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Total organic carbon distribution and budget through the Strait of Gibraltar in April 1998

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Abstract

In order to investigate total organic carbon (TOC) exchange through the Strait of Gibraltar, samples were taken along two sections from the western (Gulf of Cádiz) and eastern (Western Alboran Sea) entrances of the Strait and at the middle of the Strait in April 1998. TOC was measured by using a high-temperature catalytic oxidation method. The results referenced here are based on a three-layer model of water mass exchange through the Strait, which includes the Atlantic inflow, Mediterranean outflow and an interface layer in between. All layers were characterised by a decrease of TOC concentrations from the Gulf of Cádiz to the Western Alboran Sea: from 60–79 to 59–66 μM C in the Atlantic inflow and from 40–60 to 38–52 μM C in the Mediterranean waters, respectively. TOC concentrations in the modified North Atlantic Central Water

Strait. Our results indicate that the short-term variability caused by the tide greatly impacts the TOC distribution, particularly in the Gulf of Cádiz. The TOC input from the Atlantic Ocean to the Mediterranean Sea through the Strait of Gibraltar varies from 0.9×10^4 to 1.0×10^4 mol C s^{-1} (or 0.28×10^{12} to 0.35×10^{12} mol C $year^{-1}$, respectively). This estimate suggests that the TOC inflow and outflow through the Strait of Gibraltar are two and three orders of magnitude higher than reported via the Turkish Straits and Mediterranean River inputs. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: TOC; Distribution; Balance; Apparent oxygen utilisation; The Strait of Gibraltar

1. Introduction

The exchange between the Mediterranean and Atlantic through the Strait of Gibraltar is a key issue both for the Mediterranean environment and for global ocean circulation and climate variability (Bryden and Kinder, 1991). It is well known that the Surface Atlantic Water, which flows into the Mediterranean Sea, causes an increase of productivity in the Alboran Sea (Packard et al., 1988; Minas et al., 1991). It has also been shown that in the Atlantic inflow concentrations of the organic forms of nutrients are higher (Coste et al., 1988) and mineral forms of nutrients are lower (McGill, 1961) than

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within the Mediterranean outflow. Estimates by Greze et al. (1985) suggest that the annual zooplankton inflow from the Atlantic Ocean is twice as high as its outflow from the Mediterranean Sea.

By contrast, little is known yet about the influence of the Mediterranean outflow on the biogeochemistry of the eastern North Atlantic although the physical environment of this phenomenon has received more attention. Over the last decade, it has been found that the salinity and temperature of the Deep Mediterranean waters have increased (Béthoux et al., 1990; Rohling and Bryden, 1992; Francour et al., 1994). There are some simulations of an increase of its influence on the dynamic of the North Atlantic Ocean (Rahmstorf, 1998) and on the climate, in general (Johnson, 1997). To predict an influence of the climate warming on the cycling of the major organic nutrients in the North Atlantic and the Mediterranean Sea, we need to know in what quantity these materials are exchanged between both basins.

Polat and Tugrul (1996) estimated an organic carbon budget for the eastern part of the Mediterranean Sea through the Turkish Straits. In contrast, only indirect estimates of the organic carbon budget exist for the Strait of Gibraltar (Copin-Montégut, 1993). No reports of direct observations of organic carbon distribution and exchange through the Strait of Gibraltar have been presented up to the present. In this paper, we describe the results of total organic carbon (TOC) measurements, in terms of distribution and budget, that were estimated from the samples collected during April 1998 in the Strait of Gibraltar area.

1.1. Study area

The Strait of Gibraltar is a narrow and shallow connection between the Atlantic Ocean and the Mediterranean Sea (Fig. 1). The Strait has an east–west orientation, a 60-km-long passage with a minimum width of about 12 km on the Tarifa Narrows, and an average depth of about 600 m. Thirteen kilometres westward of the Tarifa Narrows lies the main bathymetric sill of the Strait, the Camarinal sill, with a maximum depth of about 285 m and a surface of about 7.86 km^2 (Guimerans et al., 1988). Another sill (the Spartel sill) is situated 21 km west of the

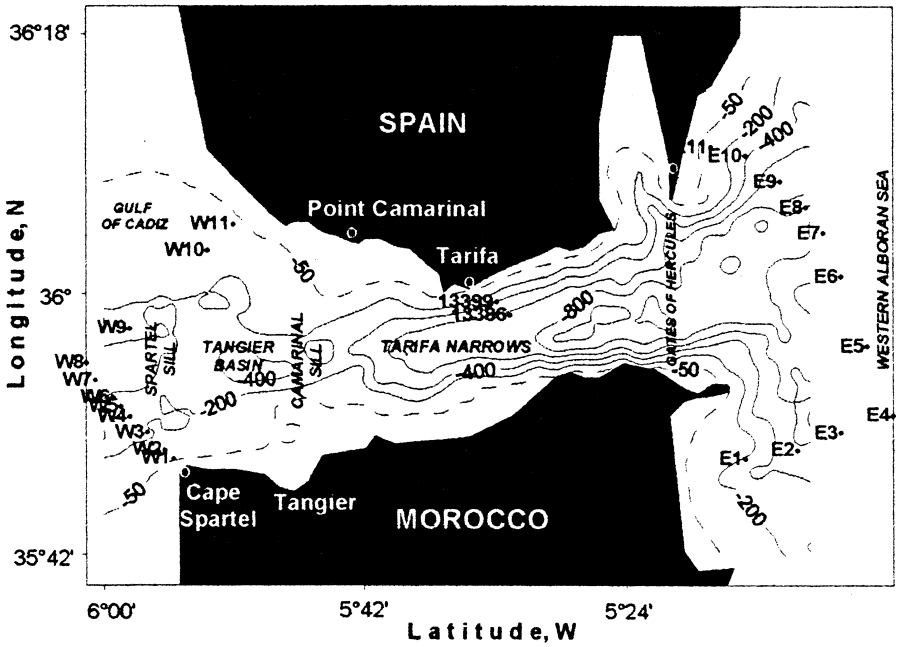

Fig. 1. Bathymetry of the Strait of Gibraltar and stations grid during cruise 232 onboard of the RRV Discovery (12–18 April 1998). To the east of the Strait lies the Alboran Sea, the westernmost basin of the Mediterranean Sea. To the west of the Strait lies the Gulf of Cádiz, an embayment of the Northeast Atlantic Ocean.

main sill and has a maximum depth of more than 350 m (La Violette and Lacombe, 1988). Between these two sills, is the Tangier Basin, with a maximum depth of approximately 640 m.

2. Materials and methods

2.1. Field sampling

Discrete seawater samples were taken from the RRV Discovery (cruise 232) at a series of stations across the Strait of Gibraltar between 12 and 18 of April 1998 (Fig. 1). A CTD rosette system (Seabird) equipped with 10 l Niskin bottles was used. Stations were chosen to cover a variety of waters from western (Stn. W1–W11, in the Spartel sill area), and from eastern (Stn. E1–E11, in the Western Alboran Sea) entrances of the Strait, and in the middle of the Strait (Tarifa Narrows, Stn. 13386 and 13399). The bottles were fired at the depths of maximum or minimum distribution of temperature, salinity, oxygen and fluorescence, within and between different water bodies and at the interface layer between the Atlantic inflow and Mediterranean outflow. Samples were taken to within a few meters of the bottom. The positions of the stations are listed in Table 1.

Samples were not filtered and were drawn as soon as possible after the rosette sampler was on the deck of the ship (either first or immediately following the gas samples). The 10 ml samples were collected in duplicate in precombusted (450°C, at least 6 h) glass ampoules (Wheaton®). During sampling, seawater was allowed to flow directly from the Niskin stopcock without the stopcock touching the tubes, to reduce the chance of contamination. All ampoules were rinsed three times with the respective sample water before filling to appropriate volumes, poisoned by addition of $HgCl_2$ (10 mg l^{-1} final concentration) and immediately after filling the ampoules were flame-sealed and stored in the dark.

2.2. HTCO analysis

The Shimadzu instrument used in this study was the commercially available Model TOC-5000 Total Carbon Analyzer with quartz combustion column in the vertical position filled with 1.2% Pt on silica pillows with approximate diameter of 2 mm (Cauwet, 1994). The furnace temperature was maintained at 680°C and the effluents passed through a mercury trap (gold wire) to remove mercury (Ogawa and Ogura, 1992). A magnesium perchlorate water trap has been added to the system located before the halogen scrubber, and an in-line membrane filter and the nondispersive infrared CO_2 detector. Prior to analysis, subsamples were acidified with 10 μl of 85% H_3PO_4 to a pH ~ 2 and sparged for 10 min with CO_2-free pure air to remove inorganic carbon as CO_2. TOC contamination from the preservation reagent and from the phosphoric acid was below the detection limit. During the sparging procedure, we followed the recommendations of J.H. Sharp (University of Delaware), i.e., care was taken such that during sparging of each sample, seawater did not overflow from the ampoules. This condition was possible at a gas flow rate of 40 ml min^{-1}. One hundred μl injections were repeated three to four times for each sample, the analytical precision of the procedure being within 3%, on average. Some variability in values from two different vials gives rise to a lower overall precision (14%). Prior to analyses of standards and samples, the catalyst bed was 'conditioned' by injecting 100 μl of acidified and sparged water from a high-quality water purifier, a Millipore Milli-Q Plus® System (hereafter, DW), until the lowest stable integrated area was obtained. To bring the blank down, the catalyst was pretreated by washing in 1% HCl and gently rinsed with DW, and dried in a furnace at a temperature of about 450°C for 10–15 min. This protocol is different from that used previously, as, for example, heating the catalyst to 500°C for 6 h in a muffle (Skoog et al., 1997).

2.3. Calibration of the instrument

Standardisation was carried out every day using potassium hydrogen phthalate (Kanto Chemical) dissolved in DW (3 concentrations) prepared just before sample analyses. The instrument response factor, measured as the slope of the standard addition to DW ($r^2 > 0.999$ for 19 runs), remained relatively constant and reproducible over the time of analysis. Calibration curves have exhibited little difference in the slope (ave. slope: 6045 ± 242 area/μM C, $n = 19$) and intersect (ave. intersect: 800 ± 164 area

Table 1
Position and depth of the stations, date and time of sampling during the cruise 232 of the RRV Discovery in the Strait of Gibraltar area (4–22 April 1998)

N stations	Station locations	Depth (m)	Sampling date, April 1998	Time of sampling
W1 (13405)	5°56′ W, 35°48′ N	128	17	16 h 17 min
W2 (13406)	5°57′ W, 35°49′ N	208	14	17 h 19 min
W3 (13412)	5°58′ W, 35°51′ N	356	18	12 h 03 min
W4 (13411)	5°59′ W, 35°52′ N	424	18	10 h 06 min
W5 (13410)	5°59′ W, 35°54′ N	126	18	09 h 04 min
W6 (13407)	6°00′ W, 35°55′ N	207	17	19 h 19 min
W7 (13408)	6°01′ W, 35°56′ N	274	17	20 h 27 min
W8 (13403)	6°01′ W, 35°57′ N	202	16	22 h 49 min
W9 (13402)	5°58′ W, 35°59′ N	172	16	21 h 20 min
W10 (13401)	5°55′ W, 36°05′ N	115	16	20 h 11 min
W11 (13400)	5°53′ W, 36°04′ N	82	16	19 h 05 min
13386	5°32′ W, 35°58′ N	668	13	14 h 45 min
13399	5°33′ W, 35°59′ N	557	15	01 h 00 min
E1 (13397)	5°16′ W, 35°51′ N	128	13	22 h 16 min
E2 (13396)	5°12′ W, 35°51′ N	437	13	20 h 55 min
E3 (13395)	5°09′ W, 35°52′ N	432	13	19 h 28 min
E4 (13394)	5°05′ W, 35°54′ N	457	13	17 h 59 min
E5 (13393)	5°07′ W, 35°58′ N	521	13	16 h 21 min
E6 (13392)	5°09′ W, 36°01′ N	562	13	14 h 38 min
E7 (13391)	5°10′ W, 36°04′ N	828	13	12 h 42 min
E8 (13390)	5°11′ W, 36°06′ N	797	14	10 h 46 min
E9 (13383)	5°14′ W, 36°07′ N	650	12	12 h 28 min
E10 (13382)	5°16′ W, 36°09′ N	357	12	10 h 30 min
E11 (13381)	5°18′ W, 36°10′ N	158	12	09 h 10 min

Number of the stations in the brackets correspond to numeration of the stations in the list of the RRV Discovery.

units, $n = 19$). The bias between slopes was approximately within 4%.

The accuracy and the system blank of our instrument were determined by analysis of the Deep Atlantic Water (DAW) reference and low carbon water (LCW) from ampoules provided by J.H. Sharp. The average dissolved organic carbon (DOC) concentration in the DAW reference and in the LCW were 45 ± 1 μM C, $n = 19$ and 3 ± 1 μM C, $n = 3$, respectively. Generally, there was no significant difference in peak areas between DW samples and the LCW standards. Individual DW blanks were rechecked after every two to four sea sample injections and were found to be about of 685 ± 198 area units, $n = 153$. Statistical analysis (ANOVA) showed no difference in the peak areas between DW blanks and LCW standards (Student's t-test was 0.13, $p < 0.05$, critical value of t at $p = 0.05$ was 4.3). TOC concentrations in sea samples were calculated on the basis of the DW blank by averaging all replicate injections of samples, subtracting the average DW value as the total blank and dividing by the slope of the standardisation curve. Our results in the most recent DOC method intercalibration, conducted by Sharp (1994); Sharp et al. (1995), were in agreement with other analysts (J.H. Sharp, personal communication). Therefore, we have confidence that TOC concentrations presented in this report have been determined within an acceptable error of 3 ± 1 μM C.

3. Results and discussion

3.1. Hydrography

A classical model of water masses exchange through the Strait suggests that two water masses flow through the Strait: Surface Atlantic Water (SAW), which spreads to the Mediterranean Sea, and

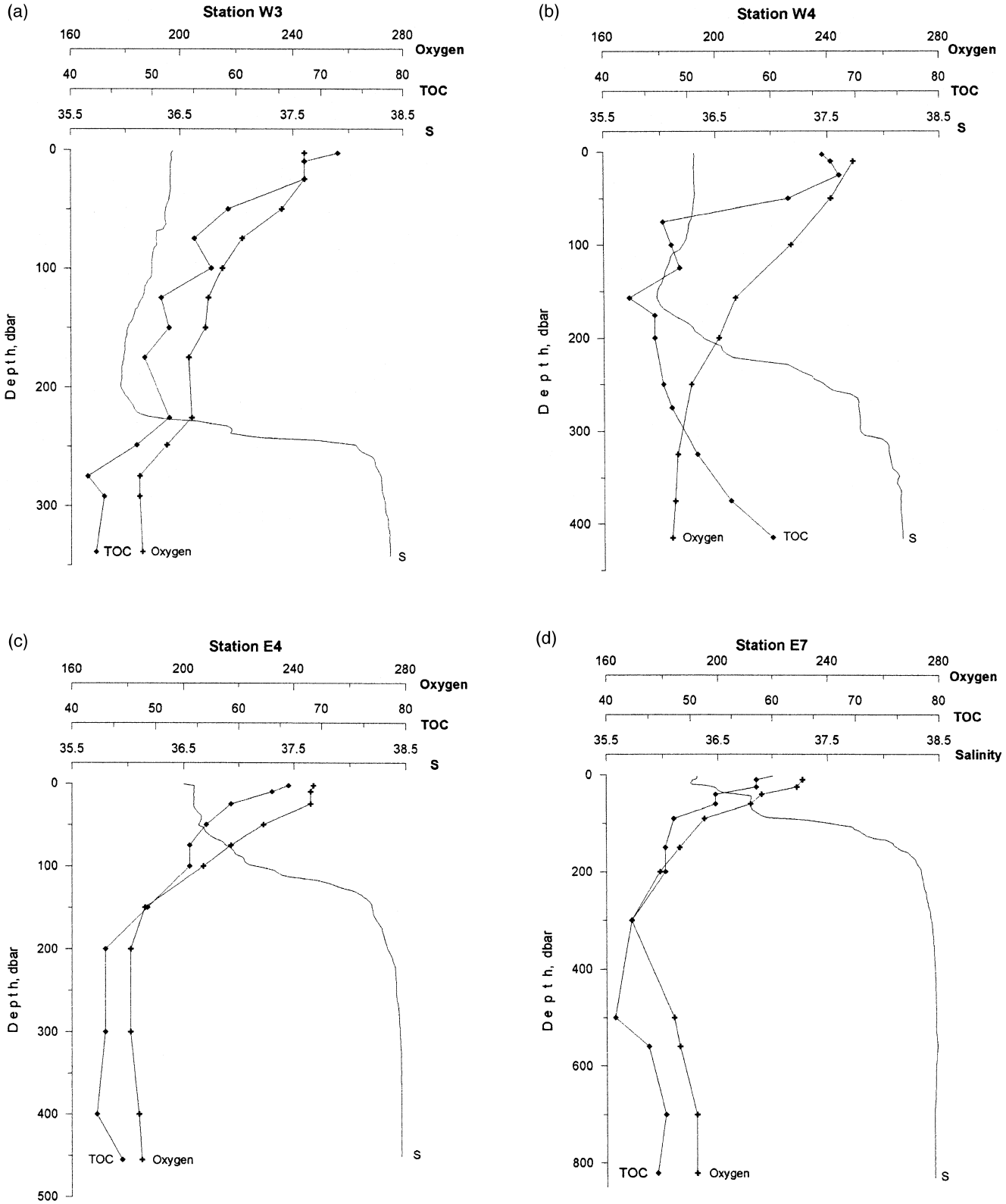

Fig. 2. Typical four vertical profiles of salinity, oxygen (μM kg^{-1}) and TOC (μM C) from the western (Sts. W3, W4) and eastern (Sts. E4, E7) sides of the Strait of Gibraltar. Minimum salinity from the western entrance of the Strait correspond to NACW. Minimum oxygen at Stn. E7 is characterised the residual core of LIW.

Mediterranean Water, which outflows from the Mediterranean Sea. Inflow slightly exceeds outflow to balance the net loss from the excess of evaporation in the Mediterranean Sea over the sum of precipitation and river discharges. The interaction of these water masses produces an extremely strong halocline (Fig. 2), which allows identification of a third, a transition or interface layer in between (Wesson and Gregg, 1994; Bray et al., 1995). Tables 2 and 3 give some characteristics of the water masses found within the Strait in April of 1998, and Fig. 3 depicts distributions of salinity along both sections.

The Atlantic inflow in the Gulf of Cádiz is formed by the mixing of the SAW (salinity about of 36.46), North Atlantic Central Water (NACW, salinity less than 36.06), and Spanish Coastal Water with salinity

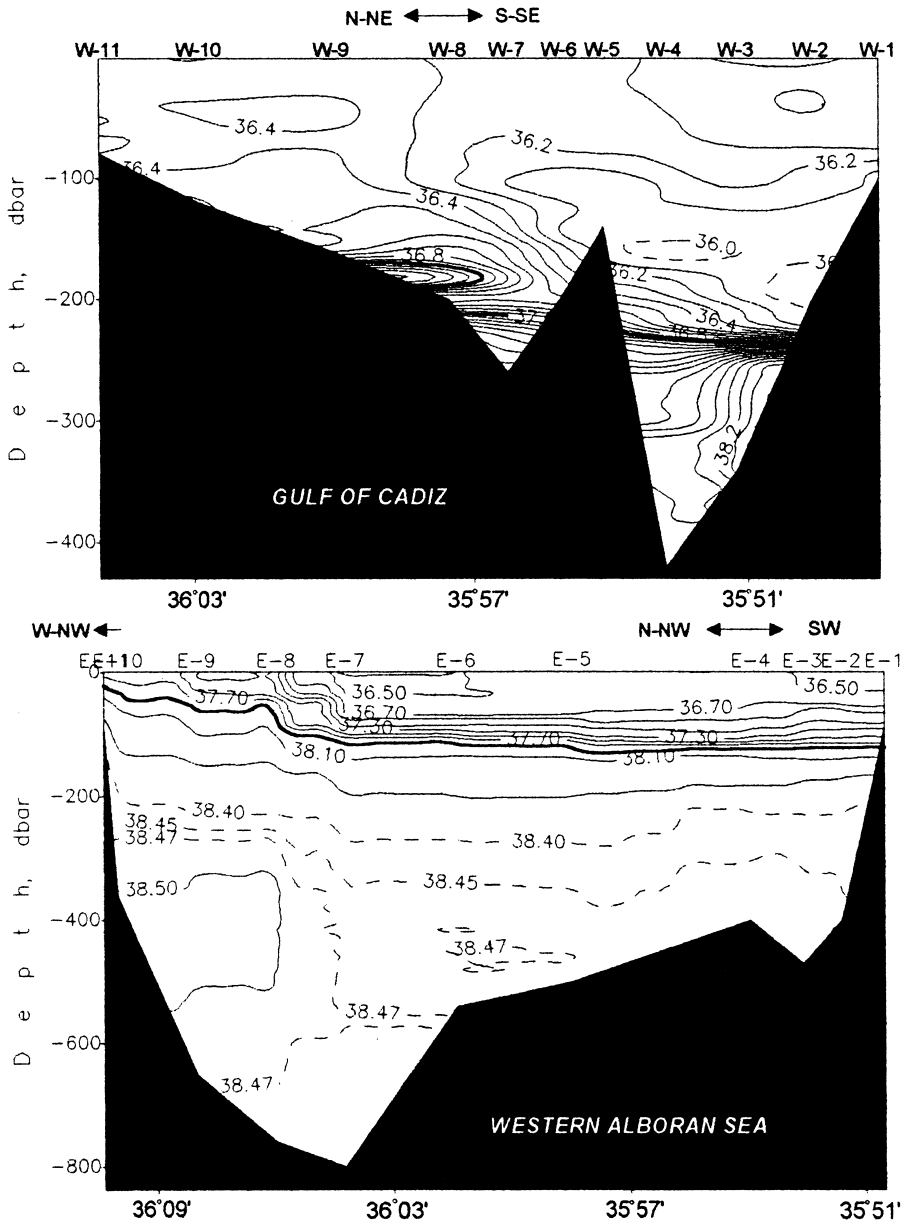

Fig. 3. Distribution of salinity on western (Gulf of Cádiz) and eastern (Western Alboran Sea) entrances of the Strait of Gibraltar. Hereafter, the bottom represents the depth observed at each station and is not typical bathymetric profiles.

Table 2
Characteristics of the different water bodies observed above the Spartel sill in April 1998

N stations	Surface Atlantic water			North Atlantic central water			Interface layer			Mediterranean deep water		
	Depth, m	Salinity	TOC, μM average	Depth, m	Salinity	TOC, μM average	Depth, m	Salinity	TOC, μM average	Depth, m	Salinity	TOC, μM average
W1	0–101	36.38–36.06	60									
W2	0–113	36.38–36.12	63	113–197	36.06–35.93	54						
W3	0–226	36.42–36.37	61	143–215	36.06–35.96	51	226–249	36.37–38.05	50	249–343	38.05–38.37	49
W4	0–207	36.31–36.21	60	125–171	36.06–35.97	46	207–313	36.52–38.02	47	313–419	38.02–38.15	55
W5	0–91	36.30–36.18	59	93–115	36.06–35.98	50						
W6	0–149	36.26–36.12	58	105–111	36.06–36.05	48						
W7	0–173	36.24–36.50	61				173–271	36.50–37.99	48			
W8	0–121	36.27–36.51	63				121–189	36.51–37.60				
W9	0–137	36.40–36.50	62				137–167	36.50–36.85	53			
W10	0–107	36.28–36.44	65									
W11	0–177	36.35–36.45	63									

Position of the interface layer was determined by the range of salinity between 36.50 and 38.00; modified NACW by salinity lower than 36.06. Stn. W8 was sampled only down to 51 m depth. Note that all stations were sampled during different tides.

< 36.10 (Van Geen and Boyle, 1989; Van Geen et al., 1988, 1991). The thickness of SAW in the Strait is highly variable and in April 1998 it decreased from about 100 m south of the Spartel sill (Table 2) to about 40–55 m at the Tarifa Narrows and to about 15–40 m in the Western Alboran Sea (Table 3).

The interface layer is defined by a well-developed halocline with a change in salinity of about 2.00 (Fig. 2). For identification of the interface layer, Lacombe and Richez (1982) have suggested a range of salinity values between 37.00 and 37.50. Bryden et al. (1989) have characterised this layer in the southern part of the Camarinal sill by a salinity range of 36.50–38.00. The interface layer was found to be deeper, thicker, fresher and colder on the west of the Strait (Table 2). The shallowest position of this layer was found in the Western Alboran Sea, where it continued to get saltier and warmer (Table 3).

The Mediterranean outflow is marked by a high salinity and temperature, and is formed by the mixing of Levantine Intermediate Water (LIW) and Western Mediterranean Deep Water (WMDW). The LIW originates in the Eastern Mediterranean and is characterised by an intermediate maximum in temperature (about 13.15°C) and salinity (about 38.47) (Parrilla and Kinder, 1987). The residual LIW is found preferentially in the northwestern part of the Alboran Sea in a depth band of 200–600 m and is essentially absent near the African coast. As shown in Fig. 3 and Table 3, we observed the salinity values close to those listed above in April 1998 at the eastern section at Stn. E6 to E10, and at the Tarifa Narrows. WMDW is characterised by a decrease in salinity and temperature (38.42–38.44 and < 12.90°C). WMDW is formed by the winter convection in the south of France (Medoc Group, 1970; Stommel, 1972). The salinity distribution in Fig. 3 demonstrates that in the Western Alboran Sea, values of salinity in the near-bottom layer were always higher than those observed for WMDW. Diluted WMDW (salinity of about 38.45) was only found at the southern most stations E5 to E2. A similar situation, which indicates a small contribution of WMDW to the outflow, has been described previously by Roether and Weiss (1975), Measures and Edmond (1988) and Minas et al. (1991).

The water exchange through the Strait is under the influence of periodic forces, such as tides (La Violette and Lacombe, 1988), and nonperiodic forces, such as atmospheric pressure (Stanton, 1983), wind

Table 3
Characteristics of the different water bodies observed at the Tarifa Narrows (Stn. 13386 and 13399), and at the Western Alboran Sea in April 1998

N stations	Surface Atlantic water			Interface layer			Mediterranean deep water		
	Depth, m	Salinity	TOC, μM average	Depth, m	Salinity	TOC, μM average average	Depth, m	Salinity	TOC, μM average
13386	0–55	36.29–36.51	54	55–110	36.51–37.98	46	110–549	37.98–38.47	39
13399	0–41	36.34–36.54	61	41–100	36.54–38.00	48	100–611	38.00–38.48	41
E1	0–63	36.51–36.80	64	63–85	36.80–37.01	60			
E2	0–29	36.35–36.51	63	29–127	36.51–38.01	59	127–435	38.01–38.45	47
E3	0–45	36.51–36.60	60	45–133	36.60–38.02	56	133–459	38.02–38.46	44
E4	0–31	36.50–36.60	63	31–129	36.60–38.01	55	129–451	38.01–38.46	45
E5	0–45	36.59–36.61	61	45–135	36.61–38.02	54	135–519	38.02–38.47	45
E6	0–67	36.46–36.54	54	67–113	36.54–38.01	50	113–557	38.01–38.47	41
E7	0–33	36.28–36.51	59	33–135	36.51–38.02	51	135–831	38.02–38.45	45
E8	0–17	36.96–37.10	66	17–77	37.10–38.01	52	77–789	38.01–38.46	42
E9	0–15	37.59–37.60	58	15–85	37.60–38.00	53	85–675	38.00–38.48	44
E10	0–37	37.54–38.00	65	37–135	38.00–38.40	50	135–353	38.40–38.48	46
E11	0–37	37.84–38.10	55	37–71	38.10–38.33	47	71–111	38.33–38.40	46

Positions of the basis of SAW and the interface layer were determined by the phenomenological criteria (vertical distribution of salinity) individually for each station. Note that all stations were sampled during different tides.

stress over the west Mediterranean Sea and the Gulf of Cádiz (Gründlich, 1981), formation of the WMDW during the winter convection, and features of the Alboran Gyre circulation (Bryden and Stommel, 1982). As a result, the water flow in the Strait does not move in the form of continuous currents but as tidal-induced pulses, which vary in the amount of water they contain according to the daily and monthly variation in the above-mentioned factors.

3.2. TOC vertical distribution

All data from the Strait of Gibraltar are presented along two sections in Fig. 4: western (Gulf of Cádiz) and eastern (Western Alboran Sea). Both these sections have been characterised by similar features of TOC distribution: (i) a decrease of TOC content from the Gulf of Cádiz towards the Alboran Sea; (ii) an increase of TOC concentrations in the Atlantic

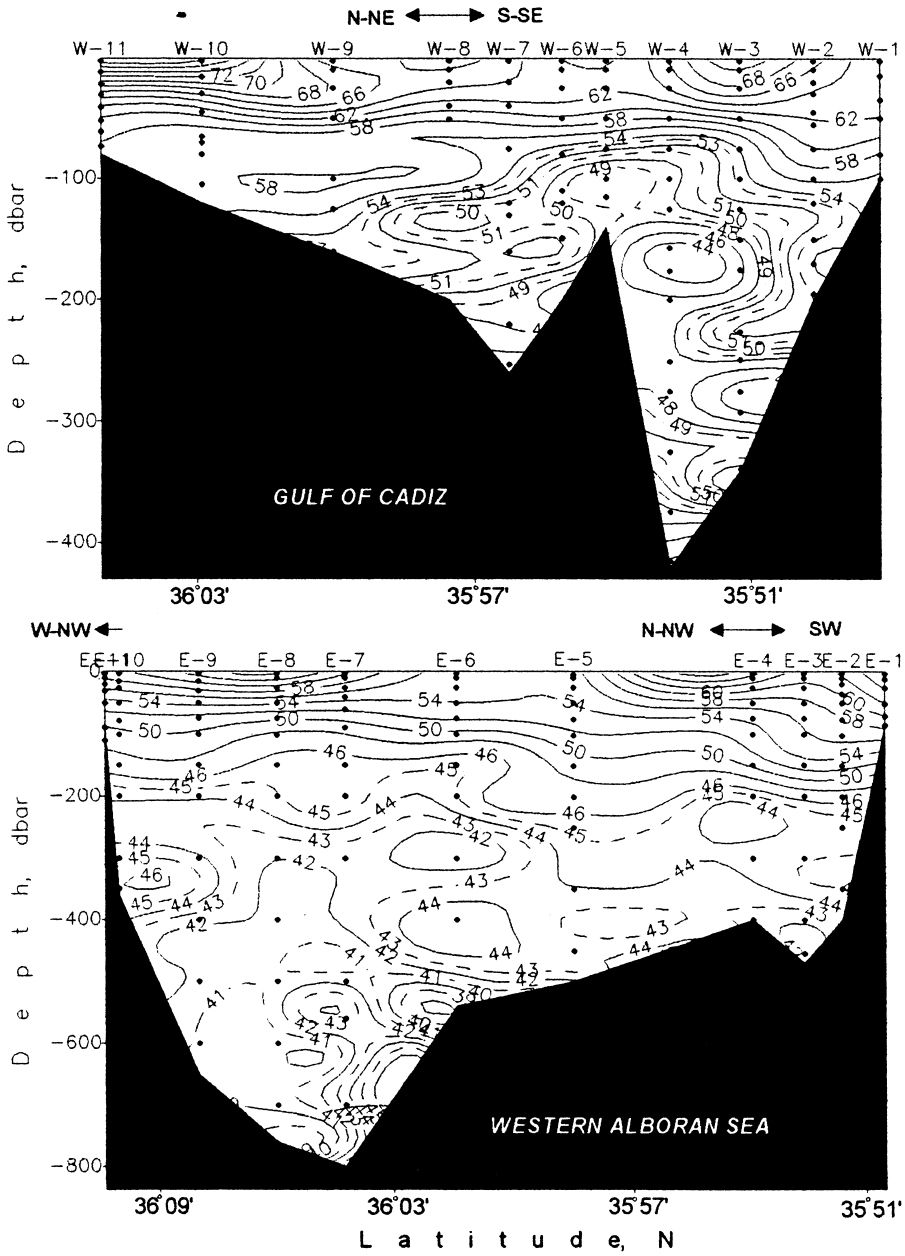

Fig. 4. TOC contour plots (μM C) along western (Gulf of Cádiz) and eastern (Western Alboran Sea) entrances of the Strait of Gibraltar.

inflow from the middle of the sections towards the continents; (iii) a decrease of TOC concentrations from the Atlantic inflow to the Mediterranean outflow, and (iv) a patchiness of TOC inventory (μM C) below the Atlantic inflow. This patchiness was due either to sampling during different times of the tide, particularly in the Gulf of Cádiz, or to different composition of the water layers from both sides of the Strait. In the Western Alboran Sea, water column was composed only by SAW, Mediterranean waters and the interface layer in between. Figs. 2 and 3, and Table 2 show that at several stations above the Spartel sill (Stn. W2–W6) additionally modified NACW was observed.

We summarize all measurements in one vertical profile (Fig. 5), which shows a large scatter of TOC concentrations in the upper 200 m (50–79 μM C) including SAW, NACW, interface layer and upper Mediterranean waters, and a decrease down to 38–48 μM C in deep waters. At several depths, the scatter is due to joining (into one profile) near-bottom measurements from the Gulf of Cádiz and pelagic observations from the same depth from the Western Alboran Sea. Some of the stations from both sides of the Strait (W4, W5, W11 and E2, E3, E4, E5, E7, E10) were characterised by an increase of TOC concentrations in the near-bottom layer (Stn. W4 and E4 in Fig. 4), which could be a result of bottom sediment resuspension.

3.3. TOC sources in the Atlantic inflow

The increase of TOC concentrations from the middle of the sections towards Spain and Morocco

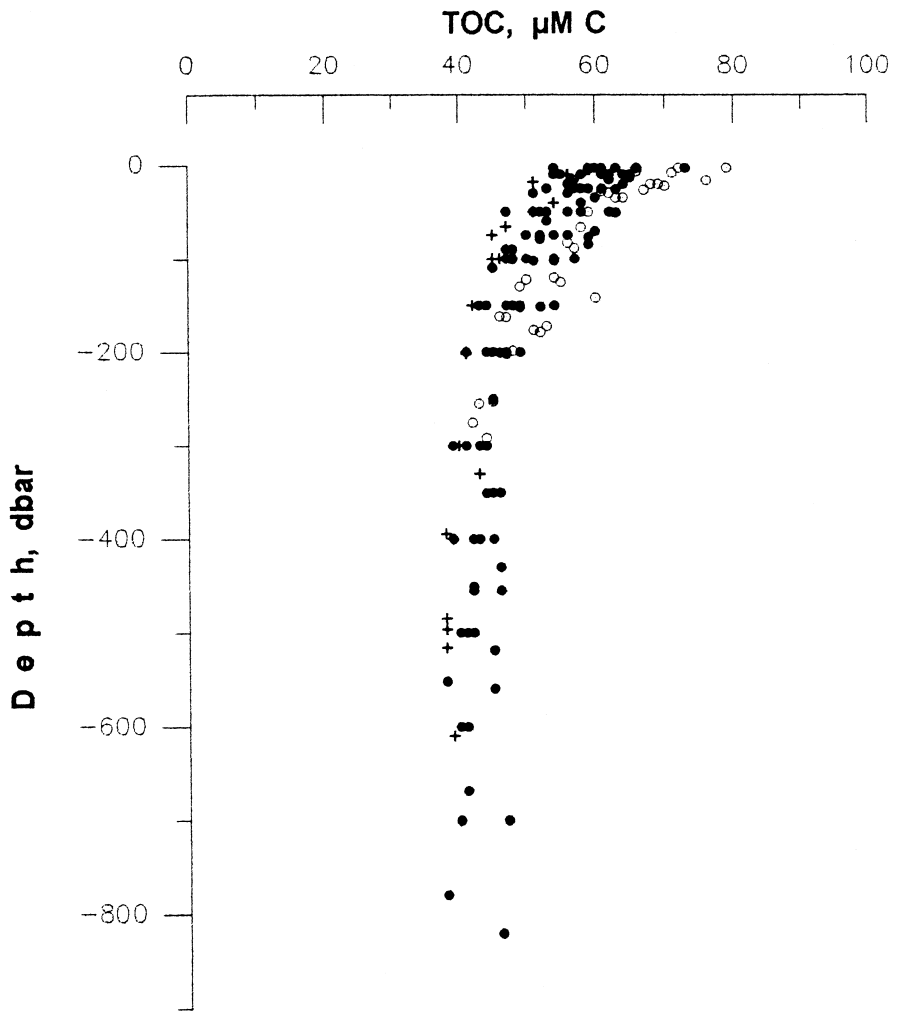

Fig. 5. Integrated TOC profile from Tarifa Narrows (+), western (○) and eastern (●) entrances of the Strait of Gibraltar.

indicate an accumulation of organic carbon along continents. Having only oxygen and fluorescence (in Volts) data, we can only hypothesize that the sources of TOC accumulation are either production of organic carbon in situ, or Atlantic inflow already enriched in organic carbon during its flow to the Strait.

In situ production can be induced by upwelling since such phenomenon, already reported between Gibraltar and the Bay of Malaga (including northeastern part of the strait), may affect the northwestern Alboran Sea (Cano, 1978; Gil and Gomiz, 1994; Rodríguez et al., 1998). Minas et al. (1991) used diagram analysis for study of water exchange through the Strait and demonstrated that in the upwelling area along the Spanish coast, nutrients are largely transported to the photic layer. They concluded that this process is responsible for bioproductivity increase along the Spanish coast and for formation of the Alboran oxygen minimum. As seen from distribution of salinity in Fig. 3, this upwelling is found in the northern part of the eastern section between stations E11 and E8. At these stations, we did not observe oxygen oversaturation (Fig. 6), but we found increased TOC concentrations up to 73 μM C. This suggests that higher TOC concentrations in proximity of Gibraltar (Stn. E11–E8) were due to organic material accumulation very likely produced in the northeastern part of the strait rather than local phytoplankton production. Fig. 6 shows also a slight oxygen oversaturation of the surface layer along the

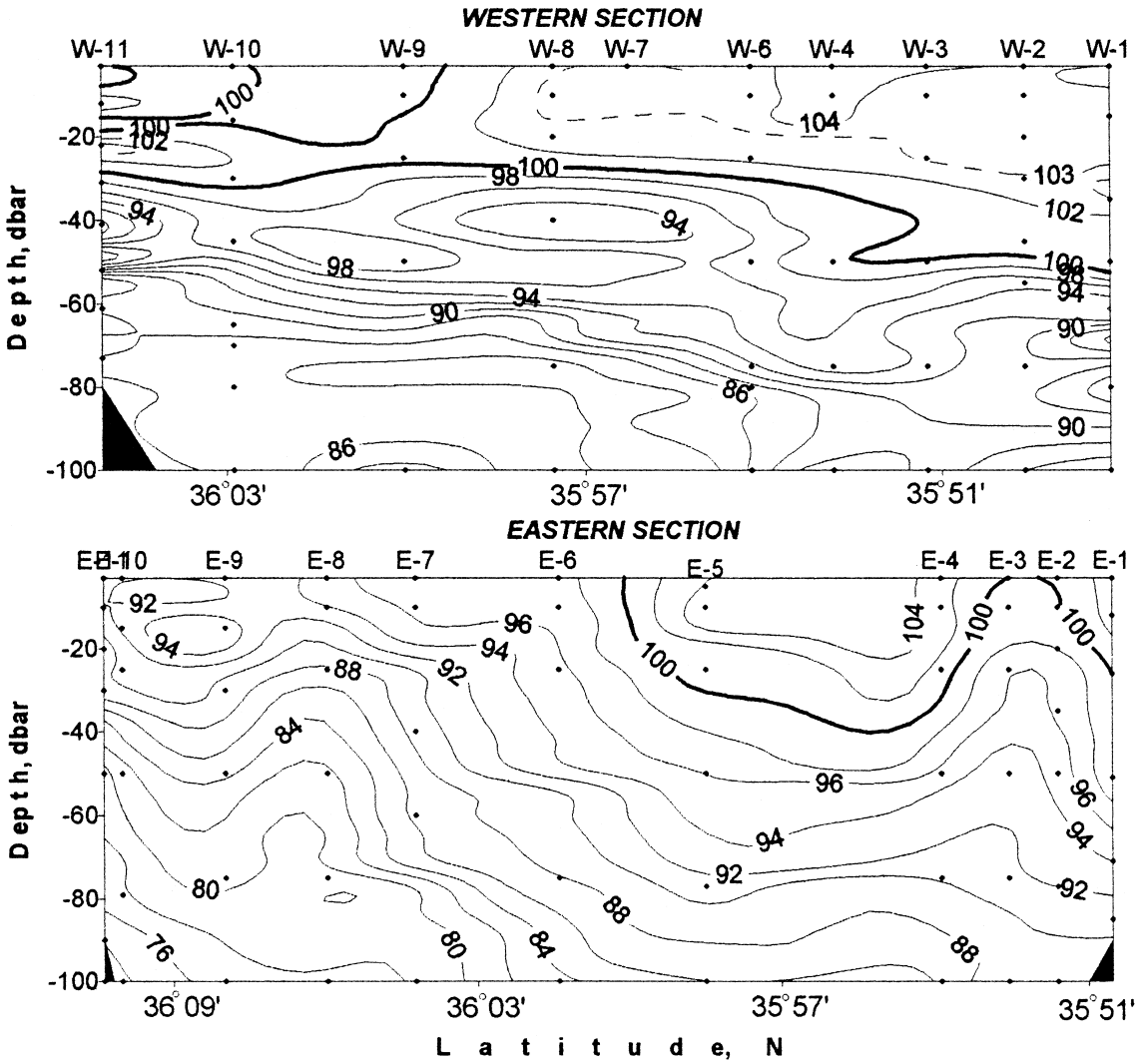

Fig. 6. Oxygen saturation (%) in the upper 100 m layer. Note that the area between Stn. E8–E10 was characterised by upwelling.

western section (up to 4%) and in the southern part of the eastern section (Stn. E1–E5, up to 5%). As indicated by Fig. 4, these areas are also characterised by high TOC concentrations that allow us to hypothesize on production of organic carbon by phytoplankton.

However, Atlantic inflow may also explain some high TOC concentrations observed in the Strait. In their paper on trace metal studies in the Atlantic inflow, Van Geen et al. (1988) have shown that high trace-metal concentrations in the surface water of the Alboran Sea may be due to enriched Atlantic waters flowing into the Mediterranean Sea through the Gulf of Cádiz. Our recent results indicate high DOC concentrations (up to 89 μM C) in the Gulf of Cádiz even during the winter season (Dafner et al., 1999). This high DOC concentration level might be due to resuspension of fresh bottom fluff settled during the last productive cycle or terrestrial input. In this case, the hypothesis of TOC enrichment in the Gulf of Cádiz due to TOC-rich Atlantic waters cannot be precluded.

3.4. TOC pool in the Mediterranean outflow

The origin of the Mediterranean outflow is an unresolved question among physical oceanographers. There is the evidence that at the time of our observations, LIW contributed to the outflow (Section 3.1) although at the southern stations (E2–E5) we have observed diluted WMDW with salinity values of about 38.45–38.46. According to extensive hydrological observations from the literature, the outflow seems to fluctuate between waters rich in LIW and waters rich in WMDW. One permanent characteristic of LIW is an oxygen minimum (Fig. 4, Stn. E7), which is located mainly in the northern sector of Alboran anticyclonic gyre and related to increased productivity in the Atlantic inflow (Packard et al., 1988; Minas et al., 1991). The upwelling in the northwestern part of the Alboran Sea and the resulting plankton growth prove that a potential source of organic matter, which is required to sustain an enhanced oxygen utilisation rate.

The lowest TOC concentrations observed in the Western Alboran Sea suggest that the refractory pool of organic carbon in the LIW is likely to range from 38 to 42 μM C. This estimate is slightly lower than the 44–52 μM C that was recently presented for this water in the Catalan-Balearic Sea (Doval et al., 1999) and the Alboran Sea (Sempéré et al., unpublished observation). The renewal time-scale of water masses, which form the Mediterranean outflow ranges from 7–10 (Andrie and Merlivat, 1988; Christensen et al., 1990) to 100 years (Lacombe et al., 1981; Gascard and Richez, 1985) for the WMDW, and from 10 to 20 years for the LIW (Stratford and Williams, 1997). Although LIW is younger than deep oceanic waters, the TOC values reported here are close to those measured for the very old deep ocean waters (Hansell and Carlson, 1998). These findings argue for the participation of bacteria turnover of the organic material inside the LIW on its pathway to the Strait of Gibraltar from the Catalan-Balearic Sea. More recently, Packard et al. (1988) have emphasised that metabolic activity, bacterial biomass, and particulate organic material should be higher in the LIW of the Western Alboran Sea than farther to the east, and especially higher than in the LIW of the Balearic Sea.

High TOC concentrations within the Mediterranean outflow (ca. 60 μM C) were found in the Gulf of Cádiz. Figs. 2 and 4 and show that at Stn. W4, TOC concentrations increased from 51 μM C at the depth of 325 m to 60 μM C in the near-bottom layer (415 m). Armi and Farmer (1989) have observed that the Tangier basin acts as a reservoir of the Mediterranean waters that fills and drains on each tidal cycle. Acoustic Doppler Current Profiler data from our cruise have shown that different layers of the Mediterranean waters in this basin could flow to the west as well as to the east, depending on the tide (A. Benabdeljelil, personal communication, 1998). This feature suggests that before overflowing through the Spartel sill, the Mediterranean outflow could delay for some time within the Tangier basin. As a working hypothesis, we assume that enrichment of the Mediterranean outflow by organic carbon in this basin occurs either via resuspension of bottom sediments or via input of particulate organic carbon from SAW and its deeper resuspension. To check this hypothesis, additional research in the Tangier basin is required.

3.5. TOC vs. salinity relationship

The analysis presented in Section 3.2 does not take explicit account of tidal variability in exchange

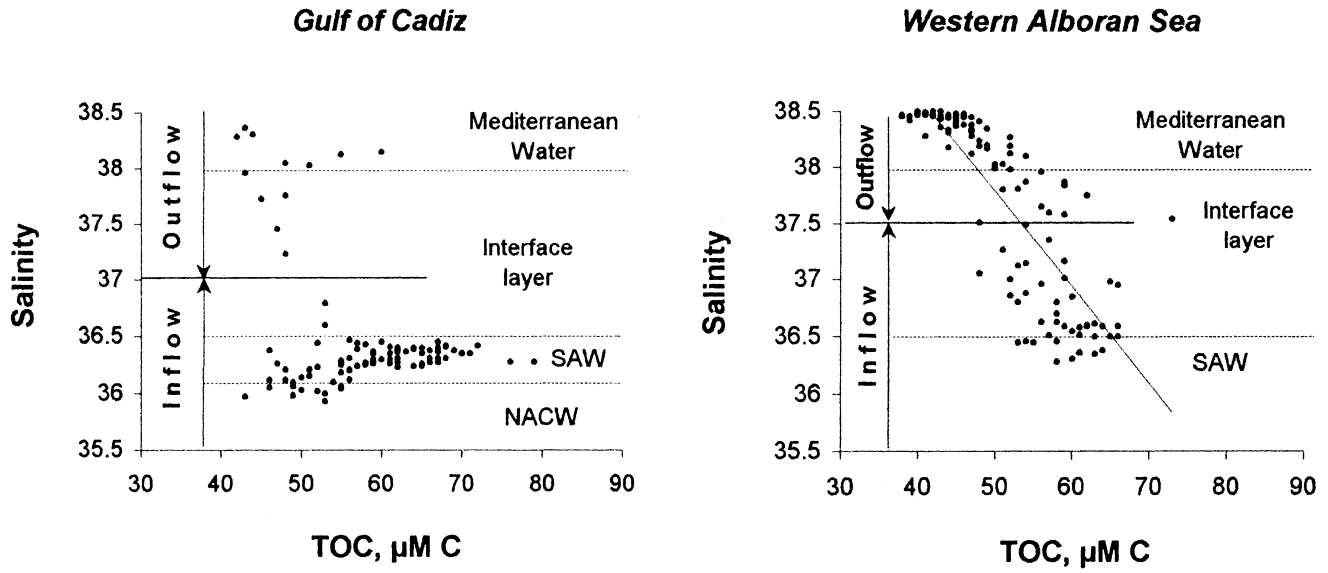

Fig. 7. Scatter plot of TOC concentrations vs. salinity. In the Gulf of Cádiz and at Tarifa Narrows, strong Atlantic inflow is marked by salinity lower than 36.50, Mediterranean outflow is traced by salinity greater than 38.00 and intermediate salinities depict interface between two layers for which substantial periods of both inflow and outflow. The 37.00 isohaline approximated an average position of the interface layer above the Spartel sill, after (Bryden et al., 1989). In the Western Alboran Sea, the average location of interface layer is shown by the isohaline 37.50. The equation of the regression line in the Western Alboran Sea is $y = -0.085x + 42.04$ ($r^2 = 0.69$, $n = 120$).

through the Strait. Most of the outflow occurs in bursts during the semidiurnal tide cycle: when the outflowing tide is strongest, the interface is relatively shallow, so there is a thick layer of the Mediter-

Table 4
Comparison of the slopes of DOC vs. AOU relationship by historical data

Slope	Location	Reference
−0.77	Marine organic matter	Redfield et al. (1963)
−0.80	NW Pacific	Sugimura and Suzuki (1988)
−1.00	Surface	Druffel et al. (1989)
−0.21	Deep Water, N Pacific	
−0.062	NW Indian Ocean	Kumar et al. (1990)
−0.24	Sargasso Sea	Bauer et al. (1990)
−1.58	Surface	Tanoue (1992)
−1.08		
−0.017	Deep water, N Pacific	
−0.047		
−0.21	N Atlantic Ocean	Kepkay and Wells (1992)
−0.25		
−0.56	N Atlantic	Peltzer et al. (unpublished), cited by Kepkay and Wells (1992)
−0.43	N Atlantic Ocean	De Baar et al. (1993)
−0.14	Equatorial Atlantic Ocean	Thomas et al. (1995)
−0.09		
−0.074	Surface	Peltzer and Hayward (1996)
0.04	Deep water, Equatorial Pacific	
−0.084	Indian sector of the Southern Ocean	Wiebinga and De Baar (1998)
−0.26	Pacific sector of the Southern Ocean	Doval and Hansell (2000)
−0.23	Central Indian Ocean	
−0.25	The Strait of Gibraltar	This study

ranean waters flowing swiftly over the Camarinal sill. Conversely, on the inflowing tide, the interface is relatively deep, so there is a thick layer of Atlantic water flowing swiftly into the Mediterranean. Such bursts account for more than half of the exchange across the sill between the Atlantic and Mediterranean basins (Bryden et al., 1989; Bray et al., 1995).

To remove discrepancies caused by the tide fluctuations, a relationship between TOC and salinity was developed. Fig. 7 shows several features of this TOC vs. salinity relationship. Firstly, in the Atlantic inflow and Mediterranean outflow, the salinity values were higher in the Western Alboran Sea than in the Gulf of Cádiz. Secondly, a larger scatter of TOC and salinity values was found in the Gulf of Cádiz than in the Western Alboran Sea. According to Bryden et al. (1989), east of the Camarinal sill salinities lower than 36.50 indicate a strong inflow. This layer is characterised by the largest scatter of TOC concentrations (48–79 μM C). Note that modified NACW was found between SAW and the interface layer or within SAW (Fig. 2, Table 2). This water mass is usually observed only above the Spartel sill and is not involved in water mass exchange through the Strait of Gibraltar, but NACW influences the properties of underlying and overlaying waters due to entrainment (Price et al., 1993). TOC concen-

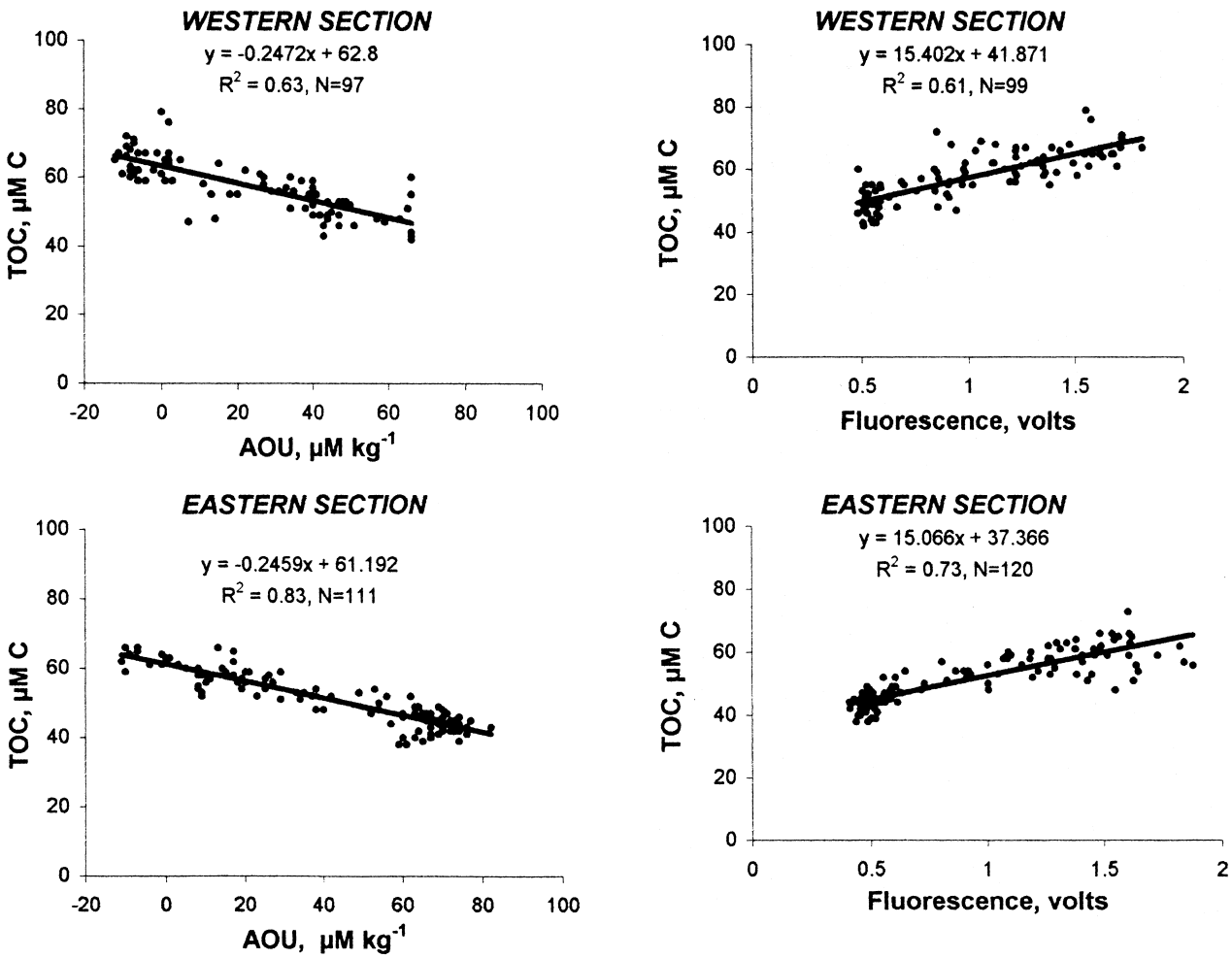

Fig. 8. Composite of TOC vs. AOU, TOC vs. fluorescence, and AOU vs. fluorescence for the western and eastern entrances of the Strait of Gibraltar.

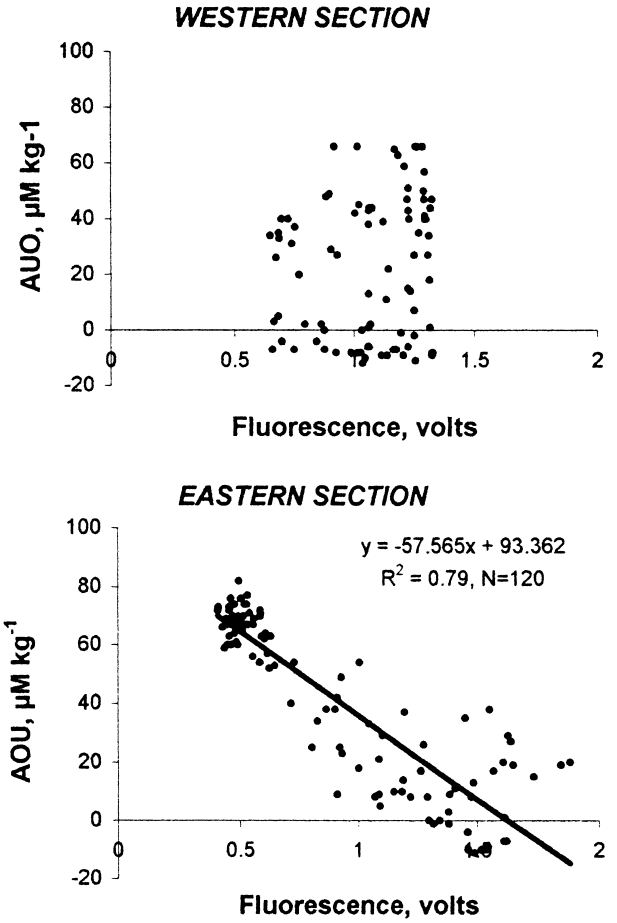

Fig. 8 (*continued*).

trations in modified NACW ranged from 43 to 55 µM C. In the Western Alboran Sea side, where the Atlantic inflow gets saltier (> 36.50) and thicker (down to 15–40 m, Table 3), we observed a lower scatter of both parameters (Fig. 7); consequently, the TOC pool correlates with salinity ($r^2 = 0.69$, $n = 120$).

For the Mediterranean waters with salinities greater than 38.00, there is strong outflow. Indeed, the lowest TOC content was found there (42–60 µM C from the Atlantic Ocean and 38–52 µM C from the Mediterranean Sea sides). For intermediate salinities, there are substantial periods of both inflow and outflow. This transition zone shows a coincidence of intermediate values of salinity as well as TOC. An average inflow is marked by a salinity lower than 37.00 along the western section and about 37.50 along the eastern section. The transition between inflow and outflow occurs, on average, at a salinity of 37.00 and 37.50, respectively (Fig. 7).

3.6. Relationships of TOC vs. AOU, TOC vs. fluorescence and AOU vs. fluorescence

Recent studies have shown an inverse relation between DOC and apparent oxygen utilisation (AOU, Table 4), since both DOC and oxygen are used by bacteria, which in turn produce CO_2 through respiration. In contrast, Martin and Fitzwater (1992) and Hansell et al. (1993) have reported weak or insignificant correlation between DOC and AOU. Our observations, pooling Atlantic inflow and Mediterranean outflow together, show the former correlation. Fig. 8 shows plots of TOC vs. AOU, AOU vs. fluorescence (in Volts), and TOC vs. fluorescence from the eastern and western entrances of the Strait. The slopes and intersects of lines drawn through the data points of TOC vs. AOU (Fig. 8) and TOC vs. fluorescence (Fig. 8) at both sections are quite similar and the differences in correlation, presumably, are due to the different number of observations.

In the Western Alboran Sea, TOC exhibits a positive linear correlation with fluorescence (Fig. 8; $r = 0.73$, $n = 120$) and increased fluorescence values in the SAW are inversely related to AOU (Fig. 8; $r = 0.79$, $n = 120$). In the Gulf of Cádiz, the relationship of AOU vs. fluorescence, by contrast, exhibits a great scatter (Fig. 8), but the TOC vs. fluorescence relationship is still significant (Fig. 8). A simple comparison between AOU and fluorescence from both sections (Fig. 8) suggests that variability of fluorescence values in the Gulf of Cádiz was lower than in the Eastern Alboran Sea. Large fluorescence scatter from the eastern entrance of the Strait is due primarily to deeper sampling (down to 800 m to the east and down to 340 m to the west of the Strait) that explains the scatter of low fluorescence values (~ 0.5 V). Secondly, in the Eastern Alboran Sea, higher photosynthetic activities could explain the scatter of high fluorescence values (> 1.5 V). SAW is almost always easily discernible in the Gulf of Cádiz and in the Alboran Sea in satellite images of chlorophyll a distribution (Minas and Minas, 1993a,b; Antoine et al., 1995).

Historical data on the DOC vs. AOU relationship, summarised in Table 4, suggest a large variability of

the slope in different areas of the ocean. One of the problems comparing the historical data in Table 4 is that prior to Peltzer and Hayward (1996) all authors used a model I regression causing a negative bias in their slopes in addition to the natural variability. Since then, most authors have used the geometric mean regression (a model II regression). Thus, some of the scatter in the numbers shown in Table 4 is due to the different statistical treatment and we cannot make corrections without the original data.

The major difficulty in interpretation of the relationship of TOC vs. AOU arises from an estimate of the preformed TOC concentrations, while the preformed AOU is at equilibrium with the atmosphere (Toggweiler, 1989, 1992). Tanoue (1992) have shown that a single linear regression analysis throughout the entire water column was inappropriate for estimations of the contribution of DOC to the utilisation of oxygen in the water column. In general, correlation was found when subsurface and intermediate levels are considered separately, i.e., variations of both AOU (and probably DOC) were as much due to a mixing as to biogeochemical processes (Thomas et al., 1995).

From both sides of the Strait of Gibraltar, we have obtained similar correlations and slopes throughout the entire water column, which lay approximately in middle of the range presented in Table 4. The inverse relationship from the Strait of Gibraltar was linear and the slope of -0.25 was lower than the -0.77 reported by Redfield et al. (1963) for organic matter of average marine composition. From only the vertical profile of both property distributions, it is impossible to conclude if these correlations are due to DOC consumption by bacteria or mixing. To evaluate the contribution of TOC to AOU, an analysis of both these properties along isopycnal surfaces is needed (Doval and Hansell, 2000), which we could not perform in this work due to a poor spatial resolution of sampling and a large variability of the dynamical environments. Theoretically, the slope, which we found in the Strait of Gibraltar area, suggests that bacterial remineralization of organic matter accounts for approximately one-third of the oxygen deficit in surface and deep waters. This value is higher than that reported by Ogawa and Ogura (1992) for the Northwestern Pacific, by Peltzer and Hayward (1996) for the equatorial Pacific and by Wiebinga and De Baar (1998) for the Indian sector of the Southern Ocean.

3.7. Organic carbon exchange through the Strait of Gibraltar

Because of the great variability of the dynamic environment, it is difficult to assign from direct observations mean values of typical water transports for a TOC balance computation. Lacombe and Richez (1982) have pointed out that with the complex spatial and temporal variations of the flow, only approximate values of transport are available. Bryden and Kinder (1988), reviewing historical balance estimations, have concluded that the flows through the Strait are apparently limited 1 to 2×10^6 m^3 s^{-1}. The new transports through the Strait of Gibraltar are 30% smaller than historical estimates and, furthermore, tidal oscillations contribute nearly half of the total transport (Bryden and Kinder, 1991). Consequently, for a TOC pool budget calculation, we cannot use general schemes of organic carbon estimation as designed for the open ocean (e.g., Walsh et al., 1992; Peltzer and Hayward, 1996).

Here, we present a TOC budget, which was calculated according to the water transport estimates based on the data of Gibraltar experiment (Bryden et al., 1994; Bray et al., 1995) and CANIGO observations summarised in Fig. 9. The estimate of the TOC transport was made by simply dividing the interface layer according to the salinity values (37.00 and 37.50 from western and eastern entrances of the Strait, respectively) and incorporating the upper part of the interface into the upper layer (Atlantic inflow) and the lower part into the lower layer (Mediterranean outflow). TOC transport in the Atlantic inflow and Mediterranean outflow was calculated as the product of the water transport and the average TOC concentration in each water layer along western and eastern sections and at Tarifa Narrows.

Fig. 9 shows that TOC transport through the Strait varies from 3.7×10^4 to 4.8×10^4 mol C s^{-1} for the Atlantic inflow and from 2.8×10^4 to 3.8×10^4 mol C s^{-1} for the Mediterranean outflow. Differences of TOC transport between Atlantic inflow and Mediterranean outflow give an estimate of TOC balance over the water column, which are in the range of 0.9×10^4 to 1.0×10^4 mol C s^{-1} (or

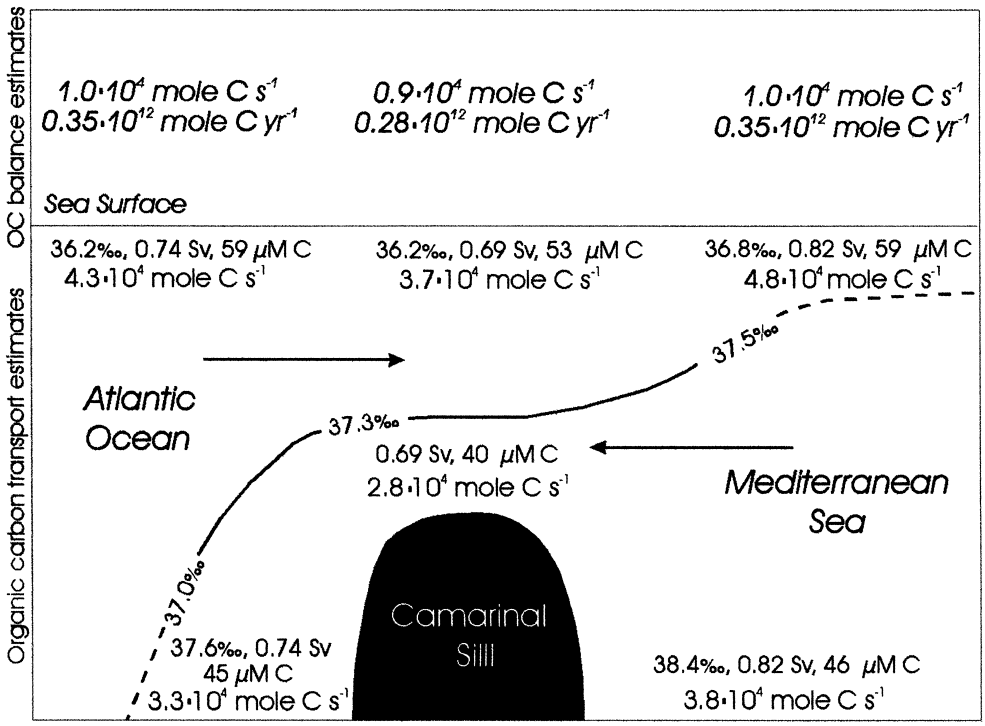

Fig. 9. Two layers model of water masses exchange through the Strait of Gibraltar with average values of salinity, mass transports in the Atlantic inflow and Mediterranean outflow based on the data of the Gibraltar experiment (Bryden et al., 1994; Bray et al., 1995) and CANIGO observations. These values of mass transport and average TOC concentration in each water layer were used for calculations of TOC transports (lower panel) and balances (upper panel) along the Strait.

0.28×10^{12} to 0.35×10^{12} mol C year^{-1}, respectively). The TOC balance is a function of water transport and TOC concentration. For example, from both entrances of the Strait, similar average TOC concentrations in the Atlantic inflow as well as in the Mediterranean outflow (59 and 45–46 μM C, respectively) were observed, but different estimates of water transport were used (Fig. 9). By contrast, at Tarifa Narrows, the water transports in Atlantic inflow and Mediterranean outflow were similar (0.7 Sv) but concentrations of TOC were different (53 and 40 μM C, respectively) and, consequently, different balance estimates were obtained.

Several authors have evaluated the budget of dissolved organic nitrogen and phosphorus through the Strait (Béthoux and Copin-Montégut, 1986; Coste et al., 1988); they have found that inflow of these organic compounds exceeded their outflow from the Mediterranean Sea. Our data together with results quoted above indicate that inflow of organic material to the Mediterranean Sea through the Strait of Gibraltar is considerably higher than outflow. We think that this feature is mostly due to the high biological productivity of the Gulf of Cádiz, where we observed high DOC concentrations (89 μM C) even in the winter season (Dafner et al., 1999).

An indirect estimate of the organic carbon budget through the Strait of Gibraltar was also recently evaluated by Copin-Montégut (1993). She presented a value as high as 1.25×10^{12} mol C year^{-1}, that is, threefold to fourfold higher than our estimates. Polat and Tugrul (1996) have obtained a value of 1.79×10^4 tons C year^{-1} (or 0.15×10^{10} mol C year^{-1}) for organic carbon export from the Marmara to the Aegean Sea and about of 0.41×10^4 tons C year^{-1} (0.34×10^9 mol C year^{-1}) for the outflow from the Aegean Sea to the Marmara Sea. River TOC inputs have been estimated to $20–83 \times 10^{10}$ mol C year^{1} (Sempéré et al., 1999 and references therein). These data indicate that TOC inflow through the Strait of Gibraltar is two orders of magnitude higher than through the Turkish Straits and than Mediterranean River inputs. The Mediterranean outflow through the Strait of Gibraltar is also higher by three orders of

magnitude than through the Turkish Straits. It is likely that these budgets are reflections of the productivity of the seas adjoining to the straits — the mesotrophic Alboran Sea to the east from the Strait of Gibraltar, and the oligotrophic Aegean Sea to the west from the Turkish Straits.

4. Conclusions

TOC concentrations found in the surface layer of the Strait of Gibraltar area are in agreement with those previously reported for the Atlantic Ocean and Mediterranean Sea (ca. 60–70 μM C). Our estimates of the TOC pool in the deep waters of the Western Alboran Sea (38–52 μM C) differ slightly from those published recently for the Mediterranean Sea, suggesting on a participation of bacteria on turnover of the organic material inside the LIW on its way to the Strait of Gibraltar. The correlation between TOC and salinity was found in the Western Alboran Sea ($r = 0.69$, $n = 120$) where the water column was characterised by a thicker layer of SAW and by a thinner layer of the Mediterranean waters. In the Gulf of Cádiz, the water column was under the influence of the short-term variability caused by tides, SAW was thicker, Mediterranean waters was thinner and an additional water body was found (modified NACW). Accordingly, this relationship was characterised by a large bias. The correlations between TOC and AOU, and TOC and fluorescence over the entire water column are observed. These correlations are due to the decrease of both properties with depth rather than biological processes.

For calculation of the TOC transport, the two-layer model of water mass exchange through that Strait was used. Estimates of the TOC budget ranged from 0.28×10^{12} to 0.35×10^{12} mol C year^{-1}. Our computations of the TOC budget suggest that TOC inflow is two-and outflow is three orders of magnitude higher through the Strait of Gibraltar then via the Turkish Straits. The amount of TOC transporting throughout the Strait of Gibraltar show that the TOC flux by Atlantic inflow and the Mediterranean outflow cannot be ignored in the modelling of carbon cycle in the Mediterranean Sea and the eastern North Atlantic Ocean.

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