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## Organic carbon dynamics in the Mediterranean Sea: An integrated study

Chiara Santinelli,<sup>1,2</sup> Richard Sempéré,<sup>2</sup> France Van Wambeke,<sup>2</sup> Bruno Charriere,<sup>2</sup>  
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[1] Total (TOC) and dissolved (DOC) organic carbon vertical profiles were analyzed from 11 stations located in various regions of the Mediterranean Sea, together with the distribution of other physical, chemical and biological parameters. TOC showed the highest concentrations (68–83  $\mu\text{M}$ ) above the pycnocline, followed by a marked decrease to values of 45–48  $\mu\text{M}$  at 100–200 m. Below 200 m, values of 40–45  $\mu\text{M}$  were observed. The excess TOC and DOC occurring at each station was calculated by subtracting 48  $\mu\text{M}$  from the observed concentrations. The stock of the excess TOC and DOC increased eastward; while surface DOC mineralization rates decreased from 1.5  $\mu\text{M d}^{-1}$  to 0.26  $\mu\text{M d}^{-1}$  eastward. The integrated average of the biological parameters in the above-pycnocline layer showed a bacterial production versus particulate primary production (BP/PPP) ratio ranging from 22% in the Ionian Sea (MIO station) to 31% in the Ligurian Sea (Dyfamed station), while bacterial carbon demand versus PPP was higher than 100%, considering a bacterial growth efficiency of both 15% and 30%. The data here reported indicate various scenarios of carbon dynamics. At the stations west of the Sardinian Channel, the microbial loop was very active, and a high flux of carbon to the microbial loop (large bacterial and protist abundance) may be hypothesized, which would result in a low DOC concentration. At the stations east of the Sardinian Channel, no significant longitudinal variation was found in DOC and BP. DOC accumulated at these stations, possibly due to bacteria P-limitation, to DOC chemical composition and/or to the occurrence of different prokaryotic populations with a different ability to consume the available DOC.

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### 1. Introduction

[2] Marine dissolved organic carbon (DOC) plays a key role in the global carbon cycle. It contains an amount of carbon ( $662 \cdot 10^{15}$  g C) [Hansell *et al.*, 2009] comparable to that occurring in the atmosphere, and it drives the good functioning of marine ecosystem. Though DOC is produced at each level of the food web, the rate of primary production determines the maximal production rate, while heterotrophic prokaryotes are the main DOC consumers [Carlson, 2002, and references therein]. Prokaryotic assimilation induces different processes, such as mineralization, transfer in the food web through bacterivores [Azam *et al.*, 1983; Cho and Azam, 1988], and/or transformation in a refractory state at

unknown proportions, fuelling the microbial carbon pump (MCP) [Jiao *et al.*, 2010]. When the production and removal processes are uncoupled, a change in the DOC concentration is observed [Carlson, 2002, and references therein]. Thus, DOC accumulates when its production exceeds consumption. The accumulated DOC can be exported to the aphotic zone via hydrodynamic processes, such as winter convection [Copin-Montégut and Avril, 1993; Hansell, 2002; Sohrin and Sempéré, 2005; Santinelli *et al.*, 2010].

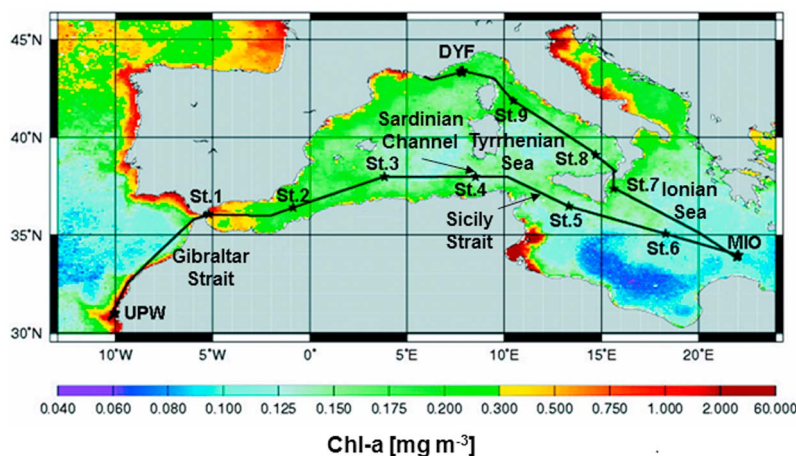
[3] Despite the occurrence of molecules with a turn-over time ranging from minutes to millennia, three main DOC fractions have been identified: (1) a labile fraction with a turn-over time of minutes-hours; (2) a semi-labile fraction with a turn over time of months-years; and (3) a refractory fraction with a turn-over time of centuries-millennia [Carlson, 2002, and references therein]. In the ocean, the refractory fraction has been hypothesized to have a uniform distribution from the surface to the bottom [Bauer *et al.*, 1992] because its average age (3700–6000 yrs) [Loh *et al.*, 2004] is higher than the time-scale of oceanic mixing. Recently, the concept of semi-refractory DOC, with a turn-over time of few decades has also been introduced [Hansell *et al.*, 2012]. The labile fraction is consumed very quickly, as a consequence, it occurs mainly at

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**Figure 1.** Study area and sampling stations of the Prosope cruise (September 1999) superimposed on a map of the average chlorophyll concentration, as measured by satellite (SeaWiifs) during the period of the cruise.

surface in nanomolar concentrations; however, its flux can be high [Keil and Kirchman, 1999]. This fraction is usually studied in ‘biodegradation’ or ‘dilution’ experiments [Kirchman et al., 1991; Carlson et al., 1994; Carlson and Ducklow, 1996; Sempéré et al., 2003]. The semi-labile fraction plays the most important role from a biological pump perspective. In fact, it escapes rapid microbial consumption so it can be accumulated and transported by water masses circulation. The concentration of the refractory and semi-labile fractions is usually determined by studying the DOC vertical profile [Hansell and Peltzer, 1998; Carlson, 2002; Sohrin and Sempéré, 2005].

[4] The Mediterranean Sea is a semi-enclosed basin with a high solar radiation level, an average depth of 2000 m, a deep temperature higher ( $>12^{\circ}\text{C}$ ) than the deep ocean ( $0\text{--}3^{\circ}\text{C}$ ), short ventilation rate and residence times for deep waters of  $\sim 70\text{--}126$  years [Schlitzer et al., 1991]. It is defined as a low-nutrient, low-chlorophyll system (LNLC) [Durrieu de Madron et al., 2011, and references therein]. Some studies indicate that the Mediterranean Sea is a P-limited system, especially in the eastern basin because phosphate availability may limit both primary and heterotrophic bacterial production [Thingstad and Rassoulzadegan, 1995; Sala et al., 2002; Van Wambeke et al., 2002a; Krom et al., 2005; Zohary et al., 2005; Pinhassi et al., 2006]. A decrease of the integrated primary production, particulate carbon export and nutrient availability toward the eastern part of the basin has been reported [Moutin and Raimbault, 2002; Van Wambeke et al., 2002a; Siokou-Frangou et al., 2010]. Recently, a west-east decreasing trend has been observed for the euphotic-layer-integrated photosynthetic production of DOC (DOCp) and particulate primary production (PPP) [López-Sandoval et al., 2011].

[5] Some papers address DOC distribution in the Mediterranean Sea with a particular focus on the intermediate and deep waters [Cauwet et al., 1990; Copin-Montégut and Avril, 1993; Sempéré et al., 2000; Dafner et al., 2001a, 2001b; Avril, 2002; Sempéré et al., 2002, 2003; Seritti et al., 2003; Santinelli et al., 2002, 2006, 2010; Pujó-Pay et al., 2011].

By contrast, very little information is available on DOC dynamics at the surface in open-seawater [Avril, 2002; Santinelli et al., 2008]. In addition, only a few papers report DOC data combined with microbiological information and these are limited to narrow areas [Yoro et al., 1997; Gasol et al., 1998, Van Wambeke et al., 2001; Sempéré et al., 2002, 2003; Van Wambeke et al., 2004; La Ferla et al., 2005; Meador et al., 2010].

[6] The primary goals of this paper are (i) to study spatial variability in DOC distribution with particular attention to the surface layer and to the Levantine Intermediate Water (LIW), (ii) to assess the flux of carbon through the microbial loop in the entire Mediterranean Sea and (iii) to investigate if significant differences can be pinpointed between the western and the eastern basins.

## 2. Study Area and Sampling Stations

[7] Samples were collected during the “Prosope” cruise from 9 September to 3 October 1999 at one station in the Atlantic Ocean and along a west–east section crossing the Mediterranean Sea (Figure 1). The station names are superimposed onto the average map of chlorophyll-a measured by satellite (SeaWiifs) during the period of the cruise. Most of the stations were characterized by very low chlorophyll-a values ( $0.08\text{--}0.2\text{ mg}\cdot\text{m}^{-3}$ ). The Atlantic station (UPW) was located in the upwelling of Morocco in order to have a reference point for a very productive area of the Atlantic Ocean. The station located in the Ligurian Sea is Dyfamed station (DYF), that has been regularly sampled since 20 years by the French community [Marty et al., 2002]. The station MIO was located in the Ionian Sea.

[8] Most of the biological and chemical data taken during this field cruise has already been published elsewhere. Therefore, the methodologies are not explained in detail. For heterotrophic bacterial production and factors limiting bacterial production, refer to Van Wambeke et al. [2002a]; for particulate primary production refer to Moutin et al. [2002]; for phosphate, refer to Moutin et al. [2001]; for

chlorophyll, picophytoplankton and other nutrients, refer to *Garczarek et al.* [2007]; for oligotrich ciliates, refer to *Dolan et al.* [2002]; for particulate organic carbon (POC), refer to *Raimbault et al.* [1999] and *Crombet et al.* [2011] and for silicates refer to *Crombet et al.* [2011].

## 2.1. Field Sampling

[9] Discrete water samples were collected from the RV *Thalassa* at one station in the Agadir coastal area (Atlantic Ocean) and at eleven stations in the Mediterranean Sea along two sections (Figure 1) using a CTD-rosette with a 20 Niskin bottle (12 l) equipped with a viton o-ring and silicone rope. Samples were not filtered and were drawn as soon as possible after the CTD was retrieved. The 10-ml samples were collected in triplicate in pre-combusted (450°C-6 h) glass ampoules, which was rinsed twice with the sample before filling. Samples were immediately poisoned by the addition of 20  $\mu\text{l}$  of  $\text{H}_3\text{PO}_4$  (final pH  $\sim 2$ ) in a laminar flow clean air bench. The ampoules were flame-sealed and stored in the dark at 4°C until analysis. Plastic gloves were worn and care was taken to minimize contamination during sampling and the following procedures.

## 2.2. HTOC Analysis

[10] We used a Shimadzu Model TOC-5000 total carbon analyzer with a quartz combustion column filled with 1.2% Pt on silica pillows with an approximate diameter of 2 mm [*Sempéré et al.*, 2003]. Prior to analysis, samples were sparged for 10 min by free  $\text{CO}_2$  pure air in order to remove inorganic carbon. One hundred microliters were injected 3–4 times for each sample and standard; the analytical precision of the procedure was 2% on average. Standardization of the instrument was performed daily using MilliQ water as blank and potassium hydrogen phthalate diluted in MilliQ water (range 0–125  $\mu\text{M}$  C) prepared just before sample analysis as a standard. The running blank was determined as the average of the peak area of the Milli-Q water acidified with  $\text{H}_3\text{PO}_4$ . The total organic carbon (TOC) concentration was determined by subtracting the running blank from the average peak area of the samples ( $n = 3$  or 4) and dividing the subtraction by the slope of the calibration curve. The acidified Milli-Q water was injected in triplicate after every 4 samples. Low carbon water (LCW) and deep seawater reference (DSR) were kindly provided by the Bermuda Biological Station and were measured daily to monitor the accuracy and the stability of the TOC analysis. The precision of the TOC analysis was determined by the standard deviation of triple or quadruple analysis of the same sample, and this value was  $\pm 1.4$   $\mu\text{M}$  on average. Samples were analyzed within 6 months of sampling.

[11] The samples collected during the Prosopé cruise were not filtered; therefore, the concentration of organic carbon is expressed as TOC. TOC is representative of DOC in intermediate and deep waters, in which the concentration of POC is lower than 0.5  $\mu\text{M}$ . Thus, the difference is within the range of the error of the DOC measurements. In the surface waters, POC contributed a larger extent to TOC. Therefore, where POC data were available, the DOC was calculated as  $\text{DOC} [\mu\text{M}] = \text{TOC} [\mu\text{M}] - \text{POC} [\mu\text{M}]$  in order to better highlight DOC dynamics. This calculation could determine an underestimation of DOC in samples where POC has a high concentration, since POC could be partially underestimated

in a 10 ml sealed ampoule due to the heterogeneity of the sample in particle rich waters.

## 3. TOC in Various Water Masses

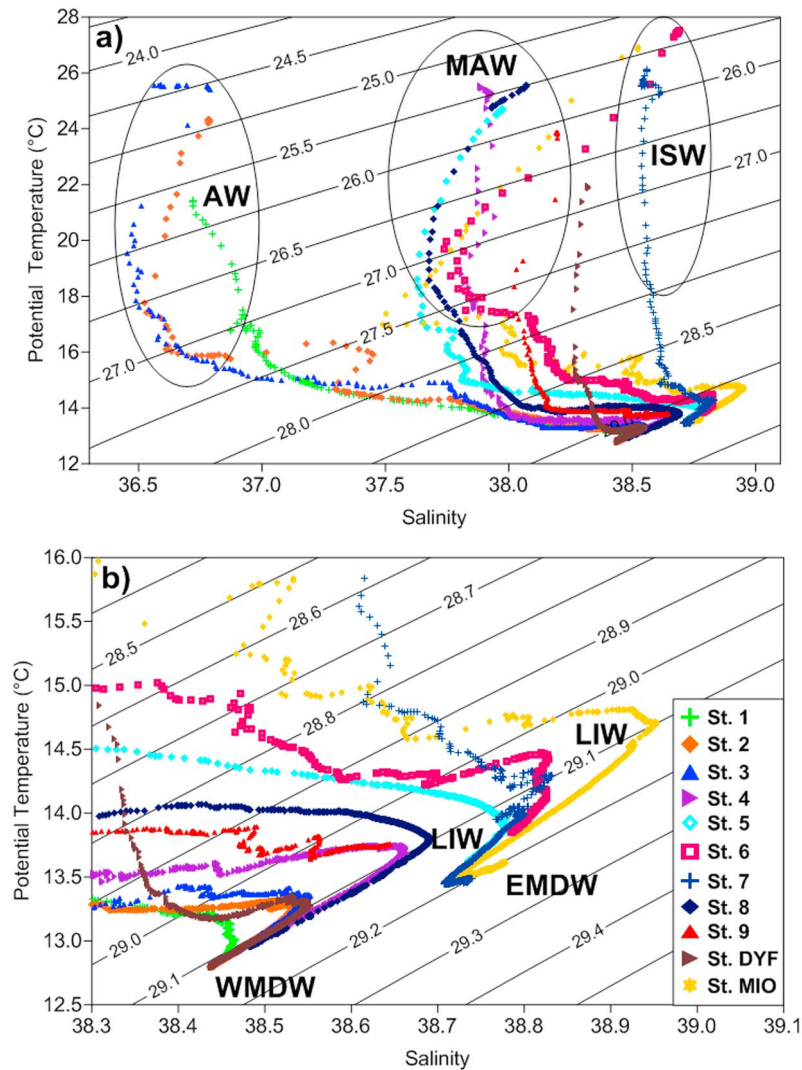
[12] The potential temperature versus salinity ( $\theta/S$ ) graphs show a net separation between the thermohaline properties of the water masses in the eastern (east Med) and western (west Med) Mediterranean Sea, with a decreasing temperature and salinity westward (Figure 2). In the surface layer (density  $< 27.0$   $\text{kg m}^{-3}$ , potential temperature  $> 18^\circ\text{C}$ ), three different water masses were identified based on salinity (Figure 2): (1) the Atlantic water (AW) ( $S < 37.0$ ) with an average TOC concentration of  $65 \pm 3$   $\mu\text{M}$  ( $n = 13$ ) St. 1–St. 3), (2) the modified Atlantic water (MAW) ( $S = 37.7$ – $38.2$ ) with an average TOC concentration of  $71 \pm 3$   $\mu\text{M}$  ( $n = 25$ ) (St. 4, 5, 6, 8, 9 and MIO), and (3) the Ionian surface water (ISW) ( $S > 38.5$ ) with an average TOC concentration of  $73 \pm 8$  ( $n = 9$ ) (St. 6 and 7). A more detailed analysis of the surface layer is reported below.

### 3.1. Intermediate Layer

[13] The intermediate layer was mainly characterized by the occurrence of different veins of the LIW that were easily recognizable by the salinity maximum at each station (Figure 2b). As expected, in the LIW core, salinity strongly decreased westward. The TOC ranged from 55  $\mu\text{M}$  in the east Med to 40  $\mu\text{M}$  in the west Med, while apparent oxygen utilization (AOU) showed higher values (74–88  $\mu\text{M}$ ) in the west than the east Med (31–70  $\mu\text{M}$ ). These data confirm that in the LIW far from its formation site, both TOC and dissolved oxygen were consumed [*Santinelli et al.*, 2010]. The ratio expected from the Redfield stoichiometry (C:O:N:P = 106:42:16:1) [*Anderson*, 1995] would predict a  $\Delta\text{C}/\Delta\text{O}$  ratio of 0.72. The relationship between TOC and  $\text{AOU-C}_{\text{eq}}$  [ $\text{AOU-C}_{\text{eq}} (\mu\text{M C}) = \text{AOU} (\mu\text{M O}_2) \cdot 0.72$ ] [*Doval and Hansell*, 2000] was studied in the samples collected in the core of the LIW ( $S > 38.70$ ) (east Med) (Figure 3) by using the Model II reduced major axis regression. A good inverse relationship ( $R^2 = 0.88$ ) with a slope of  $-0.49 \pm 0.05$  was observed (data not shown). If the samples collected in the Tyrrhenian Sea ( $S = 38.68$ – $38.70$ ) are also taken into account, the relationship improves ( $R^2 = 0.92$ ), with a slope of  $-0.46 \pm 0.03$  (Figure 3).

[14] The multiple regression between TOC,  $\theta$ , S and  $\text{AOU-C}_{\text{eq}}$  was also investigated. This relationship yields an  $R^2$  value of 0.93 and a  $\text{AOU-C}_{\text{eq}}$  versus DOC ratio of  $0.49 \pm 0.04$ . This ratio is independent of salinity and temperature variations and as a consequence it is independent of the mixing of water masses. These data indicate that in the LIW core, 49% of oxygen consumption is due to DOC mineralization during its route from the Ionian to the Tyrrhenian Sea. These values are in the range of those reported in the literature both for the Mediterranean Sea [*Dafner et al.*, 2001b; *Meador et al.*, 2010; *Santinelli et al.*, 2010] and for the oceans [*Doval and Hansell*, 2000; *Carlson et al.*, 2010].

[15] The value of the intercept of the TOC versus  $\text{AOU-C}_{\text{eq}}$  model II regression is  $64 \pm 1$   $\mu\text{M}$  (Figure 3), as a consequence 64  $\mu\text{M}$  represents the concentration of TOC during formation of the LIW ( $\text{AOU} = 0$ ). In the Sicily Channel (St. 5), the TOC concentration in the LIW core was  $\sim 41$   $\mu\text{M}$ .



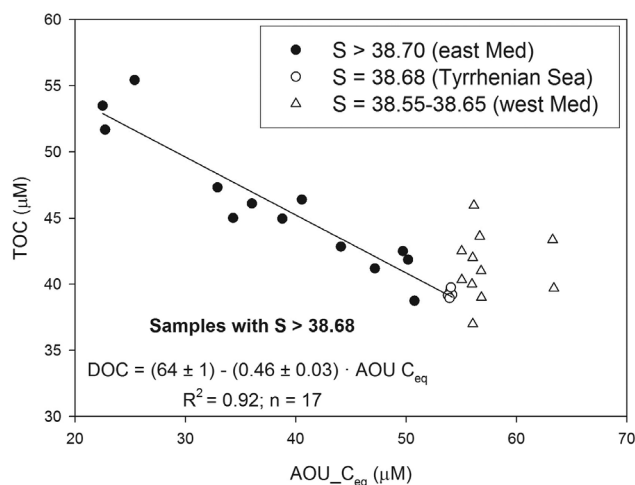
**Figure 2.**  $\theta/S$  diagram considering (a) all the samples and (b) a zoom of the intermediate and deep layers. AW: Atlantic Water; MAW: Modified Atlantic Water; ISW: Ionian Surface Water; WMDW: Western Mediterranean Deep Water; LIW: Levantine Intermediate Water; EMDW: Eastern Mediterranean Deep Water.

If we consider that the time that LIW needs to reach the Sicily Strait is about 10 years [Roether *et al.*, 1998] and that during this time the TOC decreased approximately  $23 \mu\text{M}$  ( $64 - 41 = 23 \mu\text{M}$ ), a TOC remineralization rate of  $2.3 \mu\text{M yr}^{-1}$  is estimated. This value is very similar to that reported by Santinelli *et al.* [2010], though these authors considered data collected in the core of LIW from different cruises occurring over different years. Since the results are similar, the process must be stable, confirming that the TOC removal in the LIW can be estimated when only the samples collected in its core are taken into account. When the samples collected in the LIW in the west Med ( $S = 38.55\text{--}38.65$ ) are also taken into account, the  $R^2$  decreases to 0.70 (slope  $-0.32 \pm 0.04$ ), whereas this relationship is not observed if only the samples from the west Med are considered. This can be explained using the  $\theta/S$  diagrams (Figure 2). In fact, the LIW maintains its characteristics mainly in the Tyrrhenian Sea; at the other western stations, it appears well mixed with the surrounding waters. In addition, when the LIW arrives at the Sicily

Channel, only the refractory fraction remains; therefore, the remineralization time became very long and it is possible that mixing primarily influences the TOC concentration. The mineralization rate of  $2.3 \mu\text{M C yr}^{-1}$  is higher than the DOC decay rates reported for different water masses in the North Atlantic Ocean ( $0.13\text{--}0.93 \mu\text{M C yr}^{-1}$ ) [Carlson *et al.*, 2010], while it is lower than that estimated from time series monitoring of DOC variability in the mesopelagic zone ( $7.8\text{--}8.4 \mu\text{M C yr}^{-1}$ ) [Carlson *et al.*, 1994; Soghrin and Sempéré, 2005], indicating that the semi-labile fraction of DOC is mineralized as the LIW travels from the Levantine Basin to the Sicily Channel and Tyrrhenian Sea.

### 3.2. Deep Waters

[16] Deep waters were characterized by low DOC concentrations both in the east and west Med (at these depths DOC was assumed to be equal to TOC, see section 2.2 *HTCO analysis*). A deeper analysis reveals that (1) in the east Med the ranges of DOC and AOU were 36–41  $\mu\text{M C}$



**Figure 3.** Relationship between the TOC and  $\text{AOU-C}_{\text{eq}}$  in the core of the Levantine Intermediate Water (LIW) (maximum of S).

and  $60\text{--}71 \mu\text{M O}_2$ , respectively. (2) In the west Med the ranges of DOC and AOU were almost the same than in the east Med ( $\text{DOC} = 37\text{--}42 \mu\text{M C}$  and  $\text{AOU} = 57\text{--}71 \mu\text{M O}_2$ ), with a maximum of  $44 \mu\text{M C}$  in the deepest sample of St. 3 and St. 4. The lowest DOC concentrations were found in the Tyrrhenian deep water (TDW) ( $36\text{--}38 \mu\text{M C}$ ;  $\text{AOU} = 65\text{--}71 \mu\text{M O}_2$ ) that is the oldest water mass occurring in the west Med.

[17] DOC concentrations are similar to that reported for the refractory DOC in deep oceanic waters [Hansell and Carlson, 1998] and to the DOC concentrations observed in the Tyrrhenian Sea, in the transitional Eastern Mediterranean Deep Water (tEMDW) and in the old Western Mediterranean Deep Water (WMDW) [Santinelli et al., 2010]. However, they are lower than the DOC values observed in recently ventilated deep waters. The low dissolved oxygen ( $182\text{--}200 \mu\text{M O}_2$ ) concentrations confirm the old age of the deep waters in September 1999.

#### 4. DOC Dynamics in the Surface Layer

[18] The surplus value of the data collected during the Prosopé cruise is the relative synopticity of the sampling, which gives some insight into the DOC dynamics in the surface layer at the basin scale. Figure 4 reports the vertical profiles of the TOC and bacterial production (BP) in the upper 500 m at each station. The potential density profile is added to each graph. As expected, the TOC showed the highest concentrations ( $68\text{--}83 \mu\text{M}$ ) above the pycnocline followed by a marked decrease to reach values of  $45\text{--}48 \mu\text{M}$  at  $100\text{--}200$  m. Below 200 m, values of  $40\text{--}45 \mu\text{M}$  were observed. BP was characterized by a subsurface maximum at the depth of the pycnocline; then it strongly decreased with a trend comparable to that of the TOC. The values of the exponential decay are similar to that reported for the northwestern Mediterranean Sea by Tanaka and Rassoulzadegan [2002].

##### 4.1. Excess-DOC Stock

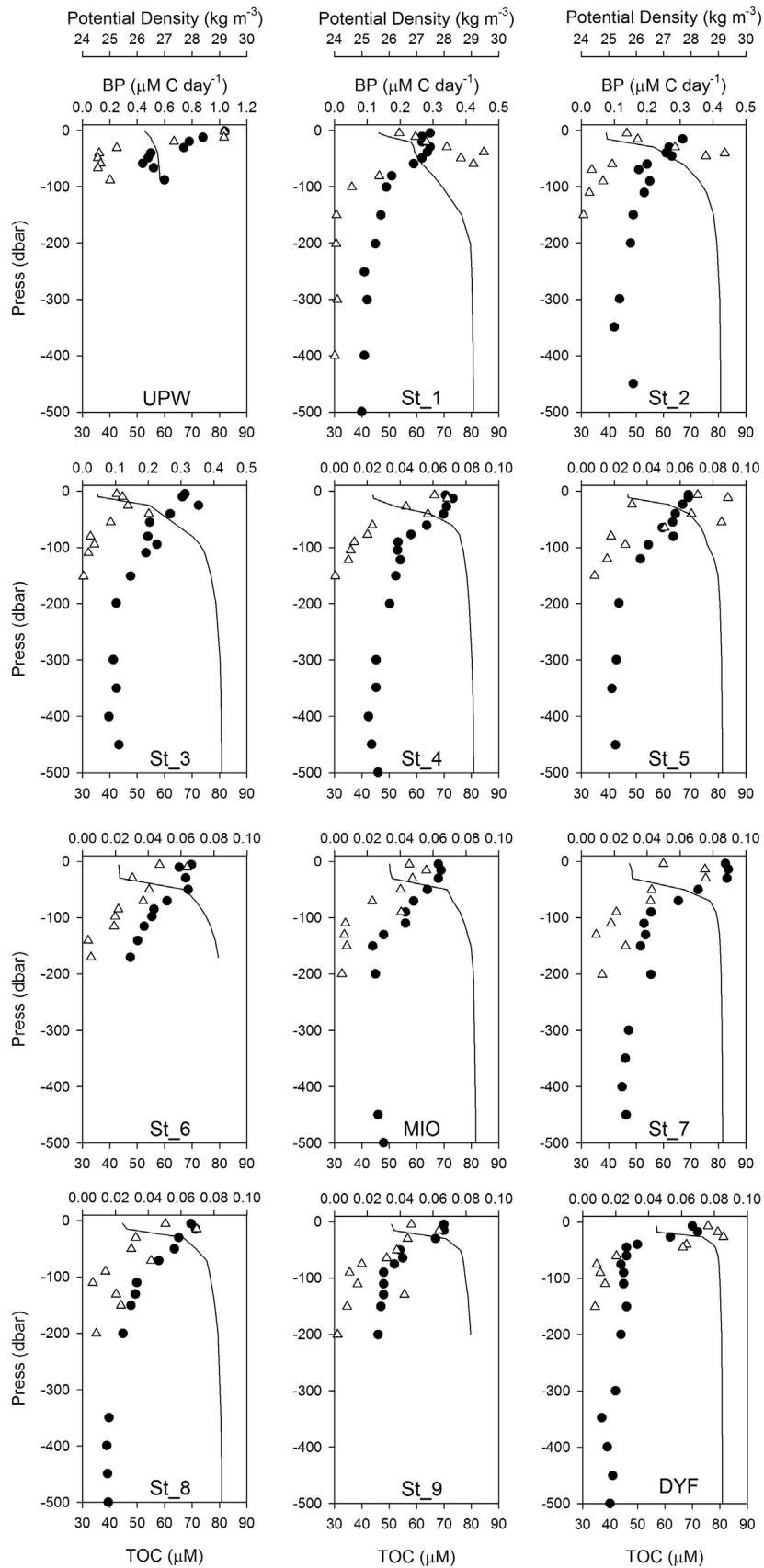
[19] The excess-DOC (ex-DOC) and TOC (ex-TOC) were calculated by subtracting  $48 \mu\text{M}$  from the observed DOC

and TOC concentrations. Forty-eight  $\mu\text{M}$  is the lowest concentration observed immediately below the pycnocline. This value is in the range of the concentrations representative of the refractory DOC in the Aegean Sea and Alboran Sea ( $44\text{--}52 \mu\text{M}$ ) [Sempéré et al., 2002, 2003], while it is higher than the concentration of refractory TOC in the LIW in the western Alboran Sea ( $38\text{--}42 \mu\text{M}$ ), as reported by Dafner et al. [2001b]. Finally, this value is slightly higher than the DOC minimum reported by Pujo-Pay et al. [2011] ( $44 \mu\text{M}$  in the east and  $39 \mu\text{M}$  in west Med). However, it is in the range of the refractory DOC concentrations observed in the oceans ( $34$  to  $48 \mu\text{M}$ ) [Hansell and Carlson, 1998]. The stock of ex-DOC was calculated as the integral of the ex-DOC from the surface to the depth at which the DOC concentration was  $48 \pm 0.5 \mu\text{M}$  ( $\text{D48}_{\text{DOC}}$  hereafter). Notably, the  $\text{D48}_{\text{DOC}}$  varied greatly among the stations (Table 1). The same calculations were made for TOC. The stock of ex-DOC and ex-TOC ranged between  $0.48$  and  $1.83 \text{ mol m}^{-2}$  and  $1.04$  and  $2.17 \text{ mol m}^{-2}$ , respectively. The minimum of ex-DOC was observed at the Gibraltar Strait (St. 1) and low values were also found in the northern Tyrrhenian Sea (St. 9) and in the Ligurian Sea (St. DYF). In these stations the DOC concentration of  $48 \mu\text{M}$  was observed at a depth of  $70\text{--}85$  m. A low ex-DOC stock was also observed at the Morocco upwelling station (St. UPW) ( $0.50 \text{ mol m}^{-2}$ ) until 59 m. The maximum ex-DOC and ex-TOC stock ( $1.83$  and  $2.17 \text{ mol m}^{-2}$ ) was observed in the Sardinian Channel (St. 4). High values were found in the Sicily Channel (St. 5) and in the Ionian Sea (St. 6). Interestingly, when only the western stations (St. 1–St. 4) are taken into consideration, a progressive increase in the ex-DOC and ex-TOC stock was observed eastward together with a deepening of both  $\text{D48}_{\text{DOC}}$  and  $\text{D48}_{\text{TOC}}$  (Table 1). If the integrated average values are taken into considerations (Table 1) it is still evident that the western stations were characterized by lower ex-DOC ( $6\text{--}8 \mu\text{M}$ ) than the eastern ones ( $9\text{--}10 \mu\text{M}$ ). The same pattern can be observed for ex-TOC. The eastward increase in the ex-DOC suggests that the west Med was probably characterized by a high flux of labile DOC (high production and high removal); in contrast, the east Med was characterized by a decoupling between DOC production and removal processes, which resulted in DOC accumulation.

##### 4.2. W-E Vertical Distribution of Organic Carbon: Physical, Chemical and Biological Parameters

[20] In order to study organic carbon dynamics in the surface layer, the TOC, POC and DOC vertical distributions (Figures 5a–5c) were studied in the upper 200 m along the W-E section (Figure 1). The vertical distribution of the other biological (bacterial abundances (BA), bacterial production (BP), abundance of oligotrich ciliates (CIL) and Chl-a; Figures 5d–5f and 5i), physical (salinity, potential temperature; Figures 5g and 5h), and chemical ( $\text{NO}_3$ ,  $\text{PO}_4$  and silicates Figures 5l–5n) parameters is also reported.

[21] The thermocline was located at about 20 m at the western stations, while it deepened to  $50\text{--}60$  m at the eastern ones. Chl-a fluorescence did not show any W-E pattern (Figure 5i). The deep chlorophyll maximum (DCM) was visible at most of the stations and it deepened eastward. The Chl-a fluorescence maxima ( $>0.4 \text{ A.U.}$ ) were observed in the Alboran Sea (St. 2 at 40 m) and in the Sicily Channel (St. 5 at 60 m) [Crombet et al., 2011]. Particulated primary



**Figure 4.** The TOC (solid circles) and bacterial production (BP, open triangles) vertical profiles in the upper 500 m. The potential density (black line) is also shown. Note difference in scale of BP for UPW and St. 1–St. 3.

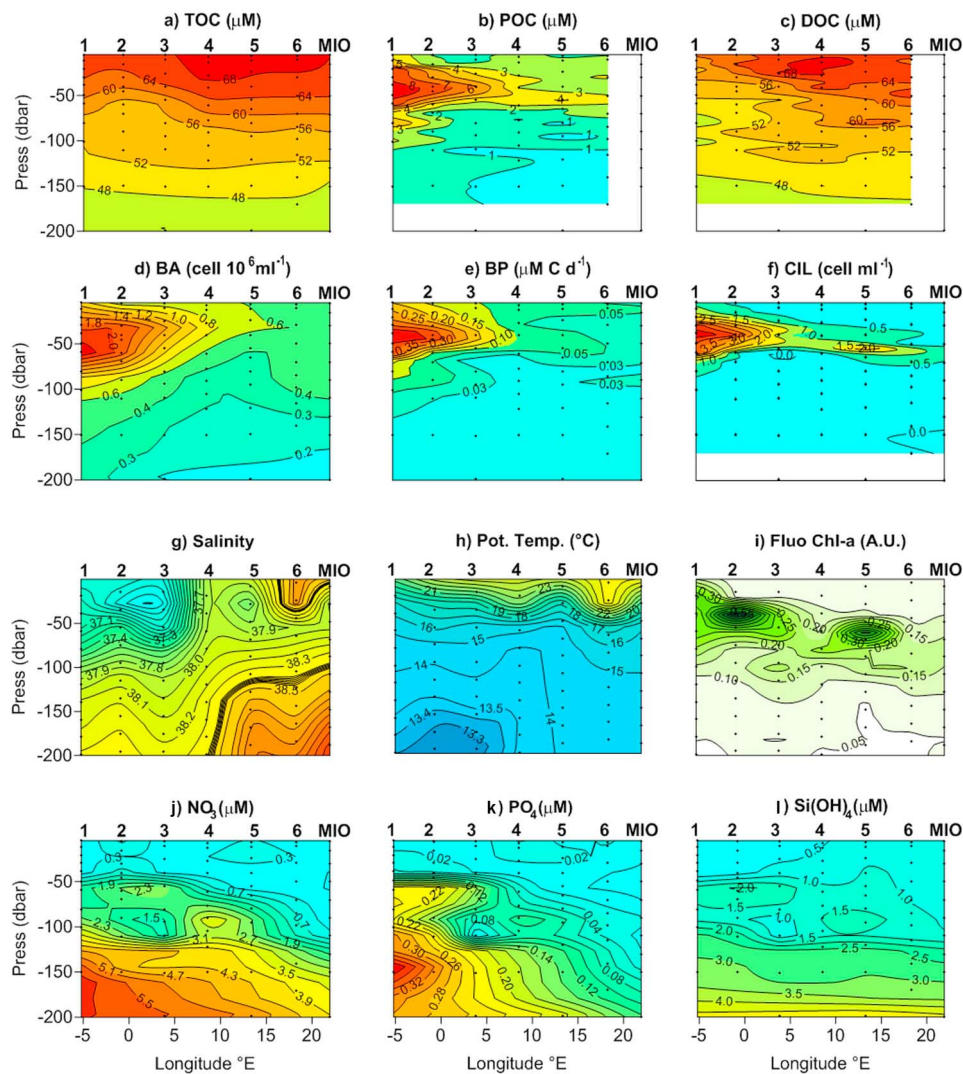
**Table 1.** Stock of DOC and Excess DOC (ex-DOC) in the Surface Layer (0 m-D48<sub>DOC</sub>) Compared to the Stock of TOC and Excess TOC (ex-TOC) in the Surface Layer (0 m-D48<sub>TOC</sub>)

Station	D48 <sub>DOC</sub> <sup>a</sup> (m)	Stock (mol·m <sup>-2</sup> )				D48 <sub>TOC</sub> <sup>a</sup> (m)	Stock (mol·m <sup>-2</sup> )			
		DOC	ex-DOC	ex-DOC <sup>b</sup> (μM)	ex-DOC (%)		TOC	ex-TOC	ex-TOC <sup>b</sup> (μM)	ex-TOC (%)
St. UPW	59	3.32	0.50	8	15	— <sup>c</sup>	— <sup>c</sup>	— <sup>c</sup>	— <sup>c</sup>	
St. 1	71	3.88	0.48	7	12	115	6.61	1.08	9	16
St. 2	150	8.09	0.89	6	11	200	10.92	1.31	7	12
St. 3	142	7.94	1.12	8	14	151	8.68	1.44	10	17
St. 4	240	13.34	1.83	8	14	240	13.7	2.17	9	16
St. 5	156	8.99	1.50	10	17	155	9.15	1.71	11	19
St. 6	160	9.18	1.50	9	16	160	9.47	1.79	11	19
St. 8	130	7.41	1.15	9	16	151	8.73	1.50	10	17
St. 9	85	4.88	0.80	9	16	90	5.39	1.07	12	20
St. DYF	70	4.08	0.73	10	18	72	4.49	1.04	14	23

<sup>a</sup>D48<sub>DOC</sub> and D48<sub>TOC</sub> indicate the depth at which DOC and TOC were  $48 \pm 0.5 \mu\text{M}$ . When the DOC or TOC value at this depth was not available, it was calculated by interpolating the available data. At St. UPW, DOC data were available to a depth of 59 m, where DOC showed a concentration of  $48.45 \mu\text{M}$ .

<sup>b</sup>The concentrations of ex-DOC and ex-TOC were calculated dividing the integral by the depth-layer at which it was calculated.

<sup>c</sup>At 88 m (the deepest sample collected) TOC showed a concentration of  $60 \mu\text{M}$ ; as a consequence, it was not possible to estimate the ex-TOC at this station.



**Figure 5.** Vertical distribution of the TOC, POC, DOC, abundance of heterotrophic prokaryotes (BA), bacterial production (BP), abundance of Oligotrich ciliates (CIL), salinity, potential temperature, fluorescence of Chl-a,  $\text{NO}_3$ ,  $\text{PO}_4$  and silicates in the upper 200 m along the W-E section, as indicated in the map in Figure 1. MIO: Ionian Sea Station. Data source is given in section 2.



**Table 2.** Weighted Average of the Chemical and Biological Parameters in the Layer Above the Pycnocline, With BCD Estimated in Relation to a BGE of 15%<sup>a</sup>

Station	D <sub>Pycnocline</sub> <sup>b</sup> (m)	BA (Cell 10 <sup>6</sup> ml <sup>-1</sup> )	BB ( $\mu$ M C)	BP ( $\mu$ M C d <sup>-1</sup> )	BCD ( $\mu$ M C d <sup>-1</sup> )	TOC ( $\mu$ M)	DOC ( $\mu$ M)	ex-DOC <sup>c</sup> ( $\mu$ M)	TT <sub>ex-DOC</sub> <sup>d</sup> (d)	PO <sub>4</sub> ( $\mu$ M)	NO <sub>3</sub> ( $\mu$ M)	Si(OH) <sub>4</sub> ( $\mu$ M)
St. UPW	45	1.79	2.23	0.571	2.79	68	58	10	4	0.273	6.08	0.0
St. 1	120	1.43	1.78	0.239	1.59	57	51	3	2	0.132	1.79	0.7
St. 2	115	1.07	1.34	0.153	1.02	57	54	6	6	0.149	1.60	1.3
St. 3	100	0.76	0.95	0.097	0.65	60	57	9	14	0.059	1.13	0.8
St. 4	80	0.57	0.71	0.042	0.28	67	64	16	57	0.023	0.43	0.7
St. 5	110	0.41	0.51	0.048	0.32	62	60	12	38	0.043	1.15	1.4
St. 6	88	0.61	0.76	0.038	0.26	65	62	14	54	0.004	0.04	0.8
St. MIO	85	0.58	0.73	0.040	0.27	64	n.a. <sup>e</sup>	n.a. <sup>e</sup>	n.a. <sup>e</sup>	0.005	0.02	0.0
St. 7	87	n.a.	n.a.	0.053	0.36	74	n.a. <sup>e</sup>	n.a. <sup>e</sup>	n.a. <sup>e</sup>	0.005	0.13	0.9
St. 8	59	0.64	0.80	0.042	0.27	66	63	15	56	0.002	0.05	0.7
St. 9	55	n.a.	n.a.	0.048	0.32	64	61	13	41	0.012	0.10	0.9
St. DYF	55	0.70	0.87	0.071	0.47	65	60	12	26	0.012	0.62	2.0

<sup>a</sup>The weighted average was calculated as the integral divided by the depth at which it was calculated.

<sup>b</sup>D<sub>Pycnocline</sub> is the maximum depth influenced by the pycnocline, and it was calculated as the depth at which the second derivative of the function of density with depth oscillates in the range of  $\pm 0.005$  kg/m.

<sup>c</sup>Ex-DOC indicate the excess of DOC with respect to 48  $\mu$ M.

<sup>d</sup>Turnover time for excess DOC (TT<sub>ex-DOC</sub> = exDOC/BCD).

<sup>e</sup>n.a.: not available.

production (PPP) was higher at St. 1 and St. 2 (5.3–5.9 mg C m<sup>-3</sup> d<sup>-1</sup>) than in the other stations (1.5–3.1 mg C m<sup>-3</sup> d<sup>-1</sup>) [Moutin *et al.*, 2002]. As expected, a clear W-E gradient was observed both for NO<sub>3</sub> (Figure 5j) and PO<sub>4</sub> (Figure 5k); in particular, a NO<sub>3</sub> maximum (>5  $\mu$ M) was detected below 150 m at the westernmost stations (St. 1 and St. 2). The same trend was observed for PO<sub>4</sub>, with two maxima at St. 1 and St. 2; the first ( $\sim 0.30$   $\mu$ M) at 75 m and the second one ( $\sim 0.47$   $\mu$ M) at 150 m [Crombet *et al.*, 2011]. This pattern can be mainly explained by the input of nutrients from the Atlantic Ocean, even if the release of nutrients due to POM and DOM mineralization cannot be excluded.

[22] The TOC showed the highest values (60–73  $\mu$ M) above the thermocline, with slightly higher concentrations (>68  $\mu$ M) in the upper 50 m of the easternmost stations (St. 4, 5, 6 and MIO). The POC had a high concentration (6.2–8.7  $\mu$ M) between 25 and 60 m at the western stations (St. 1–St. 3) with a decreasing W-E gradient. By contrast, the DOC was at a minimum (<52  $\mu$ M) between 50 and 100 m, corresponding to the high PO<sub>4</sub> concentration (Figure 5l). The DOC minimum was immediately below the maximum in the BA (Figure 5d) and BP (Figure 5e). The highest DOC concentrations were found in the upper 50 m in the Balearic Sea (St. 3) and in the Sardinian (St. 4) and Sicily (St. 5) Channels. Considering the above-pycnocline layer, DOC showed a marked W-E increase (Table 2). The distribution of BA, BP and oligotrich ciliates, is very interesting too (Figure 5). A marked maximum was observed for both bacteria and ciliate abundance in the upper 100 m of the western stations (St. 1–St. 3), with a pattern very similar to that of POC. Taking into account samples where POC and bacterial abundance were simultaneously determined and assuming a 15 fg C per bacterial cell (generally used for oligotrophic waters) [Fukuda *et al.*, 1998; Caron *et al.*, 1999], bacterial biomass represented on average 51% of POC (sd = 29%, n = 87). The size class of oligotrichs was not measured during this study; however if the biomass versus abundance relationships for oligotrich ciliates, observed along longitudinal gradient in the Mediterranean Sea in stratified conditions (BOUM cruise, June–July 2008) [Christaki *et al.*, 2011], is

taken into consideration, the biomass of oligotrich ciliates may represent on average 3.6% of the POC (sd = 3.1%, n = 6). Both bacterial abundance and production decreased from the Gibraltar Strait (St. 1) to the eastern Ionian Sea (St. MIO) (BA:  $2.0 \times 10^6$  to  $0.4 \times 10^6$  cell ml<sup>-1</sup>; BP: 0.4 to 0.04  $\mu$ M C d<sup>-1</sup>), though the strongest decrease was found from St. 1 to St. 4 (Figure 5 and Table 2). The abundance of oligotrich ciliates perfectly resembled those of bacteria, suggesting a trophic cascade effect through the microbial loop (bacteria-flagellates-ciliates). The sub-surface maximum of heterotrophic bacterial production at St. 1–St. 3 could be induced by the high POC concentrations observed at the same stations as well as by the availability of labile DOC and inorganic nutrients. It is important to remember that these stations were also characterized by high PPP. Resuming, the vertical distributions of chemical and biological parameters in the upper 200 m (Figure 5) indicate an instantaneous situation in which: (1) in the western stations (St. 1–St. 3), the DOC (or POC transformed to DOC) consumed by bacteria (low DOC), was efficiently transferred to higher trophic levels (high abundance of oligotrich ciliates), and only a small fraction of carbon was accumulated as DOC (low semi-labile DOC stock); and (2) in the eastern stations (St. 4 to St. MIO), bacteria were probably consuming carbon with low rates. Thus, the energy was accumulated as DOC (high semi-labile DOC stock).

## 5. Carbon Fluxes Through the Microbial Loop

[23] In order to get insights into the carbon fluxes in different areas of the Mediterranean Sea, the integrated average of the biological and chemical parameters in the above-pycnocline layer was analyzed in detail. This layer was chosen since it was characterized by high variability in terms of biological activity (Figure 5 and Table 2). The conversion factors used were those reported in the literature for both the oceans and the Mediterranean Sea. Bacterial carbon demand (BCD) was calculated from the BP with a unique bacterial growth efficiency (BGE) of 15%, as reported for the Sargasso Sea [Carlson and Ducklow, 1996] and for the west Med

[Sempéré *et al.*, 2003]. This value can be criticized because bacteria, which originate from different stations and depths, very likely grow with different BGE [Eichinger *et al.*, 2006, 2010, 2011]. The 15% value was used to obtain a rough estimate of the average amount of DOC needed by bacteria to sustain the observed BP.

### 5.1. DOC Mineralization Rates

[24] A rough estimate of the turn over time (TT) of the semi-labile DOC can be obtained by dividing the integrated stock of ex-DOC by the integrated BCD in the same layer [Sempéré *et al.*, 2002] (Table 2). This calculation can give some information if we assume a steady state situation in which (i) DOC is not produced, (ii) the ex-DOC is representative of the semi-labile DOC pool, and (iii) bacterial carbon demand (BCD), based on BP rate and a 15% BGE, is considered as an upper limit of semi-labile DOC consumption. However, it is important to take into consideration that BP is measured on short time incubation experiments and that on short temporal scales bacteria are mainly consuming labile DOC. As a consequence assuming that most of the ex-DOC is semi-labile, its TT could be underestimated. TT, estimated with this calculation, ranged from 2 days in the Gibraltar Straits (St. 1) to 54–57 days in the Sardinian Channel (St. 4), Ionian (St. 6) and Tyrrhenian (St. 8) Sea. These values are similar to those reported by Sempéré *et al.* [2002] for the Aegean Sea (47–80 days), which were calculated with a BGE of 14%. Based on our BP data and a BGE of 15%, the DOC mineralization rate ranged between  $1.5 \mu\text{M d}^{-1}$  (St. 1) and  $0.26\text{--}0.28 \mu\text{M d}^{-1}$  (St. 6 and St. 4) in the surface layer, with a marked decrease eastward. These rates are in agreement with the data reported by Carlson and Ducklow [1996]; the authors observed the removal of  $8 \mu\text{M}$  of labile DOC in 4 days ( $2 \mu\text{M d}^{-1}$ ) in unamended seawater cultures from the Sargasso Sea in July 1992. Our values are also similar to the mineralization rates observed by Eichinger *et al.* [2006] in the northeastern Atlantic Ocean ( $0.6 \mu\text{M d}^{-1}$ ). The decrease in the rate of DOC mineralization eastward may be due to a change in its composition, to the occurrence of different prokaryotic populations with a different ability to consume the available DOC, as well as to the increase in P limitation.

### 5.2. Bacterial Versus Primary Production Ratio

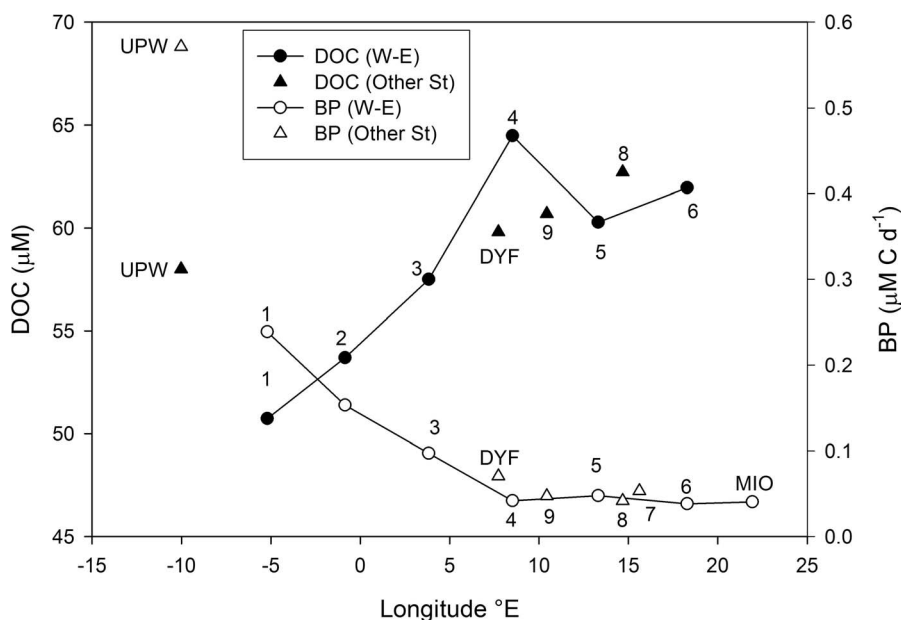
[25] The percentage of primary production (PP) used by bacteria is often considered an index of the PP flux potentially channeled through the microbial food web. Particulate PP (PPP) was measured at all the stations at one depth (10–15 m) and at three stations (St. UPW, DYF, MIO) at 6–8 depths in the upper 100 m. The integrated PPP was 13 and  $19 \text{ mmol C m}^{-2} \text{ d}^{-1}$  in the Ligurian Sea (St. DYF) and in the Ionian Sea (St. MIO), respectively. As expected, in the Morocco upwelling (St. UPW) it was more than one order of magnitude higher ( $348 \text{ mmol C m}^{-2} \text{ d}^{-1}$ ) than in the Mediterranean Sea.

[26] The BP/PPP ratio (calculated by using the integrals in the same layer at St. UPW, DYF, and MIO) showed values ranging from 8% (St. UPW) to 22% (St. MIO) and 31% (St. DYF). The relationship between BP and PPP was also analyzed taking into consideration the volumetric PPP made at a single depth (10–15 m) at every station. The slope of the relationship was  $0.41 \pm 0.10$  ( $R^2 = 0.61$ ;  $p < 0.005$ ;

$n = 10$ ), indicating a BP/PPP of 41%. This value is the same as that reported for the Atlantic tropical zone [Hoppe *et al.*, 2002]. The 41% value is also similar to the BP/PPP average reported for oceanic waters (30–40%) [Cole *et al.*, 1988; Ducklow and Carlson, 1992] and to some values observed in the Mediterranean Sea (21% west Med; 34% east Med) [Turley *et al.*, 2000] and the Almeria-Oran Front (10–20%) [Sempéré *et al.*, 2003]. Pulido-Villena *et al.* [2012] reported that the slope of the relationship between log PPP and log BP was lower in the west Med (0.29) than in the east Med (0.50), suggesting a less direct coupling between PPP and BP in the west Med.

[27] The ratio between BCD and PPP was also calculated with respect to different BGE. At a BGE of 15%, the ratio showed values of 210% at the DYF station and 148% at the Ionian Sea (St. MIO), while the BCD/PPP ratio was 54% at the Morocco upwelling. Considering sub-surface volumetric data sampled at each station, at a BGE of 15% the relationship BCD versus PPP had a slope of  $2.72 \pm 0.70$ , and at a BGE of 30% the slope was  $1.36 \pm 0.35$ , indicating that in both cases the BCD was markedly higher than the PPP. A BCD/PPP ratio greater than 100% was also observed for the Almeria-Oran Front [Sempéré *et al.*, 2003]. This finding suggests a temporal uncoupling between DOM production during the phytoplankton bloom and DOM degradation. Similar observations were also reported by Van Wambeke *et al.* [2002b]. PPP is generally measured but dissolved primary production (DOCp) should be also considered in the estimate of total primary production, particularly in oligotrophic environments. López-Sandoval *et al.* [2011] obtained a value of the percentage of extracellular release [ $\text{PER} = \text{DOCp}/(\text{DOCp} + \text{PPP})$ ] of  $\sim 37\%$ , without clear longitudinal pattern, over the whole Mediterranean Sea, in stratified conditions. Total PP (PP<sub>tot</sub>) from our data was then calculated by using their average PER of 37%. The integrated BCD/PP<sub>tot</sub> ratio ranged between 93% (St. MIO) and 132% (St. DYF), while the slope of the relationship between BCD and PP<sub>tot</sub> volumetric data at a single depth (10–15 m) at every station was  $1.71 \pm 0.44$  and  $0.86 \pm 0.22$  considering a BGE of 15% and 30%, respectively. These data indicate that even if PP<sub>tot</sub> is taken into consideration the balance is still close to net heterotrophy.

[28] These observations suggest that the Mediterranean Sea in September 1999 was an area of net heterotrophy where bacteria needed more than the organic carbon produced by photosynthesis in order to satisfy the BCD. Based on oxygen budgets, Regaudie-de-Gioux *et al.* [2009] reported that the Mediterranean open-seawaters in stratified conditions are characterized by net heterotrophy over large longitudinal gradients. This feature can be explained by a spatial and temporal decoupling between DOC production and consumption and/or by the input of DOC from the land and/or the atmosphere. The phytoplanktonic carbon dependency of heterotrophic bacteria is still the subject of controversy, even if it tends to be excluded in oceanic environments [Fouilland and Mostajir, 2010]. The numerous assumptions on conversion factors for BP and BGE, the lack of good sampling frequency as well as the problems in the measurements of particulate PP which don't take into account phytoplankton excretion, may strongly affect the BP:PPP and BCD:PPP ratios [Morán and Alonso-Sáez, 2011]. For instance, it was demonstrated that the temporal



**Figure 6.** Weighted average (calculated as the integral divided by the depth in which it was calculated) of the DOC (black symbols) and BP (white symbols) in the above-pycnocline layer. The symbols touching the line refer to the stations located in the W-E section, as indicated in Figure 1. The values for the other stations are also reported. The name of each station is indicated in the graph.

variations in substrate availability greatly influences the BGE [Eichinger *et al.*, 2010]. In oceanic systems BGE was observed to range between 37 and 72% with high values during the day [Coffin *et al.*, 1993]. As a consequence, the value of 15% for the BGE may overestimate the  $\text{CO}_2$  production by bacteria. If we consider a BGE of 50%, the BCD/PP and BCD/PP<sub>tot</sub> ratio decreases to 82% and 51%, respectively.

### 5.3. Relationship Between DOC and BP

[29] The longitudinal pattern of the integrated average of DOC and BP in the above-pycnocline layer (Figure 6) clearly showed an increase of DOC associated with a BP decrease eastward. A similar trend can be observed for TOC (Tables 1 and 2). The Sardinian Channel represented a separation point between two opposite situations: (1) in the western stations (St. 1, 2, 3, 4), a negative correlation between DOC and BP was evident, and (2) in the central (St. 5, 8, 9 and DYF) and eastern (St. 6, 7, MIO) stations, no W-E pattern was found in DOC and BP; in fact, they were essentially constant. Interestingly, the DOC versus BP trends are similar to that observed in two seawater culture experiments conducted in the northwestern Sargasso Sea [Carlson and Ducklow, 1996] and in the biodegradation experiments in the northeast Atlantic Ocean [Eichinger *et al.*, 2006] as though the longitudinal scale were a temporal scale. Carlson and Ducklow [1996] reported that when in situ DOC production and consumption processes were uncoupled, 8  $\mu\text{M}$  of labile DOC accumulated. When a surplus of labile DOC is available, bacteria grow rapidly with a BGE of 14% and consume the surplus of DOC in  $\sim 4$  days. By contrast, when in situ DOC production and consumption processes are tightly coupled, no significant variation in BP and DOC is observed [Carlson and Ducklow, 1996].

In a similar fashion, Eichinger *et al.* [2006] observed a decrease of DOC from 62 to 56  $\mu\text{M}$ , which was associated with an increase in BB from 0.7 to 2  $\mu\text{M}$ , over 10 days in a biodegradation experiment performed at 5 m in spring in the northeast Atlantic Ocean.

[30] Our data indicate a DOC accumulation of 13  $\mu\text{M}$  (and 10  $\mu\text{M}$  of TOC) that was associated with a decrease in both BB (1.07  $\mu\text{M}$ ) and BP (0.20  $\mu\text{M C d}^{-1}$ ) from St. 1 to St. 4 (Table 2). Contrarily, DOC, BP and BB were similar at the central and eastern stations. The data reported here indicate that between St. 1 and St. 3, DOC was mainly consumed by bacteria, whereas it accumulated to a similar extent at central and eastern stations. This finding suggests that the high biological activity occurring at Gibraltar Strait and in the Alboran Sea might consume all the available DOC preventing its accumulation. This observation stresses that the Sardinian Channel is a separation point between the west Med, characterized by high biological activity associated with high DOC removal and the central and eastern basins, where DOC accumulation prevails and variations in both DOC and BP are very small (Figure 6). This similarity among the central and eastern stations might be also explained by nutrient limitation of DOC consumption [Van Wambeke *et al.*, 2002a] or by the occurrence of a type of DOC that is not available for the bacterial community.

## 6. Concluding Remarks

[31] Our data confirm that in the Mediterranean intermediate water, 49% of oxygen is used for TOC mineralization with rates (2.3  $\mu\text{M C yr}^{-1}$ ) approximately double of the highest values reported for the North Atlantic Ocean. Another unique aspect of the Mediterranean Sea is the high percentage of primary production channeled into the microbial loop (41%)

as well as the very high BCD/PPP ratio (>100%). This finding may be explained by a spatial and/or temporal decoupling between DOC production and consumption processes and/or by the input of DOC from the land and/or the atmosphere. On the other hand, we cannot overlook the fact that BGE (15%–30%) may be underestimated.

[32] In September 1999, various situations can be highlighted in terms of organic carbon dynamics:

[33] 1. The stations west of the Sardinian Channel (St. 1–St. 4) were characterized by: (1) low DOC concentration with an eastward increase in its semi-labile stock, and (2) high bacterial production and high abundances of bacteria and oligotrich ciliates, which decreased eastward. The microbial loop was probably very active and most of the semi-labile DOC was utilized with a high flux of carbon into the microbial loop (high BA and high microzooplankton biomass).

[34] 2. The stations east of the Sardinian Channel were characterized by similar DOC and BP, suggesting that DOC production and consumption were coupled, resulting in no significant longitudinal variation in its stock (Figure 6). Although  $1.50\text{--}1.83\text{ mol m}^{-2}$  of DOC accumulated in the upper 200 m (ex-DOC; Table 1), this did not fuel bacteria production. This finding can be explained by nutrient limitation, the molecular characteristics of the DOC accumulated and/or the occurrence of bacterial populations that are not able to consume the accumulated DOC.

[35] 3. The Ligurian Sea was characterized by intermediate values of DOC, BP and nutrients and by a shallow pycnocline (55 m). At DYF station, experiments performed during the same cruise [Van Wambeke et al., 2002a] confirmed that bacteria were P-limited in the surface layer, whereas they were C-limited below 50 m. This finding was confirmed by the very low DOC concentration observed below the pycnocline (Figure 4).

[36] 4. Tyrrhenian Sea was characterized by a shallow pycnocline (55–60 m) and by very low nutrient concentrations. DOC and BP values were similar to those observed at the stations east of Sardinian Channel.

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