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Total organic and inorganic carbon exchange through the Strait of Gibraltar in September 1997

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Abstract

The total organic carbon (TOC) and total inorganic carbon (C_T) exchange between the Atlantic Ocean and the Mediterranean Sea was studied in the Strait of Gibraltar in September 1997. Samples were taken at eight stations from western and eastern entrances of the Strait and at the middle of the Strait (Tarifa Narrows). TOC was analyzed by a high-temperature catalytic oxidation method, and C_T was calculated from alkalinity–pH_T pairs and appropriate thermodynamic relationships. The results are used in a two-layer model of water mass exchange through the Strait, which includes the Atlantic inflow, the Mediterranean outflow and the interface layer in between. Our observations show a decrease of TOC and an increase of C_T concentrations from the surface to the bottom: 71–132 μM C and 2068–2150 $\mu mol\,kg^{-1}$ in the Surface Atlantic Water, 74–95 μM C and 2119–2148 $\mu mol\,kg^{-1}$ in the North Atlantic Central Water, 63–116 μM C and 2123–2312 $\mu mol\,kg^{-1}$ in the interface layer, and 61–78 μM C and 2307–2325 $\mu mol\,kg^{-1}$ in the Mediterranean waters. However, within the Mediterranean outflow, we found that the concentrations of carbon were higher at the western side of the Strait (75–78 μM C, 2068–2318 $\mu mol\,kg^{-1}$) than at the eastern side (61–69 μM C, 2082–2324 $\mu mol\,kg^{-1}$). This difference is due to the mixing between the Atlantic inflow and the Mediterranean outflow on the west of the Strait, which results in a flux of organic carbon from the inflow to the outflow and an opposite flux of inorganic carbon. We estimate that the TOC input from the Atlantic Ocean to the Mediterranean Sea through the Strait of Gibraltar varies from $(0.97 \pm 0.8)10^4$ to $(1.81 \pm 0.90)10^4$ mol C s^{-1} (0.3×10^{12} to 0.56×10^{12} mol C yr^{-1}), while outflow of inorganic carbon ranges from $(12.5 \pm 0.4)10^4$ to $(15.6 \pm 0.4)10^4$ mol C s^{-1} ($3.99–4.90 \times 10^{12}$ mol C yr^{-1}). The high variability of carbon exchange within the Strait is due to the variability of vertical mixing between inflow and outflow along the Strait. The prevalence of organic carbon inflow and inorganic carbon outflow shows the

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Mediterranean Sea to be a basin of active remineralization of organic material.

Keywords: Water exchange; Chemical oceanography; Carbon

1. Introduction

The average annual increase of CO_2 in the atmosphere has been estimated to be about 1.4 ppm yr^{-1}, with a year-to-year fluctuation about the mean of about $\pm$ 0.6 ppm yr^{-1} (Gammon et al., 1985; Conway et al., 1994). It has long been recognized that the oceans are the most intense sink of carbon dioxide in the global carbon cycle, absorbing about half of the carbon of anthropogenic origin released to the atmosphere (Siegenthaler and Sarmiento, 1993). The carbon dioxide sink in the ocean is dominated by the North Atlantic, despite its small area in comparison with the North Pacific (Watson et al., 1995). To improve the determination of regional or global carbon fluxes (and uncertainties), it is clear that more carbon observations are needed.

Estimates of the meridional total carbon dioxide flux have been presented for the whole North Atlantic (Martel and Wunsch, 1993) and for different parts of this ocean: the subtropical North Atlantic (Brewer et al., 1989), the tropical Atlantic (Broecker and Peng, 1992; Keeling and Peng, 1995), and the temperate North Atlantic Ocean (Tans et al., 1990). Meridional fluxes of dissolved organic matter in the North Atlantic have been calculated by Walsh et al. (1992). Recently total inorganic carbon (C_T) and dissolved organic carbon (DOC) transports have been evaluated by Stoll et al. (1996a, b) for the northern North Atlantic Ocean. These authors have pointed out that the meridional transport of DOC cannot be ignored in the total carbon flux.

One step toward better interpretation of the role of the North Atlantic in the global carbon cycle is to estimate the organic and inorganic carbon exchanges between different marine basins. The Strait of Gibraltar is of special interest in this regard, because it is a single connection between the Atlantic and the Mediterranean Sea, and a comparatively well-studied region from a physical point of view. Despite this, there exists only one indirect estimate of organic and inorganic carbon exchange through this Strait (Copin-Montégut, 1993).

In response to increased interest in global carbon change and greenhouse warming, measurements of the marine carbon system (i.e., total organic carbon, titration alkalinity, pH) were completed in the CANIGO project (Canary Islands Azores Gibraltar Observations, MAST III Programme). This program included a synoptic survey of spatial variability within the Strait with an emphasis on seasonal monitoring, primarily designed to examine temporal variability and the mechanisms controlling the carbon exchange between the Atlantic and the Mediterranean basins. In this paper, we describe the results of total organic and inorganic carbon exchange through the Strait of Gibraltar measured in September 1997.

2. Study area

The Strait of Gibraltar is a narrow and shallow connection between the Atlantic Ocean and the Mediterranean Sea (Fig. 1). It is in an east–west orientation about 60 km long with a minimum

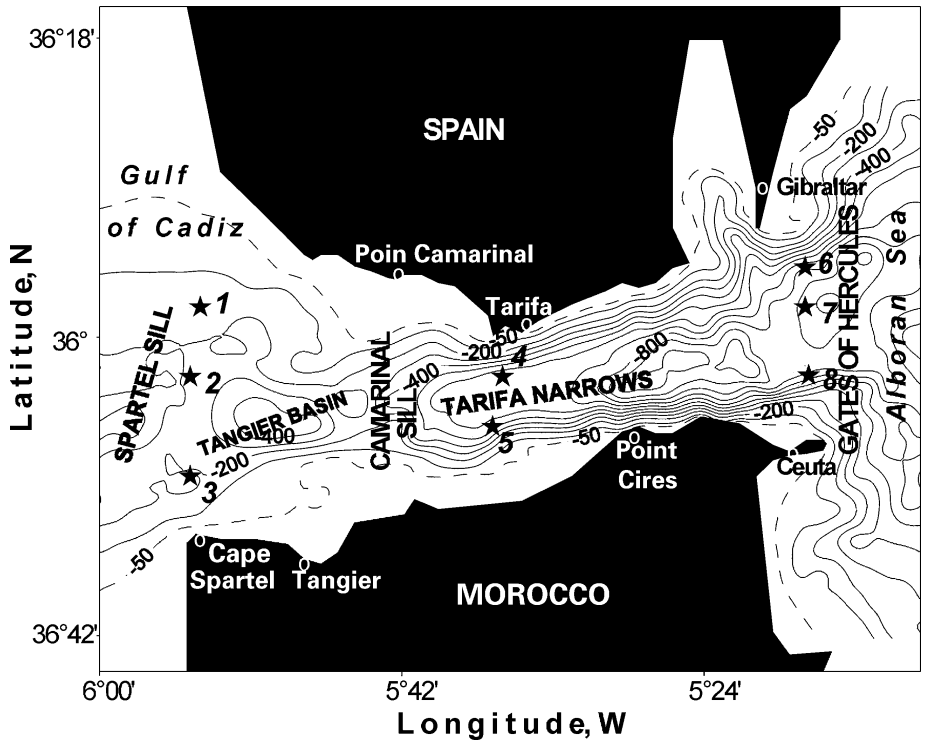

Fig. 1. Bathymetry in the Strait of Gibraltar and station grid during CANIGO 2 cruise of the RV *Thalassa* (2–9 September 1997). To the east of the Strait lies the Alboran Sea, the western-most basin of the Mediterranean Sea. To the west of the Strait lies the Gulf of Cadiz, an embayment in the northeast Atlantic Ocean. After La Violette and Lacombe (1988), the section made up of stations 1–3 is called the Spartel Sill section, between stations 4 and 5 the Tarifa Narrows section, and between Gibraltar and Ceuta the Gates of Hercules section.

width of about 12 km at the Tarifa Narrows and an average depth of about 600 m. Thirteen kilometers west of Tarifa Narrows lies the main bathymetric sill of the Strait, the Camarinal sill, with a maximum depth of about 285 m and an area of about 7.86 km^2 (Guimerans et al., 1988). Another sill (the Spartel sill) is situated 21 km west of the main sill and has a maximum depth of more than 350 m (La Violette and Lacombe, 1988). Between these two sills, is located the Tangier Basin, with a maximum depth of about 640 m.

3. Materials and methods

3.1. Sampling

The seawater samples were taken at eight stations within the Strait of Gibraltar from the RV *Thalassa* with a CTD rosette system equipped with 10 l Niskin bottles between 2 and 9 September 1997 (Fig. 1). The bottles were fired at the depths of maximum or minimum distribution of temperature, salinity, oxygen and fluorescence, within and between different water masses 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.

Table 1
Location and depth of the stations with date and time of sampling during the cruise of the RV *Thalassa*, 2–9 September 1997. Time of sampling corresponds to Greenwich Meridian Time and coincides with the beginning of the CTD cast

St. no.	Stations locations	Depth (m)	Sampling date	Time of sampling
1	5°54′W, 36°02′N	160	2.09.1997	13 h 20 min
2	5°55′W, 35°58′N	278	3.09.1997	9 h 00 min
3	5°55′W, 35°53′N	417	4.09.1997	9 h 06 min
4	5°36′W, 35°58′N	527	5.09.1997	9 h 10 min
5	5°36′W, 35°55′N	550	6.09.1997	10 h 11 min
6	5°18′W, 36°05′N	732	7.09.1997	9 h 35 min
7	5°18′W, 36°02′N	827	8.09.1997	7 h 50 min
8	5°18′W, 35°58′N	575	9.09.1997	9 h 22 min

3.2. Total organic carbon measurements

The 15 ml samples were collected in glass tubes, precombusted prior to the cruise (450°C, at least 6 h) and closed with Teflon® PFA-backed screw caps that had been rinsed with Milli-Q water and dried. 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). During sampling, seawater was allowed to flow directly from the Niskin stopcock without the stopcock touching the tubes to reduce the chance of contamination. Samples were taken in duplicate, poisoned by addition of $HgCl_2$ ($10\,mg\,l^{-1}$ final concentration), stored in the dark and analyzed in the Laboratory of Marine Microbiology, CNRS, Marseille.

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 silica pillows (Cauwet, 1994). A sample volume of 100 µl was used. Subsamples were acidified with 10 µl of 85% H_3PO_4 and sparged for 10 min at a flow rate of $50\,ml\,min^{-1}$ with CO_2-free pure air to purge inorganic carbon. Each sample, standard or blank was injected 3–4 times. The nominal analytical precision of the procedure was within 2%, but some variability in results from two different vials gives rise to an actual precision that is lower (4–6%). The catalyst bed was conditioned by injecting 100 µl of acidified and sparged Milli-Q water until the lowest stable integrated area was obtained. Standardization was carried out every day with potassium hydrogen phthalate diluted in Milli-Q water (three concentrations).

The instrument response factor, measured as the slope of the standard addition to Milli-Q water ($r^2 > 0.999$ for 11 runs), remained relatively constant and reproducible over the time of analysis. In general, calibration curves did not exhibit differences in slope (average slope: $5917 \pm 184, N = 11$), and the bias between slopes was within approximately 3%. The system blank was determined by analyzing low-carbon water (LCW) from ampoules provided by J. Sharp (University of Delaware) and was found to be about 5 µM C (the average DOC concentration in the Deep Pacific Water reference was 42 ± 5 µM C). The total organic carbon (TOC) concentrations in samples were calculated by averaging all replicate sample injections, subtracting the average LCW value as the total blank and dividing by the slope of the standard curve.

Intercalibration exercises in 1995, organized by Dr. J.H. Sharp, indicated that our instrument was suitable for marine DOC studies.

3.3. Total inorganic carbon

Total inorganic carbon (C_T) was computed from experimental values of pH_T and total alkalinity, the carbonic acid dissociation constants of Roy et al. (1993), and the boric acid dissociation constant of Dickson (1990). Several authors have examined the thermodynamic consistency of the measured components of the carbonate system (e.g., Millero et al., 1993; Clayton et al., 1995; Lee et al., 1997; McElligott et al., 1998). From these studies it appears that at present it is not possible to draw a firm conclusion regarding the best set of constants to use. Considering the accuracy of photometric pH ($\pm$ 0.002) and potentiometric total alkalinity ($\pm$ 1 $\mu mol\,kg^{-1}$) determinations (Mintrop et al., 1999), Lee et al. (1997) estimated that the probable errors in C_T determined with the Roy et al. (1993) constants is around 4 $\mu mol\,kg^{-1}$. This is slightly higher than the accuracy of the experimental value ($\pm$ 2 $\mu mol\,kg^{-1}$, Johnson et al., 1993). Recent determinations of pH_T, A_T and C_T in the Azores area have shown internal consistency among these paramenters. C_T measured was only, on average, 0.54 $\mu mol\,kg^{-1}$ higher than C_T calculated, with a standard deviation of $\pm$ 2.6 $\mu mol\,kg^{-1}$, when the Roy et al. (1993) constants were used (Mintrop and González-Dávila, unpublished observations).

The pH on the total scale was measured following the spectrophotometric technique of Clayton and Byrne (1993) using the *m*-cresol purple indicator (DOE, 1994). A system similar to that described by Bellerby et al. (1995) was developed in our lab. The pH measurements were done with a Hewlett Packard Diode Array spectrophotometer in a 25°C-thermostated 1-cm flow-cell by using a Peltier system. Using a stopped-flow protocol, seawater previously thermostated to 25°C was analyzed for blank determinations at 730, 578 and 434 nm. The flow was restarted and the indicator injection valve switched on to inject 10 µl dye through a mixing coil (2 m). Three photometric measurements were carried out for each injection in order to remove any dye effect on the seawater pH measurement.

Total alkalinity of seawater was determined by titration with HCl to the carbonic acid end point using two potentiometric systems (Millero et al., 1993) described previously (Mintrop et al., 1999). In brief, the titration systems consisted of a Titrino 702SM titrator (Metrohm, Herisau, Switzerland) and a Titrino 719S, both interfaced to personal computers. All measurements were made in thermostated plastic cells provided by F. Millero of the Rosenstiel School of Marine and Atmospheric Sciences (RSMAS), Miami, Florida. Both the acid, in a water-jacketed burette, and the seawater sample, in a water-jacketed cell, were maintained at 25°C with a constant temperature bath. The titration was performed by adding HCl to the seawater past the carbonic acid end point. A computer program was used to run the titration, record the volume of the acid added and the EMF readings of the electrodes. The HCl solution (25 l, 0.25 M) was made from concentrated analytical grade HCl (Merck®, Darmstadt, Germany) in 0.45 M NaCl, in order to yield an ionic strength similar to open ocean seawater. The acid was standardized by the titration of weighed amounts of Na_2CO_3 dissolved in 0.7 M NaCl solution resulting in a value of 0.2505 $\pm$ 0.0001 M. The acid concentration was also determined by coulometry at RSMAS (F. Millero). The results of both methods agree within $\pm$ 0.0001. The total alkalinity of seawater was evaluated from the proton balance at the alkalinity equivalence point, $pH_{equiv} = 4.5$, according to the exact definition

of total alkalinity (Dickson, 1981). A FORTRAN computer program (provided by F. Millero) was used to calculate the carbonate parameters (Millero et al., 1993). The precision of the fit (s value) is better than 0.4 $\mu mol\,kg^{-1}$ for the samples analyzed. The performance of the titration systems was monitored by titration of different batches of CRM (#35) that have known C_T and A_T. The agreement of our alkalinity values with the CRM data was within $\pm 1.5\,\mu mol\,kg^{-1}$.

4. Results and discussion

4.1. Hydrography

Over the past decade it has been shown that 'the present dynamical understanding of the exchange through the Strait of Gibraltar is that it is hydraulically controlled so that the physical dimensions of the Strait combined with the overall evaporation over the Mediterranean basin determine how much flow can get through the Strait and how much saltier the Mediterranean is than the Atlantic' (Bryden and Kinder, 1991; Kinder and Bryden, 1992). A classical model of water mass exchange through the Strait of Gibraltar suggests that two water layers interact in the Strait: the Atlantic inflow, which spreads to the Mediterranean Sea, and the Mediterranean outflow, which outflows from the Mediterranean Sea. Inflow slightly exceeds outflow to balance the net loss from the excess of evaporation over the Mediterranean Sea. The interaction of these water bodies within the Strait produces an extremely strong halocline, which allows identification of a third transition or interface layer between them (Wesson and Gregg, 1994; Bray et al., 1995). Table 2 gives some characteristics of the water bodies found within the Strait in September 1997.

The Atlantic inflow forms in the Gulf of Cádiz and is a mixture of Surface Atlantic Water (SAW; salinity of about 36.46), North Atlantic Central Water (NACW, salinity less than 36.00), and Spanish Coastal Water (SCW, salinity of about 36.10 (Van Geen et al., 1988, 1991)). The thickness of the Atlantic inflow is highly variable, and in September 1997 it decreased from about 120 m above the Southern Spartel sill to 40–50 m along the Gates of Hercules section (Table 2).

The interface layer is defined by a sharp halocline with a change in salinity of about 1.50, occurring at a depth between 40 and 230 m (Table 2). Lacombe and Richez (1982) used the salinity values 37.00–37.50, and Bryden et al. (1989) the values 36.50–38.00 to characterize the interface layer between the two flows. Following Bryden et al. (1994) and Bray et al. (1995), we have divided the interface layer at its mid-depth and incorporated the upper part of the interface into the upper layer and the lower part into the lower layer. Salinity values for the mid-depth are 37.00 for the Spartel sill section, 37.32 for the Tarifa Narrows and 37.50 for the Gates of Hercules section. The interface layer was found to be deeper, thicker, fresher and colder on the west of the Strait. As seen from Table 2, along the Spartel sill section, there is evident slope of the interface layer from the north (46 m) to the south (125 m). The shallowest position of this layer was found along the Gates of Hercules section (40–50 m), where it continued to get saltier and warmer.

The high-density Mediterranean outflow is marked by high salinity and temperature. It forms by a mixing of Levantine Intermediate Water (LIW) and Western Mediterranean Deep Water (WMDW). The LIW originates in the eastern Mediterranean and is characterized by intermediate maxima in temperature (about 13.00°C) and salinity (about 38.50) (Kinder and Bryden, 1990). The residual LIW is found preferentially in the northwestern part of the Alboran Sea in a depth band of

Table 2
Some characteristics of water masses in the Strait of Gibraltar, as observed in September 1997. TOC and C_T represent weighted average concentrations. NACW was found only above the Camarinal sill section (stations 1–3)

St. no.	Surface Atlantic Water				North Atlantic Central Water				Interface layer				Mediterranean Waters			
	Depth (m)	S	TOC (μM)	C_T (μmol kg^{-1})	Depth (m)	S	TOC (μM)	C_T (μmol kg^{-1})	Depth (m)	S	TOC (μM)	C_T (μmol kg^{-1})	Depth (m)	S	TOC (μM)	C_T (μmol kg^{-1})
1	0–46	36.08–36.44	95	2085.4	46–63	36.03–36.08	93	2138.0	63–150	36.08–37.23	83	2189.4	—	—	—	2300.2
2	0–67	36.08–36.30	115	2092.7	67–103	35.99–36.08	96	2142.8	103–220	36.08–38.23	75	2227.6	215–257	38.23–38.33	—	2306.4
3	0–125	36.08–36.34	85	2090.6	125–158	36.03–36.08	81	2127.0	158–270	36.08–38.24	75	2233.1	270–399	38.24–38.35	69	2315.9
4	0–108	36.11–36.43	87	2099.5	—	—	—	—	108–218	36.43–38.39	76	2248.7	218–503	38.39–38.48	66	2306.5
5	0–94	36.09–36.26	82	2104.5	—	—	—	—	94–285	36.26–38.37	64	2222.5	285–529	38.37–38.47	64	2316.4
6	0–41	36.40–36.50	87	2089.7	—	—	—	—	41–220	36.50–38.32	74	2266.0	220–718	38.32–38.50	69	2317.9
7	0–44	36.54–36.70	88	2111.7	—	—	—	—	44–230	36.70–38.32	80	2265.2	230-822	38.32–38.49	67	2319.7
8	0–46	36.21–36.35	—	2111.4	—	—	—	—	46–180	36.35–38.33	—	2244.4	180–552	38.33–38.49	64	—

200–600 m and is essentially absent near the African coast. The maximum salinity values (ca. 38.50) were observed at the Tarifa Narrows and along the Gates of Hercules section (Table 2). WMDW is formed by the winter convection south of France (Medoc Group, 1970; Stommel, 1972) and is characterized by decreasing salinity and temperature (38.42–38.44 and $< 12.90^{\circ}C$). The salinity distribution in Fig. 2 demonstrates that at Tarifa Narrows and along the Gates of Hercules, values of salinity in the near-bottom layer were about 38.45, always higher than those defining WMDW. A similar situation, which indicates a small contribution of WMDW to the outflow, has been described previously by a number of other investigators (Roether and Weiss, 1975; Measures and Edmond, 1988; 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 aperiodic forces, such as atmospheric pressure (Stanton, 1983), wind stress over the western Mediterranean Sea and the Gulf of Cádiz (Gründlich, 1981), formation of the WMDW during winter convection, and features of the Alboran Gyre circulation (Bryden and Stommel, 1982). As a result, the water flow in the Strait is not in the form of continuous currents but rather in tidally induced pulses, which vary in the amount of water they contain according to the daily and monthly variation in the above-mentioned factors. Additionally, tide pulses are strongly affected by the bathymetric constriction (the small cross section and the presence of the sills). These short-period pulses are able to trigger very short internal waves and current fronts in the upper layer, which propagate eastward into the Alboran Sea during the flood tide (Boyce, 1975; LaViolette and Lacombe, 1988; Alpers et al., 1996).

4.2. TOC and C_T vertical distributions

Because of the great variability of the dynamic environment, it is difficult to present any maps or vertical sections from direct observations from the Strait of Gibraltar. Moreover, our presentation here is limited to discussion of vertical profiles of TOC and C_T distributions (Fig. 2). For a general impression of spatial variability of both organic and inorganic carbon, the weighted concentrations of TOC and C_T for each water layer were also calculated (Table 2).

The main feature of the TOC vertical distribution in Fig. 2 is the presence of several maxima, located in the SAW (almost at all stations) and in the interface layer (St. 2, 4, 6, 7). The C_T vertical distribution shows an increasing concentration from the surface to the base of the interface layer and homogeneous values within the Mediterranean waters. An additional feature of the C_T vertical distribution is a subsurface maximum located in the NACW (St. 2, 3). Fig. 2 shows that the TOC concentrations in the SAW ranged from 71 μM C (St. 7, 30 m) to 132 μM C (St. 2, 60 m) while C_T ranged from 2068 $\mu mol\,kg^{-1}$ (St. 1, 17 m) to 2150 $\mu mol\,kg^{-1}$ (St. 4, 108 m). Fig. 2 also shows that the upper maximum of TOC was related to the maximum of chlorophyll *a*. Table 2 shows the decrease of TOC and the increase of C_T integrated concentrations within SAW from the Atlantic Ocean side to the Mediterranean.

Signals of the NACW, with salinity values lower than 36.08, were found only above the Spartel sill (St. 1–3) with TOC and C_T concentrations of 74–95 μM C and 2119–2148 $\mu mol\,kg^{-1}$. In the interface layer TOC concentrations ranged from 63 μM C (St. 5, 237 m) to 116 μM C (St. 7, 51 m). For this layer, C_T concentrations varied from 2123 $\mu mol\,kg^{-1}$ (St. 5, 100 m) to 2312 $\mu mol\,kg^{-1}$ (St. 4, 212 m). The lowest TOC and the highest C_T values were observed in the Mediterranean waters (Table 2): 61 μM C (St. 6, 718 m; St. 7, 61 m; St. 8, 201 m) to 78 μM C (St. 6, 100 m) and

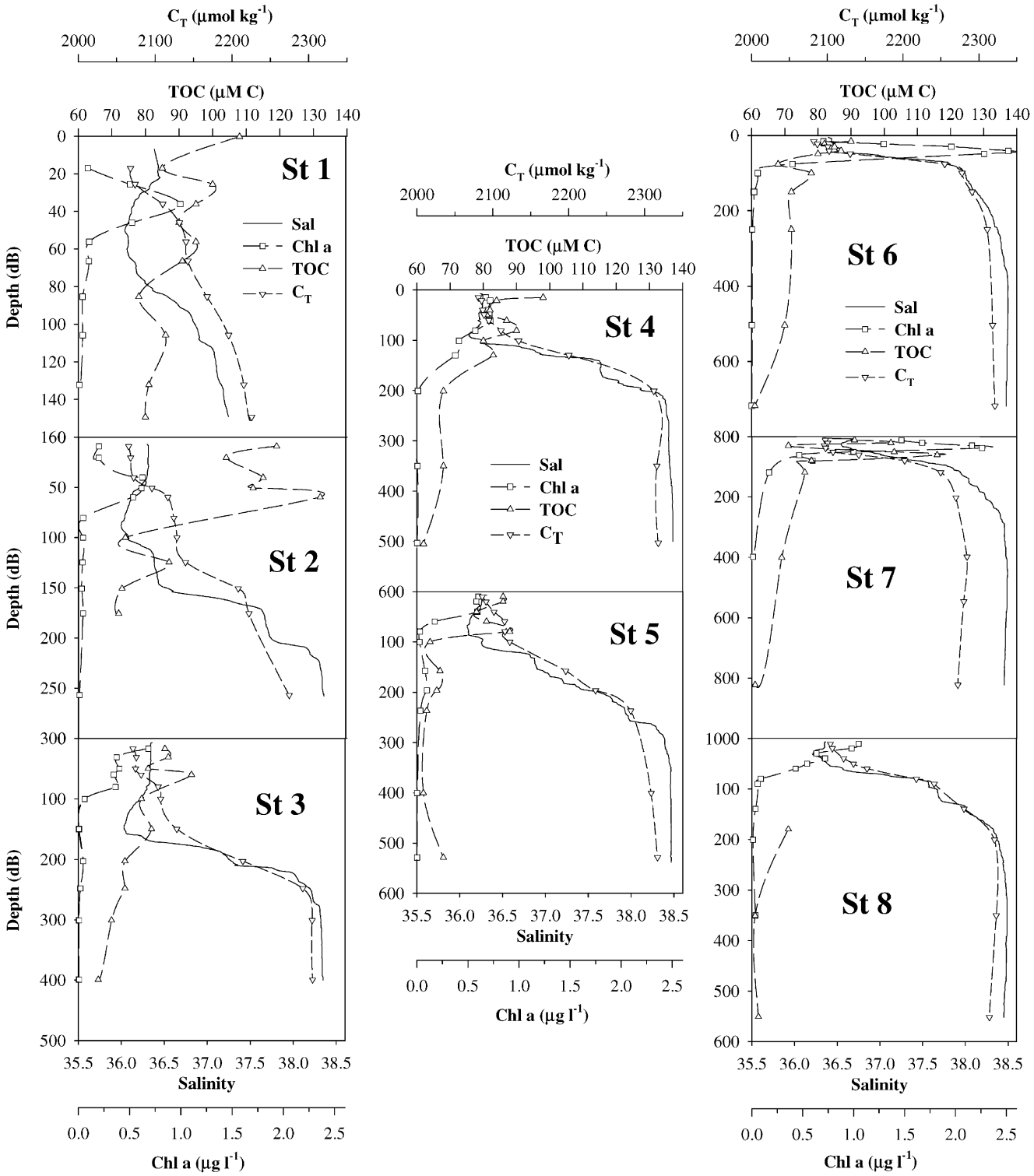

Fig. 2. Vertical distributions of salinity, chlorophyll *a* ($\mu g l^{-1}$), TOC (µM C) and C_T ($\mu mol\,kg^{-1}$) in the different parts of the Strait of Gibraltar. Stations 1–3 were situated above Spartell Sill, stations 4–5 at Tarifa Narrows, and stations 6–7 at Gates of Hercules.

2307 μmol kg^{-1} (St. 3, 301 m) to 2325 μmol kg^{-1} (St. 7, 398 m). However, in these waters, the Atlantic side in general shows higher TOC (75–78 μM C) and lower C_T (2068–2318 μmol kg^{-1}) concentration than the Mediterranean side (65–69 μM C and 2082–2324 μmol kg^{-1}). By contrast, the integrated values show (Table 2) that the difference between TOC concentrations in the Mediterranean waters above the Spartel sill and between Gibraltar and Ceuta is at the limit of TOC determination ($\pm$ 5 μM C).

TOC values measured in September 1997 are similar to those reported by various investigators in the different seas of the Mediterranean basin (Cauwet et al., 1990; Cauwet, 1991; Avril and Copin-Montégut, 1992; Copin-Montégut and Avril, 1993a, b; Cauwet et al., 1997; Yoro et al., 1997) and in the Atlantic Ocean (Carlson et al., 1994; Thomas et al., 1995; Doval et al., 1997). Similar TOC concentrations were also found in the Strait of Gibraltar in June 1997 (Dafner et al., 1999). By contrast, Gasol et al. (1998) and Doval et al. (1999) presented DOC concentrations in deep waters of the Catalan-Balearic Sea as low as 44–52 μM C. In April 1998, lower TOC concentrations (38–52 μM C) were also measured in the LIW in the western Alboran Sea (Dafner et al., 2000b). Comparison of TOC values measured near the Gates of Hercules section in June and September 1997 with observations from April 1998 suggests a seasonal cycle of organic carbon within the LIW, implying significant bacterial turnover of the organic material in this water mass (Packard et al., 1988).

In the Mediterranean Sea, no directly measured C_T values were found in the literature; all of them are based on pH–alkalinity data. The values reported by Pérez et al. (1986), Copin-Montégut (1993) and Frankingnoulle et al. (1990) for LIW in the Mediterranean Sea (2320–2330 μmol kg^{-1}) are similar to those reported here. Directly measured C_T values for the North–East Atlantic Central Water ranged from 2128 to 2135 μmol kg^{-1} (Mintrop and González-Dávila, 1999, unpublished data; Rios et al., 1995), consistent with the values reported here.

4.3. Relationships of TOC and C_T to salinity

The description of vertical distribution of TOC and C_T presented previously does not take explicit account of tidal variability in the exchange through the Strait. Most of the outflow occurs in bursts during the semidiurnal tidal cycle: when the outflowing tide is strongest, the interface is relatively shallow and so there is a thick layer of Mediterranean water flowing swiftly over the Camarinal sill. Conversely, on the inflowing tide, the interface is relatively deep and 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 Camarinal sill between the Atlantic and Mediterranean basins (Bryden et al., 1989; Bray et al., 1995).

To remove discrepancies caused by tidal fluctuations, relationships of TOC and C_T to salinity were developed (Fig. 3). Fig. 3 shows large departures from linearity in both TOC and C_T concentrations in the Atlantic inflow and in the upper interface layer (salinity lower than 37.00), but a linear decrease of TOC and increase of C_T values with salinity higher than 37.00. The departures are due either to biological processes or variability of salinity, which affects C_T content in seawater. Although the correlation between TOC and salinity is weak ($r^2 = 0.56$, $n = 25$), it is still significant. By contrast, a strong correlation is found between C_T and salinity greater than 37.00 ($r^2 = 0.97$, $n = 96$). Fig. 3 also suggests that the relationship between C_T and salinity is more significant when data from the euphotic layer are removed ($r^2 = 0.99$, $n = 131$); a lower C_T content

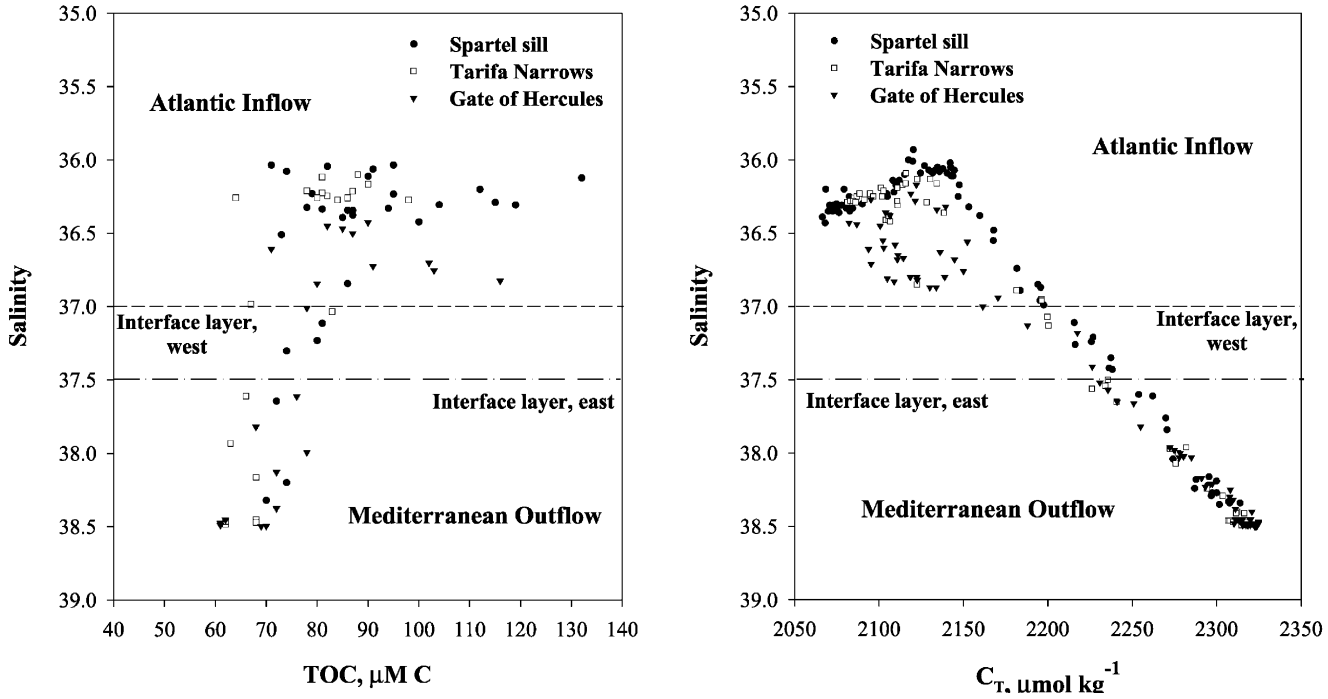

Fig. 3. Scatter plots of TOC and C_T pools vs. salinity. Strong Atlantic inflow is marked by salinity less than 36.50, the Mediterranean outflow by salinity greater than 38.00. Intermediate salinities depict the interface layer between the two layers, a zone where substantial periods of both inflow and outflow are typical. The 37.00 isohaline approximates an average position of the interface layer above the Spartell sill section, 37.32 at the Tarifa Narrows and 37.50 along the Gates of Hercules section.

is found there due to consumption of inorganic carbon by photosynthesis. The regression line is

$$C_T = 2120(\pm 1.5) + 79.24(\pm 0.83)(S - 36.00),$$

which gives C_T values similar to those obtained using only the Mediterranean outflow. No C_T variation is discernible at the computed precision between waters with the same salinity but from different depths. This indicates that biological production does not have any appreciable influence on C_T in this region and that there is only a binary mixing between the Atlantic and Mediterranean waters. Brunet et al. (1984) and Copin-Montégut (1993) have presented for the Alboran Sea similar relationships between C_T and salinity. The C_T values from them are slightly lower than those reported here, but these differences could be due to the systematic differences in the pH measurements (photometric pH vs. NBS potentiometric pH) and the error in the equilibrium constants (Roy et al. (1993) vs. Dickson and Millero (1987).

The specific total inorganic carbon (C_T/S) shows a linear relationship with salinity below 100 m. A similar relationship is found for the equivalent specific total organic carbon (TOC/S) with salinity in the whole profile except for the chlorophyll maximum (Fig. 4). The regression lines between the specific C_T (in μmol kg^{-1}) and specific TOC (in μM C) and salinity

$$C_T/S = 40.39(0.75) + 0.516(0.020)S,$$

$$\mathrm{TOC}/S = 12.46(0.92) - 0.279(0.025)S,$$

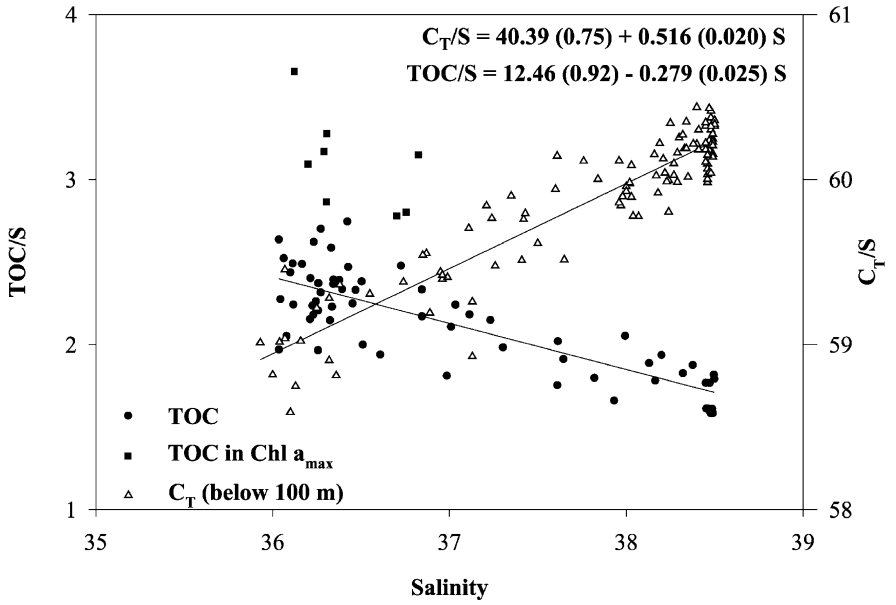

Fig. 4. Scatter plot of specific TOC and C_T vs. salinity. Linear regressions are found for C_T values below 100 m and TOC except for TOC values in the chlorophyll *a* maximum.

do not pass through the origin. The specific C_T of the Mediterranean waters is higher than that of the less saline Atlantic waters. A substantial quantity of inorganic carbon is added to seawater during its residence time in the Mediterranean Sea. This enrichment may be explained by inputs from the rivers, the Black Sea, the atmosphere and the remineralization of organic carbon. The remineralization is clearly shown in the specific TOC vs. salinity plot, where the Mediterranean inflow shows a significant reduction in TOC content with respect to the Atlantic inflow.

According to Bryden et al. (1989), at salinities less than 36.50 there is a strong inflow, which we show is characterized by highest TOC and lowest C_T concentrations (64–132 μM C and 2068–2170 μmol kg^{-1}). For the Mediterranean water salinities greater than 38.00, there is strong outflow, and the lowest TOC and highest C_T contents (75–78 μM C and 2274–2314 μmol kg^{-1} above the Spartel sill, and 65–69 μM C and 2278–2325 μmol kg^{-1} along the Gates of Hercules section) are found in the outflowing waters. For intermediate salinities, there are substantial periods of both inflow and outflow with intermediate values of TOC and C_T.

4.4. TOC and C_T balance through the Strait of Gibraltar

In reviewing different balance estimations, Bryden and Kinder (1988) have concluded that the flows through the Strait are apparently limited, from 1 to 2×10^6 m^3 s^{-1}. Later estimates suggest that 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). Because of the great variability of the dynamic environment, it is difficult to assign, from direct observations, mean values of water transports for TOC and C_T balance calculations.

For our calculations, we use the two-layer model of water mass exchange through the Strait and present TOC and C_T budgets calculated according to the water transport estimates measured

during the Gibraltar experiment (Bryden et al., 1994; Bray et al., 1995). Recent determinations in the framework of the CANIGO project have shown volume transport values for the eastern entrance of the Strait of 0.81 and -0.76 Sv with an accuracy of 0.06 Sv. These estimates are in good agreement with the measurements from Bryden et al. (1994) (0.72 ± 0.16, -0.68 ± 0.15 Sv). For the western entrance, the average outflow is –0.67 Sv and the average inflow 0.78 Sv (Tsimplis and Bryden, 1999). The inflow and outflow are in reasonable balance, with a slightly higher inflow, as expected, to balance the net evaporation over the Mediterranean basin. Table 3 shows volume transport values used in this study for each section. In turn, TOC and C_T transports were estimated by dividing the interface layer according to the salinity values (37.00, 37.32 and 37.50 from west, center and east of the Strait), and incorporating the upper part of the interface into the upper layer (Atlantic inflow) and the lower part into the lower layer (Mediterranean outflow). For budget estimations, integrated values of carbon for outflow and inflow at each station were averaged along longitudinal sections. Table 3 also shows the calculated average values of salinity, TOC and C_T for these layers, taken for the carbon fluxes estimates. Multiplying the average TOC and C_T concentrations by water transport of the upper and lower layers yields TOC and C_T transports. Summarizing all carbon transports along longitudinal sections gives the carbon balance. Results of these calculations are presented in Fig. 5.

The dominant feature of carbon exchange through the Strait of Gibraltar is organic carbon inflow to the Mediterranean Sea and inorganic carbon outflow from the Mediterranean Sea. We estimate that the TOC transport from the Atlantic to the Mediterranean Sea varies from $(0.97 \pm 0.87)10^4$ to $(1.81 \pm 0.90)10^4$ mol C s^{-1} (0.30×10^{12} to 0.57×10^{12} mol C yr^{-1}). Recently, we found that the TOC balance through the Strait was 0.45×10^{12} mol C yr^{-1} in June 1997 and 0.38×10^{12} mol C yr^{-1} in April 1998, on average (Dafner et al., 1999). This estimate is similar to the average value of TOC inflow presented here for September 1997 (0.47×10^{12} mol C yr^{-1}). The C_T balance from the Mediterranean Sea to the Atlantic Ocean varies from $(12.5 \pm 0.4)10^4$ to

Table 3
Water transport (Sv), salinity, TOC (μM C) and C_T (μmol kg^{-1}) values applied for carbon balance estimations (Fig. 5) through the Strait of Gibraltar. According to Bray et al. (1995) and Tsimplis and Bryden (1999), errors in the inflow and outflow transports are considered to be 0.06 Sv

Variables	Spartel sill	Tarifa Narrows	Gates of Hercules
Atlantic inflow			
Transport	0.74	0.69	0.82
Salinity	36.30 ± 0.06	36.42 ± 0.02	36.67 ± 0.17
TOC	95 ± 9	80 ± 8	89 ± 7
C_T	2116 ± 12	2128 ± 12	2129 ± 15
Mediterranean outflow			
Transport	0.74	0.69	0.82
Salinity	37.65 ± 0.50	38.28 ± 0.02	38.36 ± 0.02
TOC	71 ± 1	66 ± 3	67 ± 3
C_T	2277 ± 10	2301 ± 8	2310 ± 2

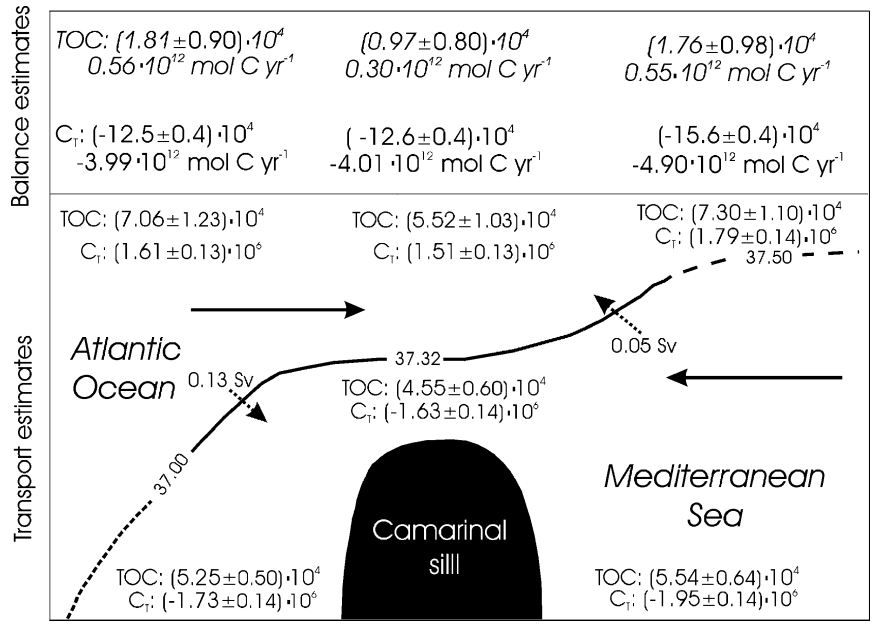

Fig. 5. Two-layer model of water mass exchange through the Strait of Gibraltar with values of TOC and C_T transports (lower panel) and balances (upper panel) along the Strait (2–9 September 1997).

$(15.6 \pm 0.4)10^4$ mol C s^{-1} for the different longitudinal sections, which gives annual estimates of 3.8×10^{12}–4.9×10^{12} mol C yr^{-1}.

The interaction between inflow and outflow results in strong shear, which induces vertical exchange between layers (Wesson and Gregg, 1994; Bray et al., 1995). In order to balance the salinity exchange in the Strait, and considering the input of water and the evaporation are negligible on this area, we estimate that the outflow increases volume transport by the entrainment at 0.13 Sv from the western entrance. By contrast, the Atlantic inflow increases its volume only by 0.05 Sv from the eastern entrance of the Strait by mixing with outflow (Fig. 5). The difference in vertical mixing between inflow and outflow from the west and east of the Strait is –0.08 Sv, in agreement with recent observation of Tsimpis and Bryden (1999). In terms of carbon, these vertical exchanges correspond to 0.87×10^6 and -0.48×10^4 mol C s^{-1} for TOC, and 0.11×10^6 and -0.3×10^6 mol C s^{-1} for C_T. The vertical mixing on the Atlantic side results in an input of organic carbon compounds from the inflow to the outflow and in the opposite direction for inorganic carbon (Tables 2 and 3).

Indirect estimates of organic and inorganic carbon balances were recently published by Copin-Montégut (1993). For DOC, she presented a value of 1.25×10^{12} mol C yr^{-1}, which is twice as high as our estimations for each longitudinal section. This difference is due to the TOC concentrations used (in her calculation she used DOC values of 67 μM C for the inflowing and 92 μM C for the outflowing waters), rather than different water transport estimates. By contrast, C_T balances obtained by Copin-Montégut and Brunet et al. (1984) (-4.6×10^{12} and -6.1×10^{12} mol C yr^{-1}) are the same as we present here despite their use of different water transport estimates. It was estimated that in the Gulf of Cádiz, entrainment increases the observed amount of carbon outflow, to about 8.6×10^6 mol C s^{-1} for C_T and 2.1×10^5 mol C s^{-1} for TOC on leaving the outer Gulf of Cádiz (Dafner et al., 2000a). It gives the net carbon transport with the Mediterranean outflow to the

Table 4
Historical estimates of meridional TCO_2 and DOC fluxes in the North Atlantic Ocean. Negative values correspond to southward transport

Areas	Carbon transport (mol $C\,s^{-1}$)	References
Section at 25°N and through the Florida Straits	-0.68×10^6	Brewer et al. (1989)
Temperate North Atlantic	-1.60×10^6	Broecker and Peng (1992)
Tropical Atlantic	$-1.05\times10^6\pm0.48\times10^6$	Keeling and Peng (1995)
Section $\sim$ 58°N, North Atlantic	-0.16×10^6	Stoll et al. (1996a)
Section $\sim$ 58°N, North Atlantic (DOC)	0.04×10^6–0.16×10^6	Stoll et al. (1996b)

open ocean of about 8.8×10^6 mol $C\,s^{-1}$. This carbon bulk is about 61.5% of the amount of fossil fuel CO_2 released into the atmosphere currently (ca. 14.3×10^6 mol s^{-1}) (Anderson et al., 1991). The estimates of carbon fluxes through the Strait of Gibraltar are similar to those presented recently for the meridional TCO_2 and DOC transports in the northern North Atlantic (Table 4). Polat and Tugrul (1996) obtained a value of 1.79×10^4 ton $C\,yr^{-1}$ (or 0.15×10^{10} mol $C\,yr^{-1}$) for the TOC export from the Sea of Marmora to the Aegean Sea and of about 0.41×10^4 ton $C\,yr^{-1}$ (or 0.34×10^9 mol $C\,yr^{-1}$) for the TOC outflow in the opposite direction. As we see, TOC inflow and outflow through the Strait of Gibraltar are two and three orders of magnitude higher than through the Turkish Straits. 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 from the Atlantic Ocean exceeds outflow from the Mediterranean Sea. Our data, together with the results quoted above, indicate that inflow of organic material to the Mediterranean Sea through the Strait of Gibraltar is considerably higher than outflow. The Mediterranean Sea acts as a sink of organic carbon and source of inorganic carbon for the Atlantic Ocean.

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