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Vertical distribution of dissolved organic carbon (DOC) in the Mediterranean Sea

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ABSTRACT: Vertical profiles of dissolved organic carbon (DOC) in different areas of the Mediterranean Sea were studied during 6 oceanographic surveys conducted between January 1999 and September 2001. The study areas were located at key points of water mass circulation of the entire Mediterranean basin. DOC showed similar behaviors at all hydrological stations, with highest values in surface waters, a minimum in the intermediate layers and slightly increasing values in deep waters. Important links were found between DOC distribution in the water column and hydrological structures. In particular, distinctive DOC concentrations were detected in the different water masses. This finding was attributed to the age, origin and route of each water mass.

KEY WORDS: DOC · Water masses · Mediterranean Sea

1. INTRODUCTION

Dissolved organic carbon (DOC) in the ocean is one of the largest reservoirs of reactive organic carbon on the Earth (Hansell & Carlson 1998). DOC in deep oceans represents a pool of carbon (~650 Gt) comparable to that of CO_2 in the atmosphere (~650 Gt) and to that of terrestrial biomass (~650 Gt) (Hedges 1992, Siegenthaler & Sarmiento 1993, Ogawa & Tanoue 2003). Growing interest devoted over the past 10 years to the study of carbon dynamics in the sea is closely tied to the recognised role of oceans in climate change; in particular, oceans can affect CO_2 concentration in the atmosphere through physical and biological pumps (Mann & Lazier 1996, Hedges 2002). Atmospheric CO_2 has increased in the 20th century, and because it absorbs infrared radiation (IR) the temperature of the Earth has increased. The consequent global warming will affect natural equilibriums in the whole planet (Mann & Lazier 1996), with consequences that are only partially imaginable.

It has been estimated that the net oxidation of only 1% of marine DOC could be sufficient to generate an amount of CO_2 equal to that released annually into the atmosphere by the combustion of fossil coals (Siegenthaler & Sarmiento 1993, Hedges 2002). Moreover, the enhancement of UV-B radiation reaching the Earth induces photochemical reactions that affect the quality and quantity of DOC in the upper layer of the water column, with important implications for CO_2 fluxes from the sea surface to the atmosphere (Moran & Zepp 1997, Blough & Del Vecchio 2002). Interest in marine DOC has been also due to its ecological significance: it represents the main substrate for the growth of heterotrophic bacteria, as well as a major intermediate in the ocean carbon cycle (Azam et al. 1983, Ducklow & Carlson 1992).

Highly labile, semi-labile and refractory fractions can be detected in the DOC pool on the basis of their biological availability (Kirchmann et al. 1993, Doval et al. 1999, Ogawa & Tanoue 2003). Biologically highly labile DOC turns over on time scales of minutes to days; this fraction is present in surface waters, where biological productivity is high, and it usually represents only a small portion of total DOC as a consequence of its rapid degradation. Biologically semi-labile DOC turns over on time scales of months to years because it is resistant to rapid microbial degradation.

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Biologically refractory DOC has a turn over of centuries to millennia; this fraction is homogeneously distributed throughout the water column and it represents approximately 70% of surface DOC in thermally stratified systems (Druffel et al. 1992, Carlson & Ducklow 1995).

Generally, biological activity and physical processes are the main mechanisms that determine DOC concentration and its distribution in the water column. In the euphotic zone, photosynthesis, together with the intense biological activity of plankton, is responsible for the high production of DOC. This DOC may be rapidly consumed by bacteria, accumulated, recycled through the 'microbial loop' or removed by photochemical oxidation, coagulation and/or adsorption on sinking particles. Some conditions such as DOC biochemical composition, molecular size, inorganic nutrient availability, grazing by protists and competition with phytoplankton determine the rate of bacterial uptake and, consequently, the control of DOC concentration (Amon & Benner 1996, Shiah et al. 1998, Søndergaard et al. 2000).

The main DOC production processes below the photic zone are: grazing by protists and copepods (Strom et al. 1997), degradation of fecal pellets, viral lysis of bacterioplankton (Fuhrman 1999) and dissolution of sinking marine aggregates larger than 0.5 µm by intense hydrolytic enzymatic activity, due mainly to the attached bacteria (Smith et al. 1992, Ploug et al. 1999). Free-living bacteria play an important role in the production of fine non-sinking particles within and below the euphotic zone, and they are also the main users of sinking carbon (Cho & Azam 1988). In bottom waters, microbial activity on sedimentary organic matter is another important source of DOC, which is then recycled to the water column (Seritti et al. 1997).

The role of physical processes, such as deep water formation, thermohaline circulation, ages and routes of different water masses and horizontal and vertical transport are other important factors that affect DOC distribution in the water column. DOC vertical transport is reduced when the water column is stratified and stable; in contrast, when the water column is subject to an intense vertical mixing, DOC is more easily transported to intermediate and deep waters. Recently, a link between DOC distribution and circulation of the main water masses in the Mediterranean Sea has been detected and the occurrence of different DOC concentrations in different water masses reported (Santinelli et al. 2002, Seritti et al. 2003).

Only a few DOC data from the Mediterranean Sea are available in the literature and they are mainly related to the Gulf of Lions and the Gibraltar Strait (Western Mediterranean) (Copin-Montégut & Avril 1993, Cauwet et al. 1997, Yoro et al. 1997, Doval et al. 1999) and to the Adriatic Sea and Aegean Sea (Eastern Mediterranean) (Pettine et al. 1999, 2001, Sempéré et al. 2002, Giani et al. 2005).

In this study, DOC distribution in areas of the Mediterranean Sea located at key points of thermohaline circulation is described. Moreover, an investigation into the links between DOC and the physical characteristics of the water column, in both western and eastern sub-basins, is reported and discussed.

2. MATERIALS AND METHODS

Seawater samples were collected during 6 field studies carried out in the Mediterranean Sea in different periods with RV 'Urania'. Fig. 1 shows all the hydrological stations at which conductivity, temperature and depth (CTD) were measured (empty symbols), in addition to stations at which seawater samples for DOC determination were also collected (filled symbols). The stations were located at key points of thermohaline circulation and they were usually positioned offshore in order to minimize the terrestrial DOC contribution. Seawater samples for DOC analysis were collected by means of a General Oceanics rosette equipped with 24 Niskin bottles, with a collection frequency of 200 and/or 500 m in order to obtain a complete profile below the euphotic zone. The rosette was assembled on the CTD SBE 911 plus probe. Seawater samples (500 ml) were immediately filtered on board through sterile 0.2 µm membrane filters (Sartorius, Minisart, SM16534 K) under low N_2 pressure and then stored in amber glass bottles at 4°C in the dark until further analysis, which was performed within 1 mo of sampling. A check of DOC variations with time, under storage conditions just described, demonstrated the absence of significant differences within 6 mo of collection.

DOC measurements were carried out by means of a Shimadzu TOC-5000 analyzer. Before analysis, samples were acidified with 50 µl of 50% H_3PO_4 and sparged for 10 min with pure 'CO_2 free' air to remove inorganic carbon. A sub-sample (100 µl) was injected in the furnace after 4 rinses with the sample to be analyzed. Replicate injections (3 to 5) were performed until analytical precision was within 2%. The calibration curve was executed daily using potassium hydrogen phthalate as standard. DOC concentrations were calculated according to Thomas et al. (1995) by subtracting the system blank area from that of the sample and then dividing for the slope of the calibration curve. The accuracy of DOC measurements and the system blank were checked daily by means of deep Atlantic water (nominal value 45 ± 1 µM, measured value 45 ± 1 µM) and low carbon (5 to 6 µM) water reference samples (provided by D. Hansell, University of Miami).

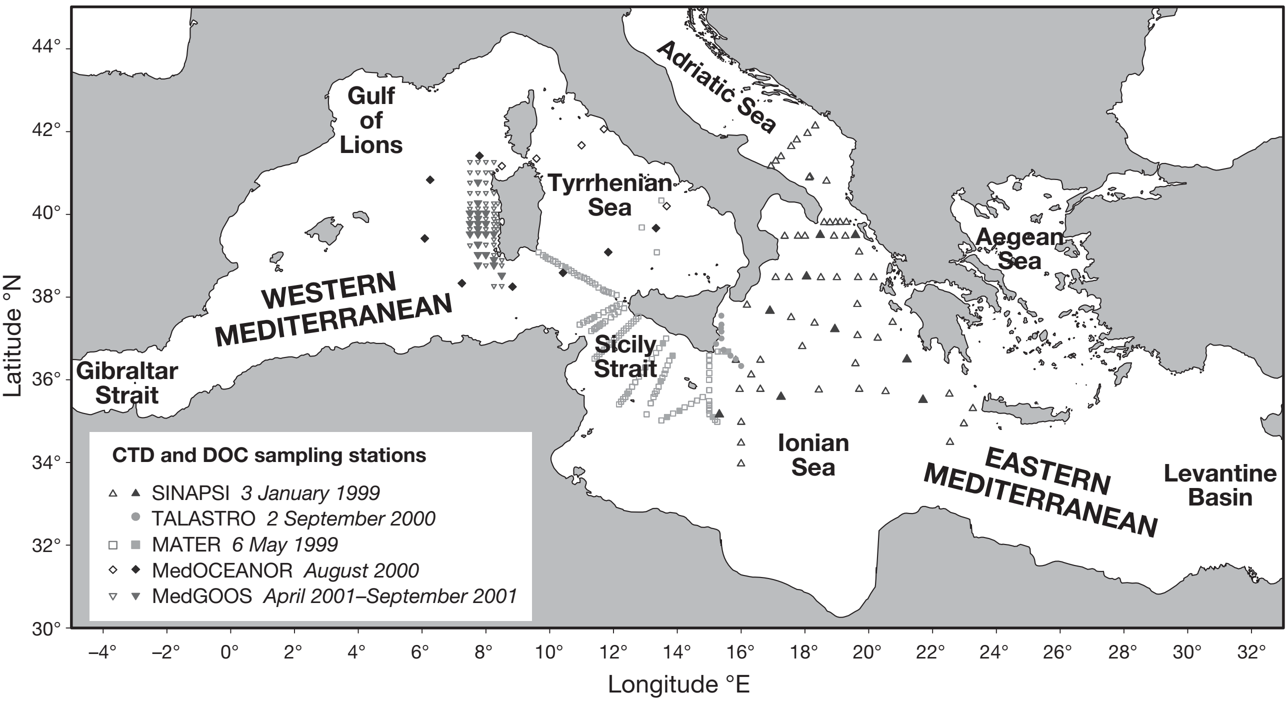

Fig. 1. Study areas investigated during 6 cruises in the Mediterranean Sea between 1999 and 2001. Empty symbols: CTD (conductivity, temperature and depth) stations; filled symbols: CTD and DOC (dissolved organic carbon) stations

3. RESULTS AND DISCUSSION

3.1. Oceanographic characteristics of the Mediterranean Sea

The hydrological stations investigated during the 6 cruises (Fig. 1) were located in the central part of the Mediterranean Sea, with the island of Crete and the Algero-Provençal basin as boundaries in the Eastern (EM) and Western Mediterranean (WM), respectively. No data from the easternmost (Levantine basin) and westernmost (Gibraltar Strait) areas were gathered.

Although the Mediterranean Sea is a small basin, its oceanographic importance is widely accepted because it is characterized by a variety of biogeochemical processes common to the world oceans, and its contribution to the global oceanic circulation has recently been reconsidered (Theocharis et al. 1998). Moreover, its small size allows it to be considered as a laboratory for the study of physical, chemical and biological processes that occur in the world oceans. In fact, the main mechanisms of dense water formation, thermohaline circulation, strait exchanges, wind-driven upwelling and the effects of the climate change can be more easily studied in the Mediterranean Sea than in the oceans (Bethoux et al. 1999).

The Mediterranean basin is characterized by 2 key points with regard to its productivity and circulation: the Strait of Gibraltar and the Sicily Strait. The Strait of Gibraltar is the only narrow connection with the Atlantic Ocean. It has a width of about 13 km and a depth at the sill of about 300 m, and therefore only the influx of surface Atlantic water (AW) and the outflow of the Levantine intermediate water (LIW) may occur; moreover, it represents a barrier to deep oceanic waters. The Sicily Strait, with a width of 140 km and an average depth of 500 m, connects the EM and the WM (Fig. 1) (Theocharis et al. 1998, Astraldi et al. 1999).

The 2 sub-basins exhibit different thermohaline characteristics: in general, the water masses circulating in the EM are saltier and warmer than those of the WM. Deep water formation in the 2 sub-basins is driven by different processes. In the EM, it is mainly due to an increase in salinity that results from intense evaporation occurring during the winter months, with the consequent increase of density, which causes the surface waters to sink to the bottom. An exception is represented by the Adriatic Sea, in which the Adriatic deep water (ADW) is formed by the cooling of surface waters induced by the Bora wind, which blows in its northern part mainly during the winter season (Astraldi et al. 1999, Lascaratos et al. 1999). In the WM, the predominant process is surface water cooling with a loss of heat due to the occurrence of the cold Mistral wind in the Gulf of Lions, which determines the decrease in temperature and the consequent sinking of surface waters to form the Western Mediterranean deep water (WMDW) (Benzohra & Millot 1995, Millot

1999, Rhein et al. 1999). The presence of a sill at the Sicily Strait hinders exchanges between the WMDW and the Eastern Mediterranean deep water (EMDW). Only the surface water (mainly AW) and the LIW can pass through the Strait, even if they assume different thermohaline characteristics in the 2 sub-basins. During its route towards the EM, the AW increases in salinity as consequence of the evaporation process, while the LIW becomes fresher as it moves away from its formation site (Levantine basin) towards the west (Astraldi et al. 1999).

In spite of very low productivity that characterizes the whole Mediterranean Sea, a relevant west-east gradient with an eastwards increase in oligotrophy, together with primary and bacterial production that is 2 to 3 times lower in the EM than in the WM, was observed (Turley 1999, Turley et al. 2000). In contrast, the phytoplankton and bacterial biomass integrated over depth were similar in the 2 sub-basins (Turley et al. 2000). Moreover, in the EM, where microheterotrophs totally dominate the food web, bacterial production was directly correlated to primary production; in the WM, bacterial production increased by (approximately) the square root of primary production. This finding suggests that bacteria in the WM are relatively decoupled from local contemporaneous primary production. In contrast, in the EM, less temporal decoupling and, therefore, a minor seasonal accumulation of DOC seems to occur (Turley et al. 2000).

3.2. DOC in the Mediterranean Sea

DOC data were plotted together in Fig. 2 in order to investigate whether the differences between WM and EM, in both physical structures and biological productivity, affect DOC distribution. DOC showed similar vertical profiles with depth in both EM and WM, albeit with high variability. The highest values (65 to 100 µM) were observed in the upper layer (0 to 100 m), even though some EM and WM stations showed lower DOC concentrations (50 to 65 µM). The high DOC values found in the surface layer should be attributed to a decoupling between production and consumption processes. Release of cell exudates by phytoplankton, grazing by zooplankton, excretion and cellular lysis by

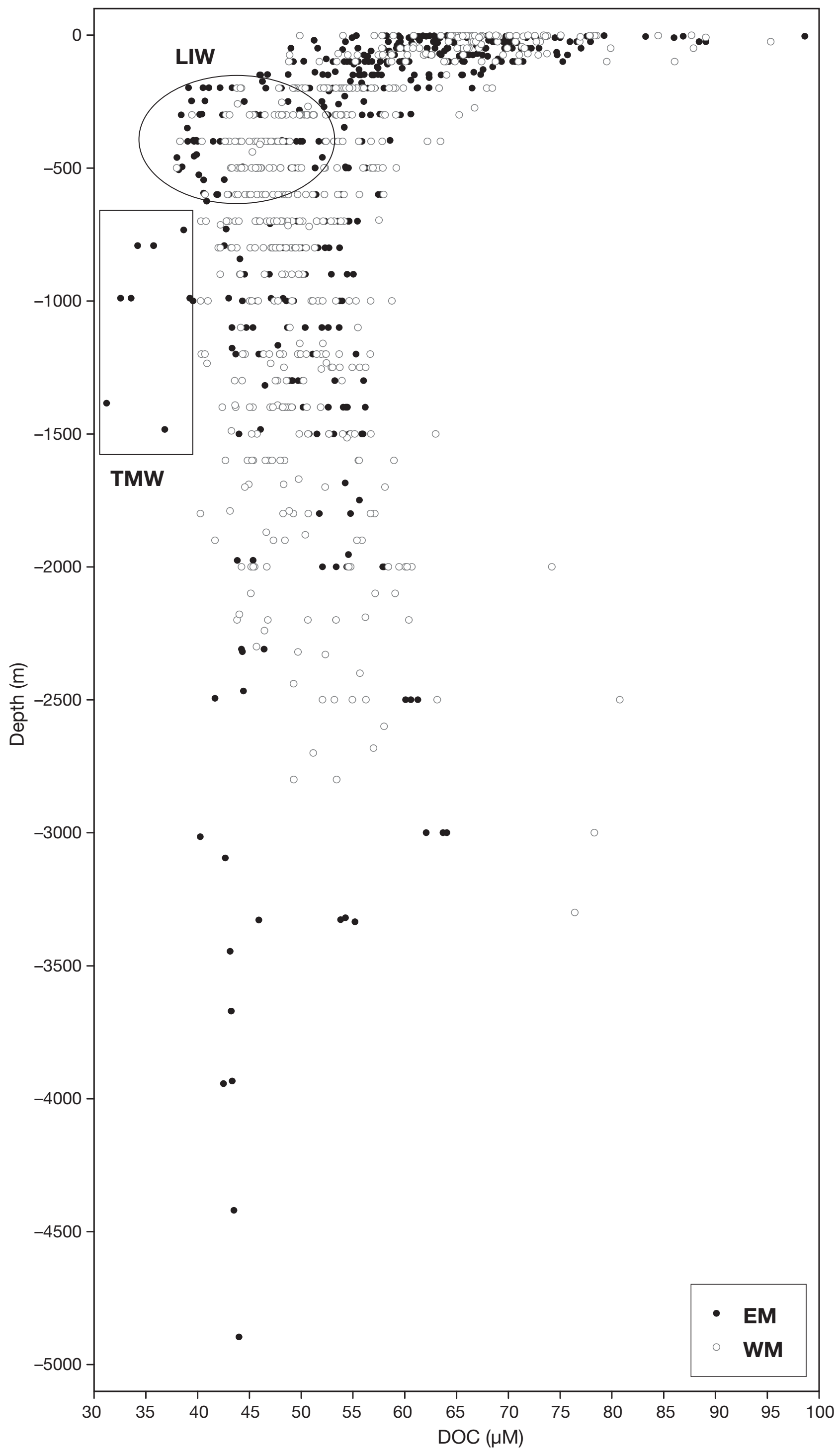

Fig. 2. DOC vertical profiles for stations located in the Eastern and Western Mediterranean (EM and WM, respectively). LIW: Levantine intermediate water; TMW: transitional Mediterranean water

viruses are the main DOC production processes in the euphotic zone, while bacteria are the major DOC consumers. Nutrient limitation or predation on bacteria may reduce DOC consumption, thereby resulting in DOC accumulation (Shiah et al. 1998). This is particularly frequent in an oligotrophic system, such as the Mediterranean, which has phosphorus as limiting factor. The high variability of DOC values in the surface layer may be related to (1) the different seasons and hours of sample collection, (2) the presence of physical processes such as upwelling or downwelling, (3) the occurrence of a phytoplankton bloom, and (4) different biological activities, which may be responsible of different rates of production and/or consumption processes, so determining a different extent of DOC accumulation.

No significant DOC differences were observed between the 2 sub-basins in the upper layer, despite differences in the extent of their oligotrophy and rate of primary production.

A portion of DOC produced in the upper layer may be transported to the subsurface waters. In the intermediate waters, between 200 and 800 m, a more or less marked minimum of DOC (37 to 55 µM) was observed in the LIW. At some stations a more pronounced minimum (<40 µM) was detected between 700 and 1500 m. These low values can be attributed to the occurrence of the transitional Mediterranean water (TMW), which is also characterized by a minimum in oxygen (Manca et al. 2002, Theocharis et al. 2002). Instead, the higher DOC values (~55 µM) observed at 200 to 600 m can be related to vertical mixing and/or to the presence of a different water mass, the younger Cretan intermediate water (CIW), observed in the EM in January 1999 (Manca et al. 2002, 2003).

In deep waters, a further peculiarity of DOC in the Mediterranean Sea was observed. DOC increased from intermediate to deep and bottom waters. In fact, below 2000 m, most samples exhibited DOC concentrations ranging from 45 to 70 µM, even reaching values of 80 µM at some WM stations. On the contrary, very low DOC values (40 to 45 µM) were found at depths below 3000 m at some EM stations (Fig. 2). This high DOC variability in deep waters is another distinctive feature of the Mediterranean Sea when compared with the literature on oceanic deep waters, which describe DOC values to be generally constant and lower than 40 µM (Carlson 2002 and references therein). The young age and different origin and route of Mediterranean deep waters, together with the central role of physical structures in DOC distribution, can explain this particular trend. A large portion of semi-labile DOC with different rates of utilization may be still present in Mediterranean deep waters, and the extent of its consumption, strongly connected to the age, origin and route of each water mass, may determine the different DOC concentrations observed in the different areas.

3.2.1. DOC vertical profiles in the eastern Mediterranean Sea

Three cruises were carried out in the EM from 1999 to 2001: SINAPSI3 (January 1999), MATER6 (May 1999) and TALASTRO2 (September 2000). The SINAPSI3 stations were located in the Southern Adriatic Sea, in the Northern and Central Ionian Sea, close to the Cretan Arc Strait on the east and to the Sicily Channel on the west (Fig. 1). Samples were collected in intermediate and deep layers every 500 m. The TALASTRO2 stations were positioned along 2 transects: one perpendicular, the other parallel to the eastern coast of Sicily (Fig. 1). Here, water collection was conducted every 200 m. The MATER6 stations were located in the Western Ionian, in the Sicily Strait and in the Sardinia Channel (Fig. 1). Only the stations located in the Western Ionian and in the Sicily Channel are immediately considered; the others, sited in Sicily Strait and in the Sardinian Channel, are taken into account when DOC in the WM is discussed (Section 3.2.2.). The study areas are important sites for the exchanges between EM and WM. In fact, they are placed in the central part of the Mediterranean Sea, where only surface and subsurface water masses, circulating in both EM and in WM, can pass through (Astraldi et al. 1999). Fig. 3 shows DOC vertical profiles of all samples collected in the EM.

Most surface (5 m) samples were characterized by a DOC concentration ranging from 55 to 75 µM in January and May 1999, respectively, while higher values (75 to 90 µM) were observed in September 2000. These differences can be attributed to the different sampling period and to a different extent of stratification, which can induce a higher accumulation of DOC in late summer than in January or May. Below, at about 100 m, almost all the samples had DOC concentrations in the range 50 to 70 µM. In the intermediate layer (200 to 600 m) a DOC minimum (37 to 47 µM in January and May 1999, and 50 to 55 µM in September 2000) was detected in most samples; moreover, a more marked DOC minimum (30 to 40 µM) was observed between 700 and 1500 m in some SINAPSI3 samples.

A slight increase in DOC concentrations (40 to 45 µM) was found in the deep waters (below 1200 m) of SINAPSI3 and MATER6 surveys, while DOC values of 60 to 65 µM were detected in TALASTRO2 samples (Fig. 3). In general, below 500 m, DOC concentrations were higher in September 2000 than in January and

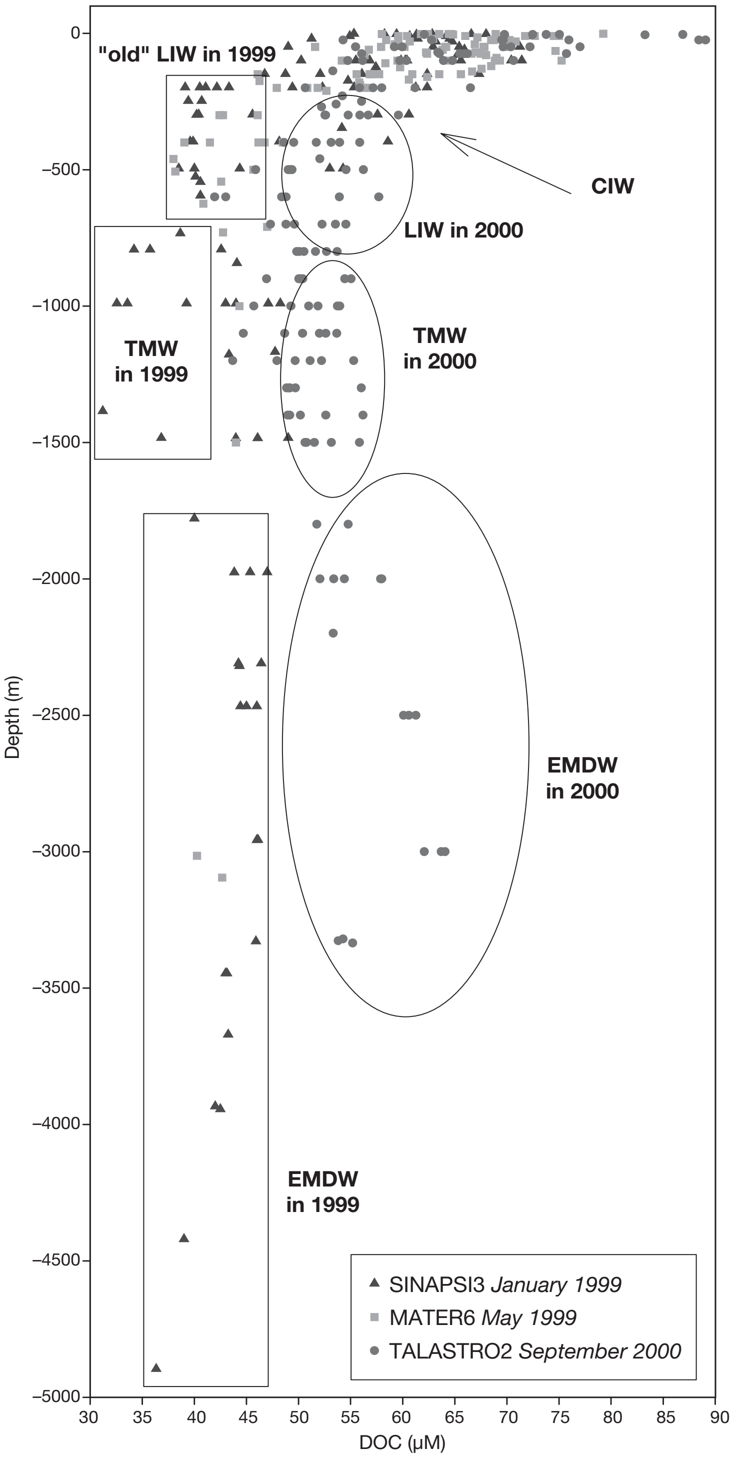

Fig. 3. DOC vertical profiles at Eastern Mediterranean stations shown in Fig. 1. CIW: Cretan intermediate water; EMDW: Eastern Mediterranean deep water; LIW: Levantine intermediate water; TMW: transitional Mediterranean water

May 1999; this was particularly evident in deep waters. Moreover, the DOC minimum, detected at both 200 to 600 m and 800 to 1200 m, was found only in samples of the SINAPSI3 survey. These patterns are related to the changes in thermohaline circulation that occurred in the 1990s, termed the eastern Mediterranean transient (EMT) (Roether et al. 1996, Lascaratos et al. 1999, Theocharis et al. 2002).

The high DOC variability observed also in deep waters can be due to different origins, routes and ages of the water masses that occurred at these depths during the 3 cruises. The DOC minimum of 37 to 47 µM, found in the intermediate waters of the SINAPSI3 survey, can be explained by the presence of an old vein of LIW, which re-circulated in the Levantine basin during the EMT; only in 1999 was it able to reach the Western Ionian. Instead, the second minimum (30 to 40 µM) observed between 700 and 1500 m in SINAPSI3 samples could be due to the occurrence of the TMW (Fig. 3). The higher values (53 to 60 µM) found at some SINAPSI3 stations between 200 and 600 m, can instead be attributed to the new CIW (Fig. 3), which was younger and closer to the source than LIW (Seritti et al. 2003). Moreover, LIW was younger in September 2000 than in 1999, because it started to move once again in an east-west direction (as in the pre-EMT period). This can explain the higher values (50 to 55 µM) observed in the intermediate waters during the TALASTRO2 cruise (Fig. 3). Similarly, the high DOC values (50 to 65 µM) found in the deep waters of the same cruise may be related to the higher contribution of new and young ADW (rich in oxygen and DOC) to the EMDW in 2000.

A comparison with literature data is not easy because they refer only to the Adriatic Sea (Pettine et al. 1999, 2001, Giani et al. 2005) and to the Aegean Sea (Sempéré et al. 2002). In general, DOC concentrations observed in the EM are lower than those reported for the Adriatic Sea, especially in surface waters (>100 µM) (Pettine et al. 1999, 2001, Giani et al. 2005). The Adriatic Sea was strongly affected by terrestrial inputs, mucilage events, as well as characterized by very shallow waters (20 to 70 m); this explains the high DOC concentrations observed. Sempéré et al. (2002) report total organic carbon (TOC) data that refer to the Aegean Sea samples collected in 1997. TOC vertical profiles were quite similar to those of the present study; in particular they found TOC concentrations ranging from 47 to 56 µM in the deep waters, which are very similar to those above reported for DOC in the EM.

3.2.2. DOC vertical profiles in the western Mediterranean Sea

Four cruises were conducted in the WM: MATER6 (May 1999), MedOCEANOR (August 2000), and 2 MedGOOS surveys (April and September 2001). As reported above, MATER6 stations covered the central part of Mediterranean (Fig. 1); therefore, only stations located in the Sicily Strait and Sardinia Channel are discussed here. MedOCEANOR stations were located in 3 areas characterized by different hydrological characteristics: the Tyrrhenian Sea, the Sardinia Channel and the Algerian Sea (Fig. 1); sampling strategy during the survey was every 100 m between 0 and 1000 m, and every 500 m from 1000 m to the bottom. MedGOOS stations were positioned in the Sardinia Sea (Fig. 1).

DOC vertical profiles from all stations sited in the WM are reported in Fig. 4. The trends of DOC in the water column here was rather similar to that observed in the EM. DOC showed highest values in the surface waters (65 to 95 µM); however, some samples collected in April 2001 (MedGOOS survey) showed surface values of about 50 to 60 µM. The DOC minimum was generally detected in intermediate layers, as follows: 38 to 43 µM between 300 and 500 m (MATER6); 40 to 60 µM between 300 and 700 m (MedGOOS, in both April and September); 47 to 57 µM between 200 and 700 m at Algerian stations, and 43 to 48 µM between 200 and 500 m at Tyrrhenian stations (MedOCEANOR). In the deep waters, DOC showed only a small increase, with most values ranging from 50 to 60 µM below 1500 m. Only the DOC data from the 2 Medgoos surveys (particularly in September 2001) were in the range of 43 to 55 µM, also in the deep waters. Finally, a very particular trend was observed below 2000 m in some Tyrrhenian stations, where DOC increased until values of about 80 µM.

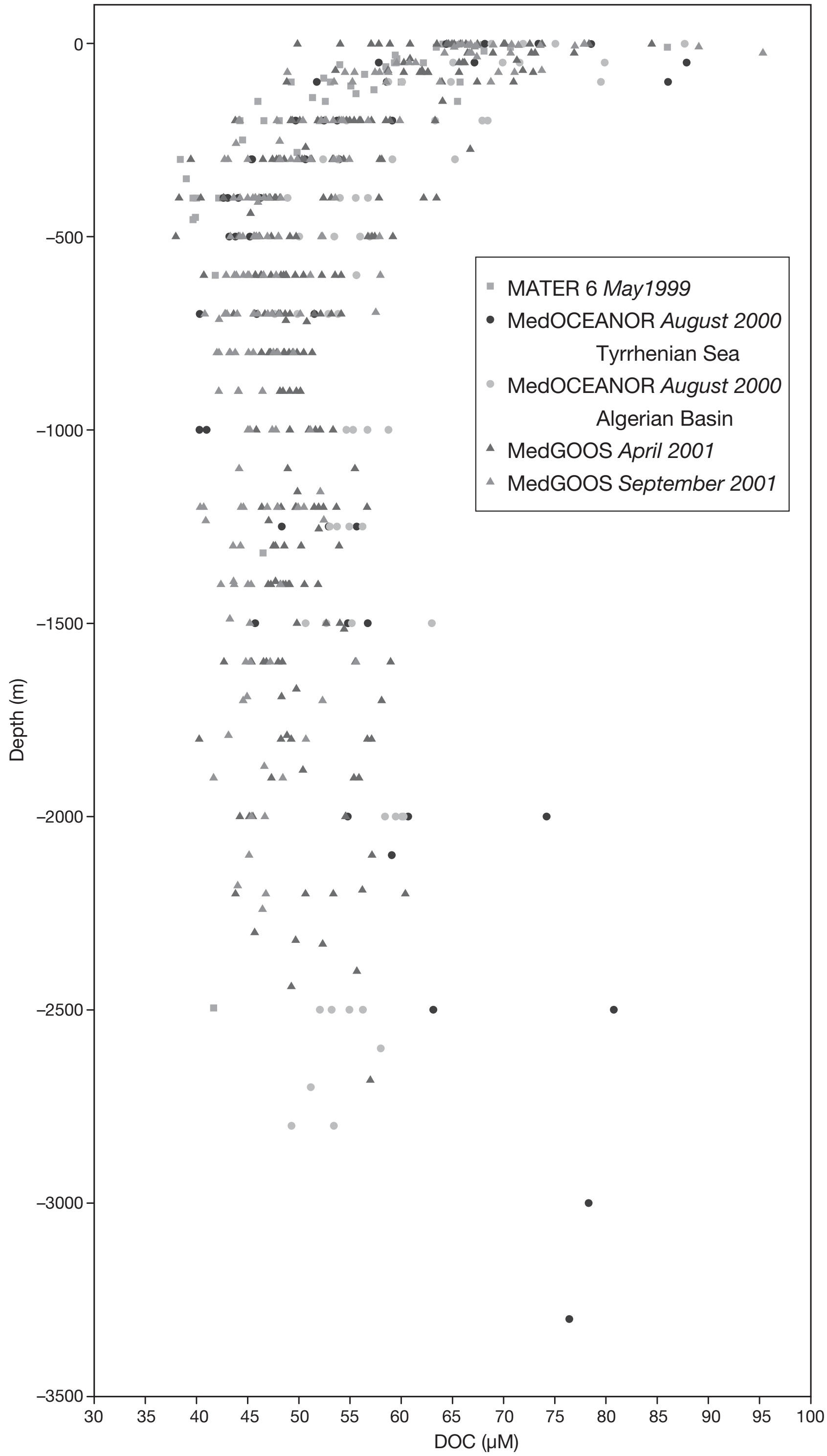

Fig. 4. DOC vertical profiles at Western Mediterranean stations shown in Fig. 1

The main feature of DOC in the WM, with respect to that observed in the EM, was a higher homogeneity along the water column and only minor variability among different stations. This may be explained by the greater extent of vertical mixing that generally characterizes the WM, particularly in the Sardinia Sea and Algerian basin. An exception was provided by DOC profiles in the Tyrrhenian Sea, where the greater extent of stratification also affects DOC distribution, with resultant major differences among the layers (Santinelli et al. 2002).

These data are in good agreement with those reported in the literature for DOC in WM (Copin-

Montégut & Avril 1993, Cauwet et al. 1997, Yoro et al. 1997, Doval et al. 1999)—especially those that refer to subsurface waters—despite the fact that these previous studies did not report a DOC increase in deep waters.

DOC variations were observed between the 2 cruises conducted in the Sardinia Sea (Fig. 4). Although seasonality cannot be excluded, in particular close to the surface, the observed variability could be also due to differences in mesoscale activity. Eddies observed near this area (Salas et al. 2002) may have influenced DOC distribution between the 2 cruises in different ways.

3.3. DOC in different water masses

A study of literature data on water mass circulation in the Mediterranean Sea during the period 1990-2002 allowed the particular features observed in the DOC vertical profiles of both EM and WM to be explained (Benzohra & Millot 1995, Roether et al. 1996, Astraldi et al. 1999, Lascaratos et al. 1999, Malanotte-Rizzoli et al. 1999, Millot 1999, Rhein et al. 1999, Manca et al. 2002). DOC distribution in LIW and in deep waters of the 2 sub-basins is reported below. The same investigation was not conducted in the upper layer because of its large variability, owing to exchanges with atmosphere and biological activity.

3.3.1. DOC in the Levantine Intermediate water

Literature data report the occurrence of LIW in both EM and WM, even if with different thermohaline characteristics (Benzohra & Millot 1995, Astraldi et al. 1999, Lascaratos et al. 1999, Malanotte-Rizzoli et al. 1999, Millot 1999, Rhein et al. 1999, Manca et al. 2002, 2003). LIW forms in the Levantine basin and then flows westward through the Sicily Strait at a depth of about 200 to 800 m. It enters into the Tyrrhenian Sea and then, exiting through the Sardinia Channel, flows northward along the western coast of Sardinia and Corsica islands, finally reaching the Gibraltar Strait, following the French and Spanish coasts. Mesoscale activity can interact with this predominant pattern (Millot 1999). In the 1990s, the occurrence of the EMT also influenced the route of the LIW, which was forced to re-circulate in the Levantine basin (owing to the presence of the new CIW) without receiving the contribution of new AW, with a consequent increase in salinity (Theocharis et al. 2002, Manca et al. 2003). With the relaxation of the formation of dense waters in the Aegean Sea and the restoration of the water mass circulation to the pre-EMT pattern, LIW was again able to flow westward, and in 1999 was detected in the Western Ionian Sea (Manca et al. 2003) with high salinity values and low oxygen concentrations (hereafter 'old' LIW). This old LIW was present at the western Ionian stations of SINAPSI3 and at some MATER6 stations located in the Sicily Channel. Table 1 provides DOC concentrations detected in the core of LIW during the 6 surveys conducted between 1999 and 2001 (Fig. 1).

Average DOC concentrations detected in samples collected in the LIW core (hereafter DOC-LIW) showed the lowest values (40 ± 1 µM) in the Ionian Sea (January 1999), a concentration of 45 ± 2 µM in the Sicily Strait and Channel (May 1999), and highest values (54 ± 4 µM) in the western Ionian Sea (September 2000) (Table 1). In the WM, a DOC-LIW concentration of 44 ± 1 µM was found in the Tyrrhenian Sea, whereas DOC-LIW concentrations of 54 ± 3 µM were detected in the Algerian basin during the same period (August 2000, MedOCEANOR cruise). Finally, mean values of 49 ± 5 µM were observed in the Sardinia Sea during both April and September 2001.

This spatial trend can be explained by the different hydrological conditions that occurred in the different areas and periods of the various cruises. The lowest DOC-LIW values found during SINAPSI3 (40 ± 1 µM) were connected to the occurrence of the old LIW in the Ionian Sea in winter 1999. This DOC-LIW concentration represents the lowest value observed in the intermediate waters of the whole Mediterranean Sea, and is similar to the concentration of the refractory DOC pool reported by Carlson & Ducklow (1995) for the central

Table 1. DOC concentrations (mean ± SE) in the core of Levantine Intermediate Water in different areas of the Mediterranean Sea, 1999 to 2001. Values in parentheses: ranges

Location and cruise	Sampling period	Depth (m)	DOC-LIW (µM)	Sample size (N)
Western-Central Ionian Sea (SINAPSI3)	January 1999	200–700	40 ± 1 (39–42)	10
Sicily Strait and Channel (MATER6)	May 1999	200–600	45 ± 2 (42–49)	20
Western Ionian Sea (TALASTRO2)	September 2000	100–400	54 ± 4 (48–60)	23
Tyrrhenian Sea (MedOCEANOR)	August 2000	300–600	44 ± 1 (43–46)	10
Algerian Sea (MedOCEANOR)	August 2000	300–600	54 ± 3 (49–57)	10
Sardinia Sea (MedGOOS)	April 2001	300–900	50 ± 4 (43–58)	65
Sardinia Sea (MedGOOS)	September 2001	300–900	49 ± 5 (42–60)	42

equatorial Pacific Ocean. The highest DOC-LIW values (54 ± 4 µM), detected in September 2000 in the Sicily transect (TALASTRO2), may have been associated with the restoration of pre-EMT circulation in the Ionian Sea, with the LIW coming directly from its source and so exhibiting a younger age than in January 1999. In the Sicily Strait in May 1999 (MATER6), DOC-LIW values slightly higher (45 ± 2 µM) than those detected in SINAPSI3 were observed. In that period the process of restoration of the pre-EMT circulation was in progress (Manca et al. 2003), therefore, the LIW flowing trough the Sicily Strait was the product of mixing of the old LIW with a certain extent of CIW, which was characterized by an higher DOC concentration (58 ± 3 µM), (Seritti et al. 2003); this may explain the small DOC-LIW differences observed. The low DOC-LIW values (44 ± 1 µM) found in the Tyrrhenian Sea 1 yr later (August 2000) may have depended on the old age of the Tyrrhenian LIW, because it was far away from its original source. In contrast, the high DOC-LIW values (49 to 54 µM) found in the Sardinia Sea and in the Algerian basin may have depended on the co-occurrence of a high productivity and high extent of vertical mixing in this area. Turley et al. (2000) reported that the vertical particle flux ratio between WM and EM was about 9:1, and that the WM:EM benthic biomass ratio between 200 and 1000 m was about 46:1. These rather large biological differences may explain the high DOC-LIW concentrations (54 ± 3 µM) found in the Algerian basin. Also, Doval et al. (1999) reported a DOC-LIW concentration of 44 to 53 µM in the Catalan-Balearic Sea.

On the basis of these data, the hypothesis that DOC values observed in the old LIW in January 1999 may be mainly ascribed to the refractory DOC fraction seems to be reliable enough. Higher DOC-LIW concentrations found in other areas and periods can be explained by the occurrence of a portion of semi-labile DOC fraction, not yet mineralized due to the younger age of LIW.

3.3.2. DOC in the Transitional Mediterranean water

Transitional Mediterranean water (TMW) occurs in the layer characterized by the minimum in oxygen: it is formed by mixing of old deep waters lifted to upper layers by the formation of new dense waters, which fill the deep layers (Theocharis et al. 2002). Generally, TMW is located at about 700 to 1500 m, even if after 1995 it was uplifted at 300–500 m. It is likely to be very old because neither surface dynamics nor deep water formation process contributed to its ventilation (Theocharis et al. 2002). The lowest DOC concentrations (33 ± 2 µM) of the whole Mediterranean Sea were found in this layer during SINAPSI3 cruise; in contrast, in September 2000, DOC in the TMW showed values of 49 ± 3 µM (Table 2, Fig. 3). This relatively large difference may depend on the circulation changes in EM (as occurred for the LIW) observed in September 2000, which were responsible of the general DOC increase, detected in the whole water column during the TALASTRO2 survey.

3.3.3. DOC in deep waters

The EMDW is the main deep water circulating in the EM. The EMT, which characterized the EM since the beginning of the 1990s, influenced the EMDW formation process and its route. In particular, in the EMT period, the major source of dense waters moved from the Adriatic Sea to the Aegean Sea, so that deep layers of the Ionian Sea were filled with new dense water of Aegean origin, termed Cretan deep water (CDW) (Roether et al. 1996, Malanotte-Rizzoli et al. 1999, Theocharis et al. 2002). With the return to pre-EMT conditions, a reduction in dense Aegean water production and the consequent restoration of the ADW as the dominant source of deep waters for the whole EM was observed (Manca et al. 2003). Moreover, the old EMDW was pushed up to the transitional layer (TMW) (Manca et al. 2002, Theocharis et al. 2002). Given these hydrological characteristics of deep waters of EM, DOC data were investigated in the core of the different deep water masses. Table 2 provides DOC concentrations detected in the core of deep waters in the EM from 1999 to 2001. In general, DOC was present in lower concentrations in 1999 than in 2000. In fact, DOC values of 44 to 48 µM and 58 to 64 µM were detected in the EMDW in January 1999 and September 2000 respectively.

During the SINAPSI3 cruise, the deep waters of the eastern stations were probably mostly characterized by the presence of CDW, with a DOC concentration of 45 ± 2 µM (Table 2). In contrast, higher DOC concentrations (62 ± 2 µM) detected in the EMDW in September 2000 may have depended on the occurrence of a significant contribution of ADW (recently formed and so rich in DOC) to the deep waters of EM.

Deep layers of the WM were characterized by the WMDW, which forms in the Gulf of Lions during winter, and by the Tyrrhenian Deep Water (TDW), which originates in the Tyrrhenian Sea as a product of mixing between LIW and WMDW (Rhein et al. 1999). Table 3 provides DOC concentrations found in the core of the deep waters of the WM from 1999 to 2001. A DOC increase towards the bottom was generally detected in the WM (see also Fig. 4), even though small DOC differences were observed in the WMDW and TDW of the different areas investigated. DOC values of about 55 µM

Table 2. DOC concentrations in the core of deep waters of the Eastern Mediterranean during different surveys conducted between 1999 and 2000. TMW: transitional Mediterranean water; EMDW: Eastern Mediterranean deep water; CDW: Cretan deep water. Values in parentheses: ranges

Location and cruise	Sampling period	Depth (m)	Water Mass	DOC (µM)	Sample size (N)
Central Ionian Sea (SINAPSI3)	January 1999	700–1500	TMW	33 ± 2 (31–36)	5
Western-Central Ionian Sea (SINAPSI3)	January 1999	1500–bottom	EMDW	46 ± 1 (44–48)	7
Eastern Ionian Sea (SINAPSI3)	January 1999	1500–bottom	CDW	45 ± 2 (43–47)	4
Western Ionian Sea and Sicily Strait (TALASTRO2)	September 2000	600–1600	TMW	49 ± 3 (44–54)	22
Western Ionian Sea and Sicily Strait (TALASTRO2)	September 2000	2000–bottom	EMDW	62 ± 2 (58–64)	7

were found in the TDW, both in the Tyrrhenian Sea and Algerian basin, while slightly higher mean values (56 to 59 µM) were found in the WMDW in the same areas. Small temporal differences (in both WMDW and TDW) were detected in the Sardinia Sea, where DOC concentrations were lower in September (47 ± 3 µM in TDW; 46 ± 1 µM in WMDW) than in April 2001 (50 ± 2 µM in TDW; 55 ± 3 µM in WMDW) (Table 3).

In general, deep waters in the WM were characterized by DOC concentrations higher than those detected in the LIW; this behavior was particularly evident in the Tyrrhenian Sea. The small differences between DOC in TDW and in WMDW can be attributed to the fact that TDW forms by mixing between LIW and WMDW; moreover, the large extent of vertical mixing observed in the Algerian basin and Sardinian Sea can drive the transport of DOC from the upper layer to intermediate and deep waters, so reducing the differences in DOC between LIW and deep waters.

Table 3. DOC concentrations (mean ± SE) in the core of deep waters of the Western Mediterranean during different surveys conducted between 1999 and 2001. WMDW: Western Mediterranean deep water; TDW: Tyrrhenian Deep Water. Values in parentheses: ranges

Location and cruise	Sampling period	Depth (m)	Water Mass	DOC (µM)	Sample size (N)
Tyrrhenian Sea (MedOCEANOR)	August 2000	900–1500	TDW	55 ± 3 (51–58)	6
Tyrrhenian Sea (MedOCEANOR)	August 2000	1700–bottom	WMDW	59 ± 3 (55–63)	4
Algerian Sea (MedOCEANOR)	August 2000	900–1500	TDW	55 ± 2 (51–59)	11
Algerian Sea (MedOCEANOR)	August 2000	1700–bottom	WMDW	56 ± 4 (49–60)	12
Sardinia Sea (MedGOOS)	April 2001	1000–2000	TDW	50 ± 2 (47–55)	22
Sardinia Sea (MedGOOS)	April 2001	1800–bottom	WMDW	55 ± 3 (49–59)	15
Sardinia Sea (MedGOOS)	September 2001	1200–2000	TDW	47 ± 3 (43–56)	16
Sardinia Sea (MedGOOS)	September 2001	2000–bottom	WMDW	46 ± 1 (44–47)	6

4. CONCLUSIONS

DOC in the water column showed similar trends in the EM and WM; this can be explained by (1) the study areas, which are mainly located in the central Mediterranean (with the exceptions of the easternmost and westernmost areas), and (2) the surveys, which were not synoptic but conducted in different years and seasons—the absence of a temporal sampling strategy could have minimized differences in DOC patterns.

DOC variability in the intermediate and deep layers in both sub-basins may be linked to the occurrence of a high fraction (20 to 30%) of semi-labile DOC, which may be degraded to different extents in each water mass. The relatively high temperature (~13°C), the high availability of nutrients, oxygen and DOC, together with the absence of competition with phytoplankton, are factors that can support bacterial and protist activity in the deep layers.

Data reported in this study represent a broad confirmation of the firm link observed between DOC distribution and physical structures in a large part of the Mediterranean Sea. DOC exhibited different concentrations in various water masses that can be attributed to their origin, route and age. The modification of thermohaline circulation in the EM during the EMT also affected DOC values, which were lower in 1999 than in 2000 in the subsurface waters. The greater homogeneity of DOC values in the water columns in the Sardinian Sea and Algerian basins was attributed to the dominant role of vertical mixing in these areas of the WM. In contrast, in the Tyrrhenian Sea, where the water column exhibited greater stratification, DOC exhibited larger variations with depth.

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LITERATURE CITED

Amon RMW, Benner R (1996) Bacterial utilization of different size classes of dissolved organic matter. Limnol Oceanogr 41:41–51

Astraldi M, Balopoulos S, Candela J, Font J and 5 others (1999) The role of straits and channels in understanding the characteristics of Mediterranean circulation. Prog Oceanogr 44:65–108

Azam F, Fenchel T, Field JG, Gray JS, Meyer-Reil LA, Thingstad F (1983) The ecological role of water-column microbes in the sea. Mar Ecol Prog Ser 23:37–49

Benzohra M, Millot C (1995) Characteristics and circulation of the surface and intermediate water masses off Algeria. Deep-Sea Res I 42:1803–1830

Bethoux JP, Gentili B, Morin P, Nicolas E, Pierre C, Ruiz-Pino D (1999) The Mediterranean Sea: a miniature ocean for climatic and environmental studies and a key for the climatic functioning of the North Atlantic. Prog Oceanogr 44:131–146

Blough NV, Del Vecchio R (2002) Chromophoric DOM in the coastal environment. In: Hansell DA, Carlson CA (eds) Biogeochemistry of marine dissolved organic matter. Academic Press, San Diego, CA, p 509–546

Carlson CA (2002) Production and removal processes. In: Hansell DA, Carlson CA (eds) Biogeochemistry of marine dissolved organic matter. Academic Press, San Diego, CA, p 91–151

Carlson CA, Ducklow HW (1995) Dissolved organic carbon in the upper ocean of the central equatorial Pacific Ocean, 1992: daily and finescale vertical variations. Deep-Sea Res II 42:639–656

Cauwet G, Miller A, Brasse S, Fengler G, Mantoura RFC, Spitzy A (1997) Dissolved and particulate organic carbon in the Western Mediterranean Sea. Deep-Sea Res I 44:769–779

Cho BC, Azam F (1988) Major role of bacteria in biogeochemical fluxes in the ocean's interior. Nature 332: 441–443

Copin-Montégut G, Avril B (1993) Vertical distribution and temporal variation of dissolved organic carbon in the North-Western Mediterranean Sea. Deep-Sea Res I 40:1963–1972

Doval MD, Pérez FF, Berdalet E (1999) Dissolved and particulate organic carbon and nitrogen in the Northwestern Mediterranean. Deep-Sea Res I 46:511–527

Druffel ERM, Williams PM, Bauer JE, Ertel JR (1992) Cycling of dissolved and particulate organic matter in the open ocean. J Geophys Res 97:15639–15659

Ducklow HW, Carlson CA (1992) Oceanic bacterial production. In: Marshall KC (ed) Advances in microbial ecology, Vol 12. Plenum Press, New York, p 113–181

Fuhrman JA (1999) Marine viruses and their biogeochemical and ecological effects. Nature 399:541–548

Giani M, Savelli F, Berto D, Zangrando V, Ćosović B, Vojvodić V (2005) Temporal dynamics of dissolved and particulate organic carbon in the northern Adriatic Sea in relation to the mucilage events. Sci Total Environ 353: 126–138.

Hansell DA, Carlson CA (1998) Deep ocean gradients in dissolved organic carbon concentrations. Nature 395:263–266

Hedges JI (1992) Global biogeochemical cycles: progress and problem. Mar Chem 39:67–93

Hedges JI (2002) Why dissolved organic matter. In: Hansell DA, Carlson CA (eds) Biogeochemistry of marine dissolved organic matter. Academic Press, San Diego, CA, p 1–33

Kirchmann DL, Lancelot C, Fasham M, Legendre L, Radach G, Scott M (1993) Dissolved organic matter in biogeochemical models of the oceans. In: Evans GT, Fasham MJR (eds) Towards a model of ocean biogeochemical processes. Series I: Global environmental change, Vol 10. Springer Verlag, Berlin, p 209–225

Lascaratos A, Roether W, Nittis K, Klein B (1999) Recent changes in deep water formation and spreading in the eastern Mediterranean Sea: a review. Prog Oceanogr 44: 5–36

Malanotte-Rizzoli P, Manca BB, Ribera D'Alcalà M, Theocharis A, Brenner S, Budillon G, Ozsoy E (1999) The Eastern Mediterranean in the 80s and in the 90s: the big transition in the intermediate and deep circulations. Dyn Atmos Oceans 29:365–395

Manca B, Klein B, Kress N, Ribera d'Alcalà M (2002) Low-frequency changes of water masses structure, flow patterns and biochemical exchanges through the Eastern Mediterranean regions. In: Briand F (ed) Tracking long-term hydrological change in the Mediterranean Sea. CIESM workshop Monogr 16:61–70

Manca BB, Budillon G, Scarazzato P, Ursella L (2003) Evolution of dynamics in the eastern Mediterranean affecting water mass structures and properties in the Ionian and Adriatic Seas. J Geophys Res 108:8102, doi:10.1029/2002JC001664

Mann KH, Lazier JRN (1996) The oceans and global climate change: physical and biological aspects. In Mann KH, Lazier JRN (eds) Dynamics of marine ecosystems: biological-physical interactions in the oceans, 2nd edn. Blackwell Science, London

Millot C (1999) Circulation in the Western Mediterranean Sea. J Mar Syst 20:423–442

Moran MA, Zepp RG (1997) Role of photoreactions in the formation of biologically labile compounds from dissolved organic matter. Limnol Oceanogr 42:1307–1316

Ogawa H, Tanoue E (2003) Dissolved organic matter in oceanic waters. J Oceanogr 59:129–147

Pettine M, Patrolecco L, Manganelli M, Capri S, Farrace MG (1999) Seasonal variations of dissolved organic matter in the Northern Adriatic Sea. Mar Chem 64:153–169

Pettine M, Capri S, Manganelli M, Patrolecco L, Puddu A, Zoppini A (2001) The dynamics of DOM in the Northern Adriatic Sea. Estuar Coast Shelf Sci 52:471–489

Ploug H, Grossart HP, Azam F, Jørgensen BB (1999) Photosynthesis, respiration, and carbon turnover in sinking marine snow from surface waters of the Southern California Bight: implications for the carbon cycle in the ocean. Mar Ecol Prog Ser 179:1–11

Rhein M, Send U, Klein B, Krahmann G (1999) Interbasin deep water exchange in the western Mediterranean. J Geophys Res 104:23495–23508

Roether W, Manca BB, Klein B, Bregant D, Georgopoulos D, Beitzel V, Kovacevic V, Luchetta A (1996) Recent changes in Eastern Mediterranean deep waters. Science 271: 333–335

Salas J, Millot C, Font J, García-Ladona E (2002) Analysis of mesoscale phenomena in the Algerian basin observed with drifting buoys and infrared images. Deep-Sea Res I 49:245–256

Santinelli C, Gasparini GP, Nannicini L, Seritti A (2002) Vertical distribution of dissolved organic carbon (DOC) in the Western Mediterranean Sea in relation to the hydrological characteristics. Deep-Sea Res I 49:2203–2219

Sempéré R, Panagiotopoulos C, Lafont R, Marroni B, Van Wambeke F (2002) Total organic carbon dynamics in the Aegean Sea. J Mar Syst 33–34:355–364

Seritti A, Nannicini L, Del Vecchio R, Giordani P, Balboni V, Miserocchi S (1997) Optical properties of sediment pore waters of Adriatic Sea. Toxicol Environ Chem 61: 195–209

Seritti A, Santinelli C, Manca BB, Murru E, Boldrin A, Nannicini L (2003) Relationships between dissolved organic carbon (DOC) and water mass structures in the Ionian Sea (winter 1999). J Geophys Res 108:8112, doi:10.1029/2002JC001345

Shiah FK, Kao SJ, Liu KK (1998) Bacterial production in the Western Equatorial Pacific: implications of inorganic nutrient effects on dissolved organic carbon accumulation and consumption. Bull Mar Sci 62:795–808

Siegenthaler U, Sarmiento JL (1993) Atmospheric carbon dioxide and the ocean. Nature 365:119–125

Smith DC, Simon M, Alldredge AL, Azam F (1992) Intense hydrolytic enzyme activity on marine aggregates and implications for rapid particle dissolution. Nature 359: 139–142

Søndergaard M, Williams PJleB, Cauwet G, Riemann B, Robinson C, Terzic S, Woodward EMS, Worm J (2000) Net accumulation and flux of dissolved organic carbon and dissolved organic nitrogen in marine plankton communities. Limnol Oceanogr 45:1097–1111

Strom SL, Benner R, Ziegler S, Dagg MJ (1997) Planktonic grazers are a potentially important source of marine dissolved organic carbon. Limnol Oceanogr 42:1364–1374

Theocharis A, Gacic M, Kontoyiannis H (1998) Physical and dynamical processes in the coastal and shelf areas of the Mediterranean coastal segment. In: Robinson AR, Brink KH (eds) The sea, Vol 11. Wiley Interscience, New York, p 863–887

Theocharis A, Klein B, Nittis K, Roether W (2002) Evolution and status of the Eastern Mediterranean Transient (1997–1999). J Mar Syst 33–34:91–116

Thomas C, Cauwet G, Minster JF (1995) Dissolved organic carbon in the equatorial Atlantic Ocean. Mar Chem 49: 155–169

Turley CM (1999) The changing Mediterranean Sea — a sensitive ecosystem? Prog Oceanogr 44:387–400

Turley CM, Bianchi M, Christaki U, Conan P and 6 others (2000) Relationship between primary producers and bacteria in an oligotrophic sea—the Mediterranean and biogeochemical implications. Mar Ecol Prog Ser 193:11–18

Yoro SC, Sempéré R, Turley C, Unanue MA, Durrieu de Madron X, Bianchi M (1997) Cross-slope variations of organic carbon and bacteria in the Gulf of Lions in relation to water dynamics (northwestern Mediterranean). Mar Ecol Prog Ser 161:255–264

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