–100)	60 ± 9 (46–91)		77
	Intermediate (200–500)	46 ± 4 (39–54)	48 ± 7 (28–59)	39
	Deep water (800-bottom)	54 ± 6 (46–66)	30 ± 5 (26–48)	31
EM (*June* 2007)	Surface (0–100)	64 ± 5 (54–75)		26
	Intermediate (200–500)	46 ± 4 (40–52)	46 ± 7 (36–56)	13
	Deep water (2750-bottom)	41 ± 4 (34–47)	46 ± 3 (39–48)	13
Ionian Sea (*March* 2008)	Surface (0–100)	58 ± 6 (50–73)		47
	Intermediate (200–500)	45 ± 4 (37–51)	56 ± 7 (42–68)	30
	Deep water (3000-bottom)	45 ± 4 (37–50)	49 ± 4 (44–55)	19

average concentrations (± standard deviation) in the surface (0–100 m), intermediate (200–500 m), and deep waters (DW, the deepest 1000 m and the deepest 300 m in the Adriatic Sea, due to its low depths) of the same stations are reported in Table 2.

In general, DOC and AOU vertical profiles were opposite as also observed for oceanic waters (Guo et al., 1994; Álvarez-Salgado et al., 2001; Arístegui et al., 2002). DOC values were similar to those reported for oceanic waters (Hansell, 2002) and for other Mediterranean Sea areas (Cauwet et al., 1990; Copin-Montegut and Avril, 1993; Dafner et al., 2001a, 2001b; Avril, 2002; Sempéré et al., 2003; Santinelli et al., 2006; 2008). AOU values were similar to those previously reported for the Mediterranean Sea (Avril, 2002; Copin-Montégut and Bégovic, 2002; Santinelli et al., 2002; 2008), but they were generally lower (24–89 μM) than those observed in oceanic waters (50–200 μM) (Guo et al., 1994; Hayase and Shinozuka, 1995; Doval and Hansell, 2000; Álvarez-Salgado et al., 2001; Arístegui et al., 2002). AOU data in the surface layer are not reported in Table 2, because most of them are affected by oxygen super saturation.

DOC in the surface layer (0–100 m) showed the highest and most variable concentrations (46–100 μM). The seasonality (Avril, 2002), the trophic characteristics of the different areas (D'Ortenzio and Ribera d'Alcalà, 2009), and the occurrence of cyclonic and anticyclonic eddies (Hansell, 2002; Santinelli et al., 2008) have been demonstrated to affect surface DOC distribution and concentrations. The average values ranged between 57 and 68 μM, with the lowest values in the WM and in the Ionian Sea in March 2008 and in the Tyrrhenian Sea (Table 2), and the highest value in the Ligurian Sea. No significant differences between WM and EM in DOC surface values were observed, even with the W-E increasing oligotrophy and the phosphorus limitation of bacteria DOC consumption in the EM (Krom et al., 2005; Zohary et al., 2005; Pinhassi et al., 2006).

In the intermediate layer (200–500 m), DOC and AOU average values ranged between 44–53 and 46–77 μM, respectively in most of the profiles; in addition a maximum of DOC (53 ± 4 μM) and low values of AOU (49 ± 11 μM) were observed in the Ionian Sea in 2002. DOC and AOU distributions in this layer are strongly affected by the occurrence of the LIW, which is generally characterized by minima in DOC and DO (maximum in AOU) (Santinelli et al., 2002, 2006, 2008). The highest DOC values, observed in the Ionian Sea in 2002, could be attributed to mixing between the LIW and the Cretan Intermediate Water (CIW) characterized by high DOC and DO concentrations (Seritti et al., 2003).

Surprisingly, DW were characterized by high variability in the whole range of both DOC (34–76 μM) and AOU (26–73 μM), with the average values ranging between 41 and 63 μM for DOC and between 30 and 64 μM for AOU. High DOC and DO values were previously observed in the Mediterranean Sea in correspondence with newly formed DW (Santinelli et al., 2006; Seritti et al., 2003). The DOC vertical profiles reported in Fig. 3 showed two characteristic behaviors. In some areas, like the Tyrrhenian Sea, the WM in 2008, the EM in 2007, and the Ionian Sea in 2008, DOC profiles were very similar to those observed in the Arabian Sea (Hansell and Peltzer, 1998), Sargasso Sea (Hansell and Carlson, 2001), central equatorial Pacific Ocean (Carlson and Ducklow, 1995), and Mediterranean Sea both in the WM (Cauwet et al., 1990; Copin-Montegut and Avril, 1993; Doval et al., 1999; Avril, 2002) and in the EM (Seritti et al. 2003, Krom et al., 2005). These profiles showed the highest average values in the surface layer (57–64 μM), a decrease until a concentration of 44–46 μM at 200–500 m, and almost constant values (41–45 μM) until the bottom (Fig. 3, Table 2). In some of these profiles a slight DOC increase in the samples close to the bottom was observed. In contrast, in the WM in 2005, in the Ionian Sea in 2002, and in the Adriatic Sea in 2006, DOC showed a marked increase (to values > 60 μM) in the DW (Fig. 3). These profiles were also characterized by a high variability among the stations (indicated by the error bars). Finally, the average DOC vertical profile for the Ligurian Sea was characterized by almost constant values (50 ± 5 μM) below 500 m with a slight increase close to the bottom. It is interesting to note that the very low DOC concentrations (42 ± 3 μM), found below 300 m in both the Tyrrhenian Sea and in the WM in 2008, were associated with high AOU values (> 60 μM). In contrast, in the DW of the Adriatic Sea, the Ligurian Sea and the WM in 2005, the increase in DOC was associated with a decrease in AOU. This finding suggests that the higher DOC concentrations in DW can be due to a minor extent of mineralization. Finally, in the Ionian Sea in 2002, the expected marked decrease in AOU was not observed in correspondence to the increase in DOC in the DW. This could be related to the very low values of DO observed in the EM during the EMT (Klein et al., 2003). As a consequence, the increase in DO, due to deep-water ventilation, could be masked by mixing with the old resident waters poorer in DO than those occurring in June 2007 and March 2008.

3.2. DOC horizontal maps

In order to describe the general features of the DOC dynamics in the Mediterranean Sea, horizontal maps of DOC concentrations are reported in the core of the LIW (Fig. 4) and at bottom depths (Fig. 5). These maps can be useful to get a general trend of DOC in the Mediterranean Sea, but it is very important to keep in mind that they were obtained by combining data collected in different seasons and in different years.

3.2.1. Intermediate layer

In the Mediterranean Sea, the DOC distribution in the water column is strongly affected by water masses circulation (Santinelli et al., 2006). The biggest problem in the estimation of DOC consumption rates is to follow the core of a water mass, due to the extent of the mixing. The only water mass that can be clearly identified, by its S maximum, is the LIW, even if the mixing with the overlying thermocline and underlying DW affects its core during its route. Due to winter surface cooling and evaporation, a surface mixed layer of about 100 m, with LIW characteristics, occurs in the northeastern Levantine basin. LIW subducts and spreads on isopycnal surfaces along pathways determined by cyclonic/anticyclonic structures of the upper thermocline circulation (The LIWEX group, 2003). The LIW represents the Mediterranean contribution to the oceanic thermohaline circulation. For these reasons, horizontal maps of S, DOC, and AOU at the maximum of S in the intermediate layer 200–700 m (LIW core) are reported in Fig. 4.

LIW route is rather complicated and it follows different paths because it is trapped by eddies (Millot, 1994, 1999) (see black arrows superimposed to the S map, Fig. 4A). LIW moves westward from its formation site; one vein flows northward toward the Adriatic, the other passes through the Sicily Strait and it enters in the Tyrrhenian Sea, following the east side due to the Coriolis force. It emerges from the Sardinian Channel flowing northward very close to the Sardinian western coast. It reaches the Ligurian Sea, the Gulf of Lions, and then flows toward the Algerian Basin (Millot, 1994), finally reaching the Gibraltar Strait. In general, DOC and AOU showed opposite patterns moving from the Levantine Basin to the WM: DOC decreased from 68 to <40 μM (Fig. 4B), while AOU increased from 10 to >90 μM (Fig. 4C). An absolute minimum of DOC was observed in the southern part of the Algerian Basin in correspondence to a maximum of AOU. This area is known to be characterized by structures, named extra-minimum oxygen (Minas et al., 1991), in which the biological activity determines a strong decrease in DO concentrations (and a consequent increase in AOU). The region is recognized for high primary productivity at the surface and high remineralization rates at depth, perhaps explaining the low DOC values associated with the maximum in AOU.

3.2.2. DOC consumption at long temporal scale: the LIW case

In order to estimate DOC consumption in the LIW, the DOC distribution is assumed to be stable in this water mass. This means that the DOC concentration, when LIW forms (in the Levantine Basin), and the DOC consumption rate is considered almost the same each year in its core. The contribution of DOC mineralization to oxygen consumption was determined by converting AOU to carbon equivalents ($\text{AOU-C}_{\text{eq}}=\text{AOU}\cdot 0.72$) (Doval and Hansell, 2000) and considering only the samples collected in the LIW core, that is the samples characterized by a $S>38.70$. A linear relationship between DOC and AOU-C_{eq} was observed. The slopes of the reduced major axis linear regression (model II) was -0.53 ± 0.03, with an R-square of 0.50 ($n=229$). This value indicates that 53% of oxygen consumption in the LIW core is due to DOC mineralization. The role of mixing in this relationship has to be taken into account, so multiple regression of DOC with AOU and S was calculated. This relationship yields an R-square value of 0.51; the P-value is 0.3 for S and <0.0001 for AOU, suggesting that the relationship between DOC and AOU-C_{eq} is not significantly affected by mixing. The AOU-C_{eq} ratio, in which the effect of mixing has been removed, decreases to -0.38 ± 0.02, indicating that DOC mineralization accounts for 38% of oxygen consumption in the core of the LIW. This value is comparable to the highest value reported by Carlson et al. (2010), to the DOC:AOU ratios observed in the South Pacific (-0.15, -0.34) and in the Indian Ocean (-0.13, $-0{,}31$) at depths <500 m (Doval and Hansell, 2000), and to the ratio of 32% calculated by considering all the samples collected in the EM by Meador et al. (2010).

In order to estimate the DOC removal rate in the core of the LIW we considered the value of the Y intercept in the model II regression (67 ± 1 μM) as the concentration of DOC in the LIW when it is just formed ($\text{AOU}=0$ μM). This DOC is mineralized en route toward the WM. The lowest DOC concentration observed in the samples, considered for the relationship ($S>38.70$), was 45 μM. By choosing samples with $S>38.70$, only those collected in the Levantine Basin and the Tyrrhenian Sea were considered (Fig. 4). Since the estimated time for the LIW to reach the Sicily Strait is of ~10 years (Roether et al., 1998) and ~22 μM have been consumed in that period, the removal rate in the core of LIW is 2.2 μMC yr^{-1}. This value is about double the highest values reported for the open ocean (Carlson et al., 2010).

3.2.3. Deep waters

Mediterranean DW circulation is complex. Each winter DW forms in both EM (mainly in the Adriatic and in the Aegean Sea) and WM (mainly in the Gulf of Lions, but also in the Ligurian Sea). The recently formed DW are subjected to mixing with resident DW and this process determines a change of their chemical and physical characteristics; as a consequence, it is not simple to follow their routes and it is much more difficult to estimate DOC consumption rates in their core. Although samples were collected at the same locations in two consecutive years, it is probable that the DW sampled were different. In addition, recently ventilated DW usually replenishes the deepest layer. For these reasons, we report the bathypelagic DOC horizontal map by considering only the deepest samples collected at each station (Fig. 5); samples from <1000 m were excluded. The contour map of the depth at which samples were collected (Fig. 5A) corresponds to the bathymetry of the study area and shows that the range of depth is 1027 to 3609 m in the WM and 1040 to 4262 m in the EM. The EMDW and the western Mediterranean DW (WMDW) cannot mix due to the sill at the Sicily Strait (~500 m). They are also characterized by different ranges of S (38.64–38.80 in the EM and 38.43–38.65 in the WM), of σ_θ, (29.16–20.31 kg m^{-3}, in the EM and 29.00–29.13 kg m^{-3}), and by a θ of 12.75–13.67 °C in both basins.

Due to the high spatial and temporal variability of DOC (Fig. 3 and Section 3.1) this map can only give a general picture of the DOC distribution in the Mediterranean bathypelagic layer. Inter-annual variability and/or particular features will be discussed in the following sections. AOU is mapped as well (Fig. 5C), giving an indication of the relative "age" of the DW. In fact, when a new

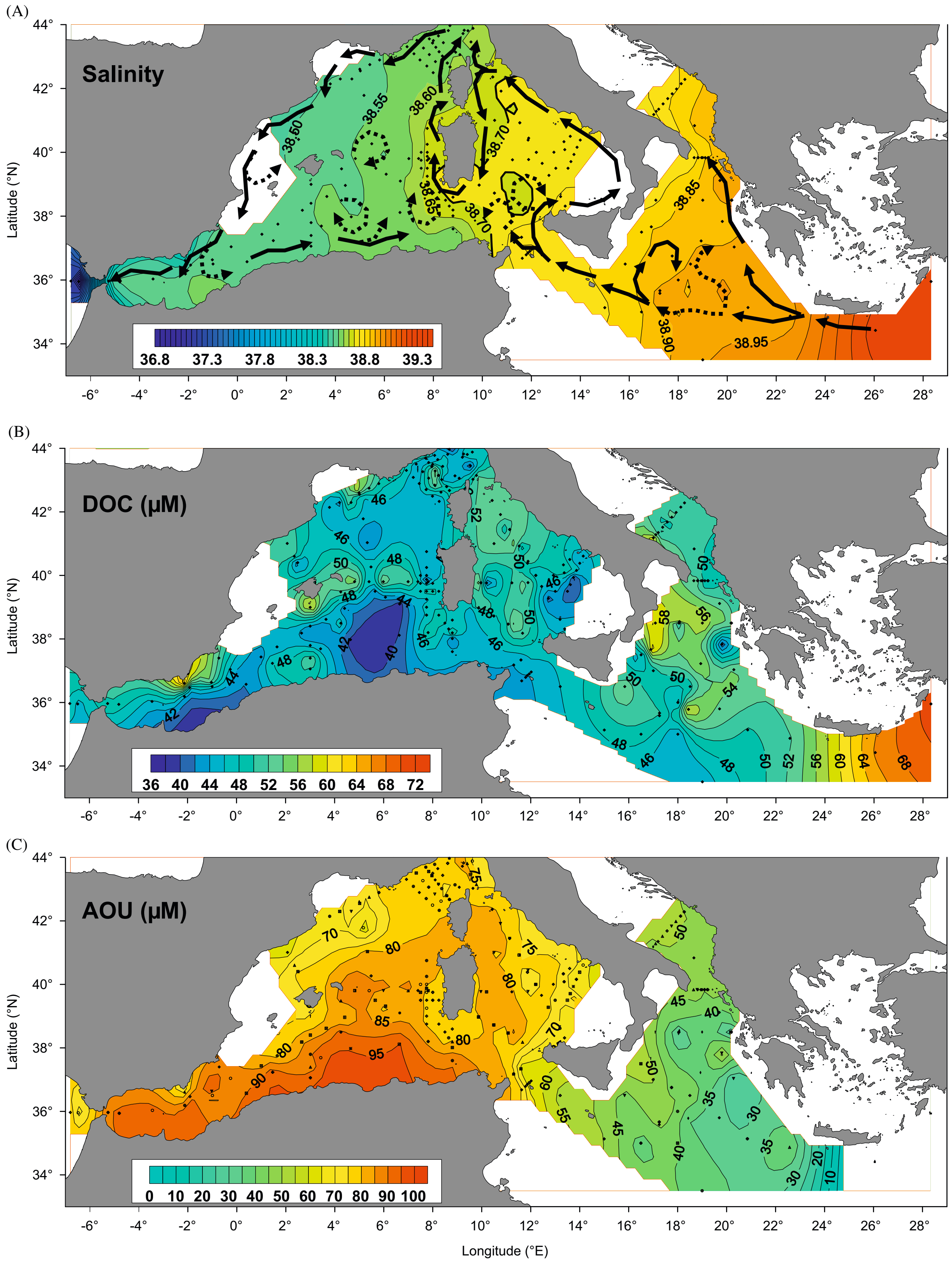

Fig. 4. Horizontal distributions of salinity, DOC (μM) and AOU (μM) determined in the core of the Levantine intermediate water (LIW), identified by its salinity maximum (in the intermediate layer 200–700 m). The black points indicate the positions of the stations used for the map. The simplified main flow path of LIW is superimposed on the salinity map (adapted from Millot, 1994 and Malanotte-Rizzoli et al., 1997). Negative values of AOU in the easternmost part of the map have been removed.

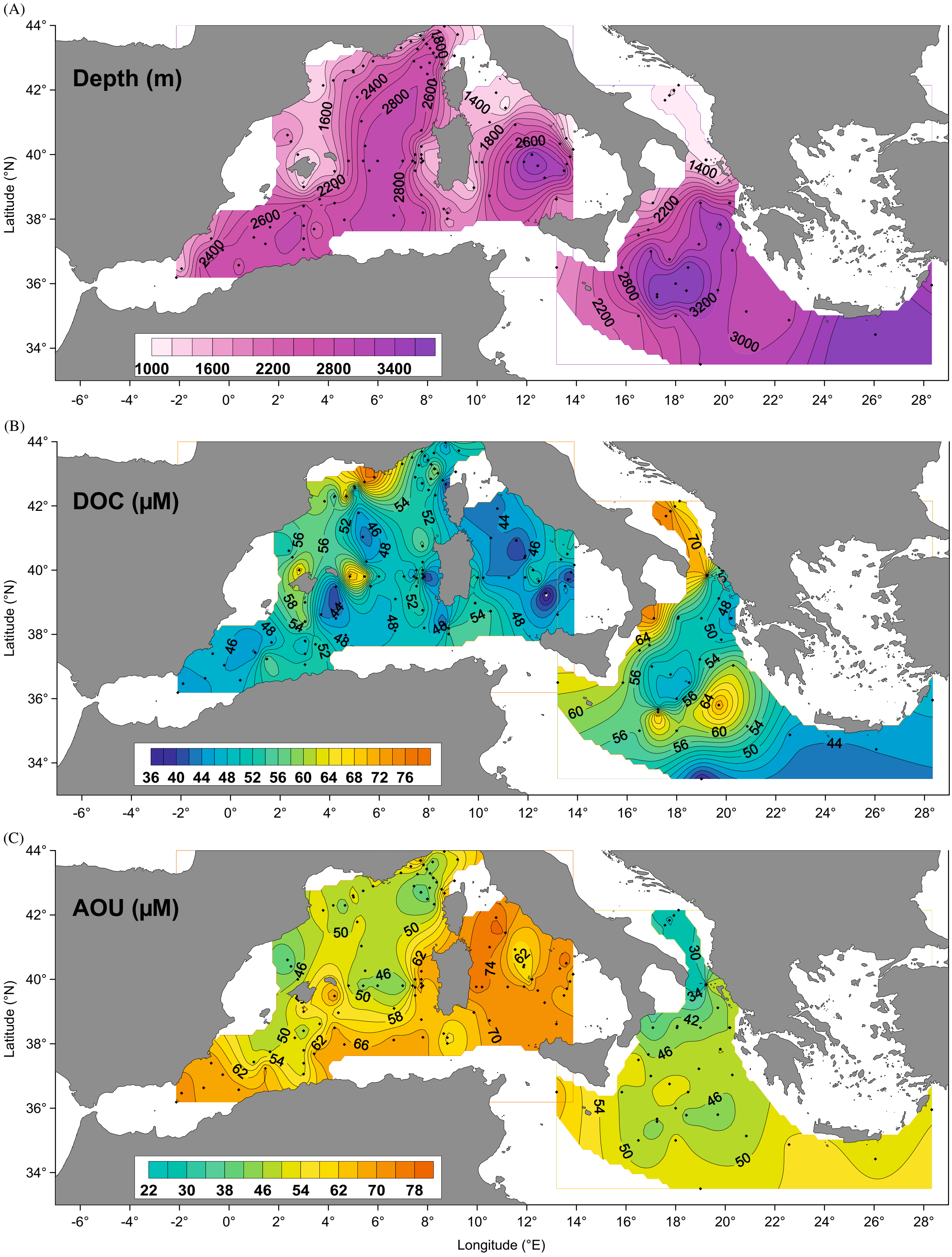

Fig. 5. Horizontal distributions of (A) bottom depth (m) and (B) DOC (µM) and (C) AOU (µM) at those depths, considering the deepest sample collected in each station (stations with a depth <1000 m were excluded). The black points indicate the positions of the stations used for the map.

input of a recently ventilated DW occurs, this results in an increase in DO (and a consequent decrease in AOU), therefore the oldest resident waters are characterized by higher AOU concentration due to the extent of mineralization. In the Mediterranean bathypelagic layer, two main features can be observed: (1) DOC concentrations are highly variable, ranging between 36 and 76 μM; (2) DOC values are very high if compared to those reported for the oceanic waters and they are generally higher than those observed in the LIW. These surprising findings pose intriguing questions about carbon export at depth and on the role of DOC in supporting the deep-water ecosystem in the Mediterranean Sea.

In general, the bathypelagic horizontal map shows: (i) A marked increase in DOC (> 60 μM), associated with a minimum (< 47 μM) in AOU in the Gulf of Lions, in the Southern Adriatic Sea and in the Ionian Sea; these regions are influenced by DW formation (Theocharis et al., 1998). (ii) DOC concentrations of 49 ± 5 μM in the southern WM (36–39°N, 0–8°E). These values result from a survey in October 2004 when only the 'typical' WMDW was observed (Schroeder et al., 2008b); this water mass was characterized by an AOU of 62–67 μM. (iii) A minimum of DOC (< 45 μM) associated with a maximum AOU (> 72 μM) in the Tyrrhenian Sea.

The highest DOC concentrations (55–76 μM) in the WM were detected in May 2005. This finding can be attributed to the particular DW formation event observed by Schroeder et al. (2006) during the same cruise. In the following sections the areas characterized by a marked DOC increase in the DW are discussed in detail.

3.2.4. *DOC export during WMDW formation*

Due to rapid changes in WMDW, DOC vertical distributions along a section in the Algero-Provençal Basin is reported for both 2005 (Fig. 6A) and 2006 (Fig. 6B), together with the DOC distribution in a southern W-E section in March 2008 (Fig. 6C).

The vertical distribution of S, θ and DO in 2005 and 2006 along the same transect and the overall θ/S diagrams are shown in Schroeder et al. (2006, their Fig. 2) and Schroeder et al. (2008a, their Figs. 2–3; 2008b, their Figs. 1–3).

In 2005 at > 1500 m, DOC showed (i) a maximum (> 55 μM) in the westernmost stations (AOU < 47 μM), (ii) values ranging between 50 and 55 μM in the central part of the section (AOU = 50–54 μM), and (iii) a minimum (< 40 μM; AOU > 60 μM) in the easternmost stations (Fig. 6A). In 2006, DOC in the DW changed; at > 2000 m, DOC was higher (> 50 μM) than in 2005 and its maximum was observed in the eastern side of the section (Fig. 6B). These high DOC values completely disappeared in 2008 (Fig. 6C). These features can be explained by physical processes; in spring 2005, a layer of newly formed WMDW was found in the bottom waters of the Gulf of Lions, Balearic Sea, Algero-Provençal Basin and northern Algerian Basin (López-Jurado et al., 2005; Schroeder et al., 2006; Santinelli et al., 2007). In addition, Canals et al. (2006) observed in the Gulf of Lions a major dense shelf water cascade in February-March 2005. This process transported large amounts of sediment and organic matter to the DW, so it is very probable that it affected DOC concentrations, in particular in the DW of coastal origin. They estimated a total organic carbon transport of 15×10^9 gC d^{-1}. In addition, in 2006 at > 1800 m the resident DW was completely renewed by newly formed DW (θ = 12.85–12.88 °C, S = 38.45–38.47, DO = 200–207 μM, AOU = 52–60 μM) (See Fig. 3 in Schroeder et al., 2008b). This observation explains the general increase in DOC at > 2000 m. In 2008, the significant decrease in DOC was not supported by the AOU, which ranged between 50 and 60 μM. This finding, together with the DOC homogeneity, is not easy to explain, but underlines the high seasonal and interannual variability of DOC also in DW.

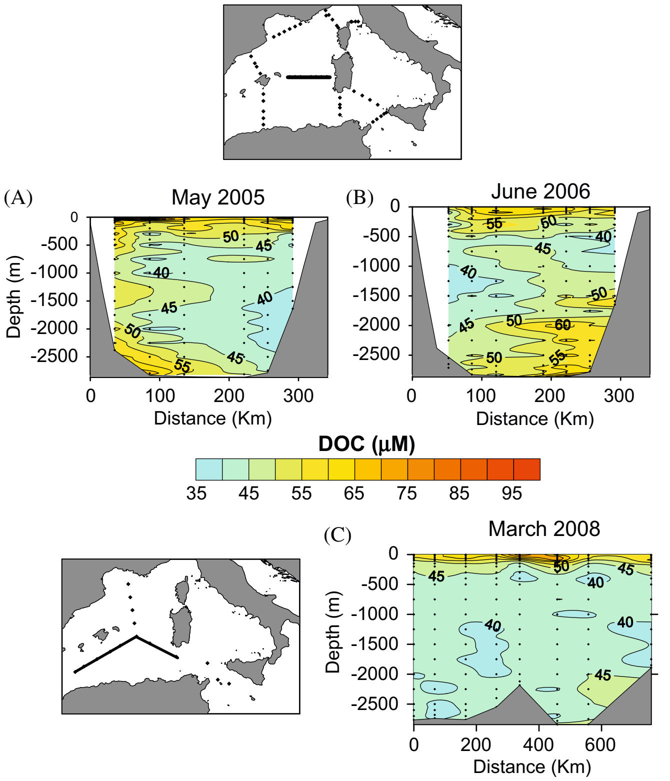

Fig. 6. Vertical distribution of DOC on a section between the Balearic Islands and the Sardinian Sea (see inset map) visited in both May 2005 (A) and June 2006 (B) and a southern section (see inset map) visited in March 2008 (C).

An estimation of the amount of DOC exported during DW formation in 2005 can be done by considering the mean production rate of DW reported by Schroeder et al. (2008b) (2.4 Sv, that is 2.4×10^6 m^3 s^{-1}) and assuming that winter surface DOC concentrations ranged between 50 and 80 μM (the typical range of surface DOC values in the whole Mediterranean Sea, Table 2, Fig. 3). This range is in agreement with the DOC values observed in the upper 50 m from September to December (1991–1994) in the Dyfamed station (Ligurian Sea, Avril, 2002). In contrast these values are lower than those measured in the Gulf of Lions in November 1991 (85–250 μM) (Cauwet et al., 1990) and in November 1994 (80–110 μM) (Yoro et al., 1997), so the export could be underestimated. Considering 40 μM as representative of DOC in DW, a ΔDOC (DOC at surface-DOC at depth) of 10–40 μM can be calculated. Given these assumptions, the export of DOC during DW formation in 2005 ranged between 0.29–1.15×10^6 g C s^{-1} (0.76–3.02 Tg C month^{-1}). These values are two orders of magnitude higher than the input of DOC by the Rhone River (1.1×10^{-2} Tg C month^{-1}) estimated by Sempéré et al. (2000). Assuming that the lowest DOC concentration observed in Mediterranean waters (34 μM) represents the refractory fraction, all the DOC exported at depth is semi-labile.

Our data support the theory of Christensen et al. (1989) that the input of DOC is almost sufficient to explain the high respiration rates found. The DW formation rate of 2.4 Sv (Schroeder et al., 2008b) is similar to that calculated using tritium profiles (2.5 Sv), (Andrie and Merlivat, 1988), but it is significantly higher than the values of 0.14–1.2 Sv reported by Rhein (1995). If DW forms with these lower formation rates, an export ranging between 0.045 and 1.52 Tg C month^{-1} is estimated. As a consequence, different DW formations rates result in vastly different DOC export rates.

3.2.5. DOC consumption at short temporal scale: the Adriatic Sea case

In the framework of the Italian National projects SINAPSI and VECTOR, DOC samples were collected in January 1999, April 2002, January and June 2008 in the Southern Adriatic Sea (Fig. 7). This is an important region of DW formation, where the water masses occurring in the deep layer are renewed by winter convection and by a vein of denser and DO rich water flowing into the southern Adriatic depression, presumably from the north (Manca et al., 2006). DOC and AOU at the deepest station, located in the central part of the basin, were compared between the different periods (Fig. 7). The DO data for the Adriatic Sea were kindly provided by G. Civitarese (CNR-ISMAR).

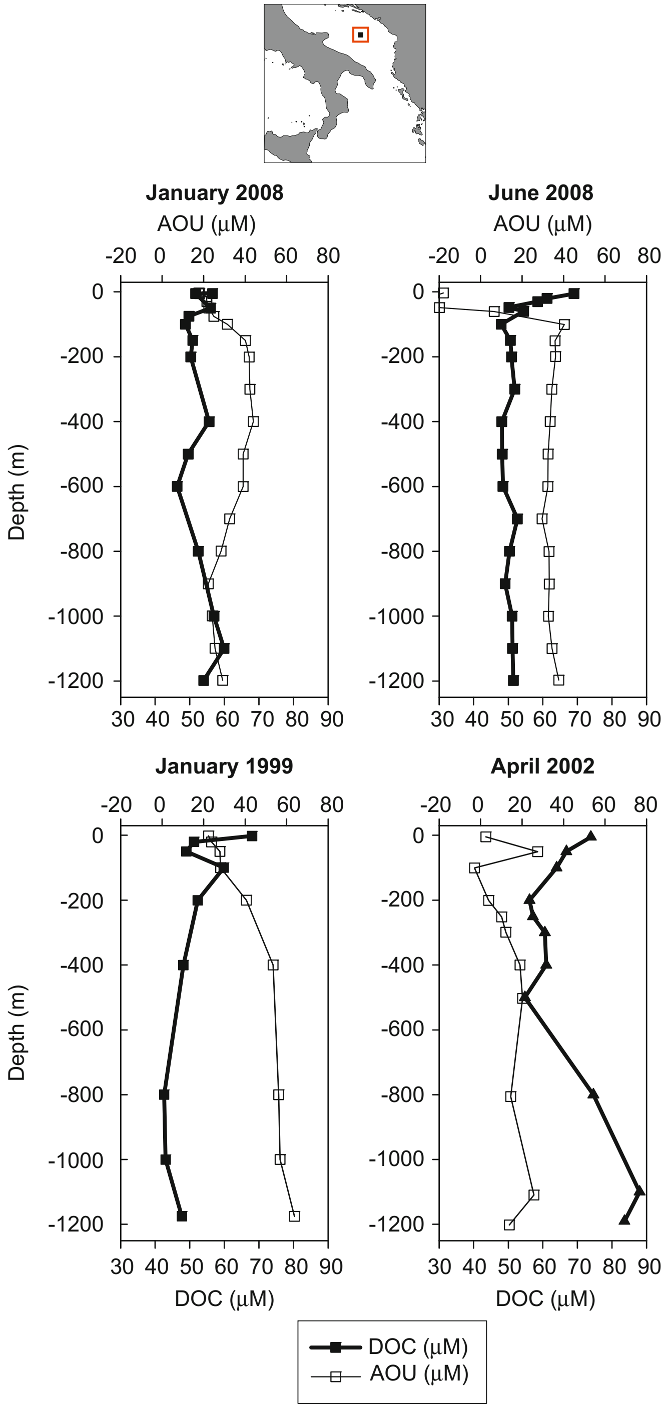

Fig. 7. Vertical distribution of DOC and AOU at the station located in the central part of the southern Adriatic Sea (see inset map), in January and June 2008, in January 1999 and in April 2002.

Vertical profiles in January and June 2008 were used to estimate DOC consumption at short temporal scale. During January 2008 an event of DW formation occurred and this probably caused the high DOC (52–60 μM) and the low AOU (22–29 μM) concentrations, clearly visible in the deepest samples (Fig. 7). This signal disappeared in June, when values of 49–51 μM for DOC and of 33–38 μM for AOU were observed below 800 m. This station is characterized by particular physical features; the waters in the deepest layer are not able to flow into the Ionian Sea, due to the Otranto Sill (850 m), unless there is a big input of water from the north, but this occurs mainly in winter. S and θ values below 1000 m (January 2008: $S=38.73$, $\theta=12.95$ °C; June 2008: $S=38.73$, $\theta=12.96$ °C) confirm that the DW present was hydrographically the same in the two periods; as a consequence, we can suppose that the DOC decrease, observed from January to June, was due mainly to DOC bacterial mineralization. DOC and AOU mean values from 1000 m to the bottom (1250 m) in January were 57 and 26 μM, respectively, and in June were 51 and 35 μM, respectively. These data indicate a decrease of 6 μM in DOC and a correspondent increase of 9 μM in AOU in the Adriatic DW in 5 months. The ratio between DOC and AOU-C_{eq} is -0.92, suggesting that about the 92% of oxygen consumption was due to DOC mineralization. These data suggest a DOC microbial utilization rate of 1.2 μM C month^{-1}. This value is 10 times higher than the values observed by Carlson et al. (2010) in the Atlantic Ocean. Obviously, these rates are strongly affected by the quality of DOC; we may suppose that semi-labile DOC transported to depth during DW formation should be more quickly used than the older fraction, and also that with time and progression of mineralization, the DOC utilization rate decreases. In fact, it is probable that where DOC concentrations are higher, a higher fraction of semi-labile DOC occurs and as a consequence it is mineralized faster. This supports the Carlson et al. (2010) finding that DOC decay rates decreased exponentially as a function of decreasing mean layer DOC concentration; but, for a mean DOC concentration of 56 μM, they observed a DOC removal rate of 0.8–1.0 μMC yr^{-1}. The difference could be due to the fact that the highest DOC concentrations were found by Carlson et al. (2010) in the upper thermocline where bacteria could be limited by nutrients. The high DOC removal rate in the Adriatic DW (ADW) supports the increase in oxygen consumption rate in the EMDW as a consequence of the EMT (Klein et al., 2003). In fact, this may be linked to the fast consumption of the high fraction of semi-labile DOC exported during DW formation in the Cretan Sea (Seritti et al., 2003).

To emphasize the importance of this area for DOC export to depth and the influence of water masses circulation changes, the DOC vertical profiles in January 1999 and April 2002 were investigated (Fig. 7). In the deep layer (> 800 m), DOC concentration was low (44 ± 3 μM) in January 1999, whereas a surprising DOC increase occurred in April 2002 (82 ± 7 μM). AOU vertical profiles completely support the DOC trend, as below 800 m values of 60 ± 4 and 18 ± 7 μM AOU were observed in January 1999 and in April 2002, respectively. A decrease in AOU of 42 μM corresponded to an increase in DOC of 38 μM. A possible explanation for this behavior is related to the physical processes in the area. These two years were differently affected by the EMT (Roether et al., 1996; Malanotte-Rizzoli et al., 1999). In 1999, the southern Adriatic Sea was characterized by the occurrence of old DW (very low DO values), because the main source of the ADW was shifted to the Cretan Sea. In 1999, this water was estimated to be about 12 years old using radioactive tracers (Delfanti et al., 2003, data collected in 1999, during the same cruise). In contrast, in April 2002, ventilation of the bottom layer of the southern Adriatic Sea was observed during the same cruise (Manca et al., 2006). This substantial replenishment of the deepest layer with recently ventilated waters was not observed during the last two decades. This could justify both the low DOC values observed in 1999 and the marked increase of DOC, due to the replacement of the old bottom water with recently ventilated waters in 2002. The high input of DOC during DW formation in the southern Adriatic Sea supports the higher CDPR values observed there relative to other areas of the Mediterranean Sea (La Ferla et al., 2003).

3.2.6. *DOC in the transitional Eastern Mediterranean Deep Water*

DOC concentrations as low as 33–38 μM were observed in some areas of the Mediterranean Sea, such as the Tyrrhenian Sea and the Ionian Sea. These very low DOC concentrations were usually found between the LIW and the DW. This layer is occupied by the transitional EMDW (tEMDW), which is the oldest water mass detected in the Mediterranean Sea. Its renewal time has been estimated to be 126 years (Roether and Schlitzer, 1991; Schlitzer et al., 1991) and this water is always characterized by a minimum of DO (<186 μM, Manca et al., 2006). The tEMDW can pass through the Sicily Strait, below the LIW, and it was reported to sink to a depth of ~1850 m in the Tyrrhenian Sea (Sparnocchia et al., 1999). The minimum DOC observed in both basins may be a characteristic signature of this old water mass.

3.2.7. *DOC refractory fraction in the Mediterranean Sea and in the Ocean*

Mediterranean waters are younger than oceanic ones by an order of magnitude. Maximum renewal time estimated for WMDW is about 100 years (Lacombe et al., 1981; Gascard and Richez, 1985), but it could be as low as 11 years (Andrie and Merlivat 1988; Christensen et al., 1989). Mediterranean DW are characterized by higher θ (12.7–13.7 °C) than the deep Atlantic (2–3 °C). In addition, each winter DW formation events occur both in the EM (Adriatic Sea) and in the WM (Gulf of Lions and/or Ligurian Sea). Depending on the preconditioning phase (in a more cold and dry winter, more water will sink) different volumes of water are exported, but in any case, it drives a significant amount of energy to deep-water ecosystems.

DOC showed concentrations of 40–48 μM in DW not recently ventilated and concentrations as low as 33–38 μM in the tEMDW (Figs. 3A and 3B). Hansell and Carlson (1998) reported a gradient in DOC concentration in DW from 48 μM in the Northern North Atlantic to 34 μM in the Northern North Pacific; 34 μM is the lowest DOC concentration observed in the oceanic waters and is reported to be the concentration of the refractory fraction of DOC (Carlson, 2002). The weighted mean turnover time for deep-water dissolved organic matter (DOM), using $\Delta^{14}C$, was estimated to be 3700–6000 yr in the North Atlantic and North Pacific Oceans, respectively (Loh et al., 2004). A surprising finding is that in the Mediterranean Sea almost the same concentration gradient (48–34 μM) is observed. More surprising is that a DOC concentration as low as that observed in oceanic DW is found in waters characterized by an estimated renewal time an order of magnitude lower. This finding can be explained if: (1) 34 μM represents the concentration of the refractory fraction of DOC in the Mediterranean Sea, regardless of the younger age of its waters; (2) the concentration of the refractory fraction in the Mediterranean Sea is lower than that observed in the oceanic waters, as a consequence the concentration of 34 μM can be reached in a shorter time.

Some hypotheses can be formulated to explain the first consideration:

i. A different functioning of the microbial loop in the Mediterranean Sea, with a more efficient mineralization of DOC. Some features reported in the literature for the Mediterranean Sea can support this idea, including: the very high viral abundance reported for Mediterranean DW (Magagnini et al., 2007), respiration rates higher than those observed in the Oceans (Christensen et al., 1989), and the finding that respiration in the deepest Mediterranean waters accounts for a greater percentage of the upper aphotic respiration ($>45\%$) than that found in the open ocean ($<21\%$) (La Ferla et al., 2003). In addition, the DOC consumption rate estimated in this study (2.2–14.4 μM C yr^{-1}) is much higher than those observed in the open ocean (0.1–0.9 μM C yr^{-1}) (Carlson et al., 2010).

ii. High DOC mineralization rates in Mediterranean meso- and bathypelagic layers are supported by the high θ (12.7–13.7 °C). Temperature regulation of bacterial abundance, production, and specific growth rate was reported (Shiah and Ducklow, 1994; Bendtsen et al., 2002; Hoppe et al., 2002; La Ferla et al. 2005). In addition, Carlson et al. (2010) observed an exponential decrease of DOC decay rates with decreasing water mass temperature. Their data suggest that an increase in temperature from 3 to 14 °C results in an increase in DOC removal rate from 0.2 to 0.3 μMC yr^{-1}.

iii. The occurrence in Mediterranean DW of different microbial communities with respect to those present in deep open-ocean waters, due to the different environmental conditions. Very few data are available to test this hypothesis (Alonso-Sáez and Gasol, 2007; Martín-Cuadrado et al., 2007). In addition, the high ectoenzymatic activities, measured under in situ pressure, suggest that microbes are probably able to use complex carbon compounds in the northwestern Mediterranean Sea (Tamburini et al., 2002).

iv. The input of a high fraction of semi-labile material during DW formation may induce high bacterial production, capable of mineralizing the less labile material. This hypothesis could explain the increase of oxygen consumption rate in the EMDW as a consequence of the sinking of DW rich in semi-labile DOC during the EMT (Klein et al. 2003; Seritti et al., 2003).

On the other hand, the concentration of the refractory DOC fraction may be lower in the Mediterranean waters than in other oceanic waters, due to the fact that refractory fraction has less time to accumulate. DOM stoichiometry could give some information about the nature of DOM, but very few data are available for the Mediterranean Sea (Doval et al., 1999; Moutin and Raimbault, 2002; Krom et al., 2005).

The most probable hypothesis is that 34 μM represents the concentration of the refractory DOC also in the Mediterranean Sea. Otherwise, it would be strange that the lowest DOC concentration observed in the Mediterranean is exactly the same found in the oceanic waters. This could be confirmed in the high degree of similarity in proton nuclear magnetic resonance (H^1 NMR) spectra observed for high molecular weight (HMW) DOM collected in the Atlantic and Pacific Ocean, as well as for terrestrial HMW-DOM samples (Repeta et al., 2002), and in the striking similarity between H^1 NMR spectra obtained for the samples collected from the Ligurian Sea (DYFAMED) and from other oceanic environments (Jones et al., 2005). This observation suggests that refractory DOM has the same composition in very different environments.

Finally, the role of Archaea must be clarified (Karner et al., 2001; Herndl et al., 2005). They may be able to remove the refractory DOC more efficiently in the Mediterranean Sea in terms of time and/or concentration, as Teira et al. (2006) observed in the meso- and bathypelagic waters of the North Atlantic. But only one paper reports the distribution and activity of Bacteria and Archaea in the Mediterranean Sea, and it is limited to the Tyrrhenian Sea (Tamburini et al., 2009). In addition, $\Delta^{14}C$ could give important indications about the average age of the DOC in the Mediterranean Sea, but no data are yet available.

4. Conclusions

The data reported here demonstrate the heterogeneity and dynamic nature of Mediterranean DOC pool and its high variability both in the surface and deep layers. They also indicate that DW formation could strongly impact deep-water ecosystems by bringing to depth high amounts of semi-labile DOC.

Two different conceptual models represent the distribution of the various fractions of refractory, semi-labile and labile DOC in the Mediterranean Sea (Fig. 8). One (Fig. 8A) is the same as proposed for the open ocean (Carlson, 2002) while the other (Fig. 8B) is an adaptation in which the occurrence of semi-labile DOC at depth is evidenced and the DOC minimum is reached between LIW and DW. The availability of semi-labile DOC at depth represents an important input of energy for deep-water microbial loop. The amount of DOC exported to depth will depend both on the DOC concentration at surface and on the amount of DW formed. The first is influenced by biological activity at surface (both DOC production and consumption processes); the second by climatic conditions. In general, the semi-labile DOC at depth is very quickly consumed and this signal disappears in a few months. A consequence of this finding is that the export of DOC during DW formation plays a key role in the global carbon cycle by linking atmospheric and surface water dynamics with deep water ecosystems.

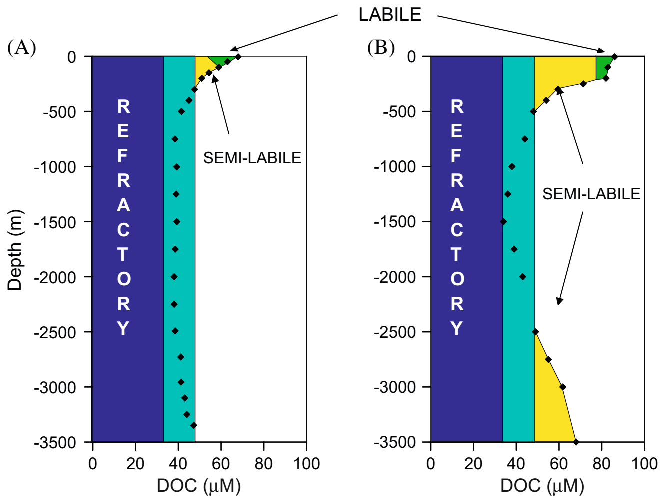

Fig. 8. Two conceptual models for the distribution of refractory (cyan and blue), semi-labile (yellow) and labile (green) fractions of DOM in the Mediterranean Sea. The refractory fraction was divided in two broad pools based on DOC gradient observed in the Mediterranean deep waters, in the same way as reported by Carlson (2002) for the open ocean. The lowest concentration of DOC (34 μM) was observed in the tEMDW (estimated age of 126 years), while concentrations of 44–48 μM were found in the old WMDW (residence time of 10–20 years). (A) The model proposed for the open ocean (Carlson, 2002) and supposedly valid for some Mediterranean regions; (B) a model adapted for specific areas of the Mediterranean Sea impacted by deep water formation, in which high amounts of semi-labile DOC are exported to depth (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Finally, our data indicate the need for further interdisciplinary studies focused on DOM dynamics, covering this marginal sea both spatially and temporally. These studies should combine measurements of the whole DOM pool ($\Delta^{14}C$, DOC, dissolved organic nitrogen (DON), dissolved organic phosphorous (DOP), and chromophoric DOM (CDOM)) with analyses at the molecular level. In addition, microbial studies should be done in order to identify differences between microbial populations in Mediterranean and oceanic DW. All these studies should be combined in a modeling effort of the carbon cycle in the Mediterranean Sea.

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