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Tidal-induced inorganic carbon dynamics in the Strait of Gibraltar

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ABSTRACT

This study presents the distribution of dissolved inorganic carbon (DIC) along the Strait of Gibraltar, its tidal-induced variability, as well as the inorganic carbon exchange between the Atlantic Ocean and Mediterranean Sea. During November 2003, water column samples were collected at nine stations to measure total alkalinity (TA), pH, and dissolved oxygen (DO) for the spatial characterization of the carbonate system. At the same time, anchored samplings were carried out, above the Camarinal Sill and in the Eastern Section of the Strait, in order to assess the tidal mixing effects for oxygen and DIC distribution on the water column. Three distinct water masses can be discerned in this area: the Surface Atlantic Water (SAW), the Mediterranean Water (MW), and the less abundant North Atlantic Central Water (NACW). The observations show an increase in the DIC and a decrease in oxygen concentration with depth, related to the different physico-chemical features of each water mass. The results show the high time-dependence of the vertical distribution of DIC with the interface oscillation, affected by the intense mixing processes taking place in the Strait. Intense mixing episodes over the Camarinal Sill are responsible for an increase in the DIC concentrations in the upper layer of the Eastern Section of the Strait. Higher DIC concentrations in the Mediterranean than in the Atlantic waters are responsible for a net DIC transport of $1.47 \times 10^{12}\,\text{mol C yr}^{-1}$ to the Atlantic Ocean. Nevertheless, the net exchange is highly sensitive to the interface definition, as well as to the estimate of water volume transport used.

1. Introduction

The Strait of Gibraltar is the only connection of the Mediterranean Sea with Atlantic Ocean. The Mediterranean outflow plays an important indirect role in the North Atlantic circulation (Reid, 1979) and, consequently in the thermohaline "conveyor belt" at global scales and on time scales of global climate change (Wu and Haines, 1996). The Mediterranean Sea provides an interesting case study for the processes that take part in the atmospheric sequestration of CO_2 through the outflow of deep waters across the Strait of Gibraltar, which transfers carbon from the sea surface to the intermediate waters of the Atlantic, where it is isolated from the atmosphere for several centuries (Bethoux et al., 2005); in part, this interest rests on the fact that the Mediterranean Sea is one of the few places in the world where deep convection and water mass formation takes place, and thus it constitutes a strong marine sequestration of anthropogenic CO_2 (hereinafter Cant). Furthermore, in the Gulf of Cadiz, the entrainment of central waters to depth when Mediterranean Water spills out of the Strait of Gibraltar is an important mechanism by which surface Cant is injected to depth and then distributed at intermediate levels into the North Atlantic. Recently, Alvarez et al. (2005) estimated that this mechanism drives the transfer of $151 \pm 14\,\text{kmol s}^{-1}$ ($4.7 \times 10^{12}\,\text{mol C yr}^{-1}$) from the surface to intermediate levels, and $88 \pm 8\,\text{kmol s}^{-1}$ ($2.8 \times 10^{12}\,\text{mol C yr}^{-1}$) are exported northward with the MW into the North Atlantic. These quantities highlight the role of the MW in the Cant oceanic budget which should be taken into account in future long-term monitoring programs and model studies about feedback between thermohaline changes affecting MW formation and circulation and the oceanic Cant budget (Alvarez et al., 2005).

Studying the biogeochemical properties of the Mediterranean and Atlantic water masses constitutes a good way to track the water exchange through the Strait of Gibraltar. In this context, several biogeochemical research studies have been carried out previously in the area, for example, on the nutrients pattern and its associated biological effects (Minas et al., 1991; Gómez et al., 2001; Echevarría et al., 2002; Macías et al., 2006) but relatively

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few studies have been made of the carbonate system. The European funded CANIGO project, with the observation published by Dafner et al. (2001a) and Santana-Casiano et al. (2002) are the most specific studies conducted on the Gibraltar Strait. Other studies carried out on the region but not specifically designed to study the Strait include those by Aït-Ameur and Goyet (2006), which was centred on the Gulf of Cadiz and the Western entrance of the Strait, and by Copin-Montégut (1993) on the Alboran Sea.

The changes in the biogeochemical parameters of waters interacting through the Strait are largely controlled by hydrodynamic phenomena. In the Strait of Gibraltar, a variety of physical processes are superimposed on the average Mediterranean–Atlantic flows, with large fluctuations at different time scales, and even greater variability is observed on the tidal scale (García-Lafuente et al., 2000). This is mainly due to the interaction of the average flow with the shallow topography at the Camarinal Sill (300 m depth), which produces large fluctuations at the interface between the upper Atlantic layer and the deeper Mediterranean layer, favouring the formation of internal hydraulic jumps, especially at spring tides (Armi and Farmer, 1988), or the arrested internal waves (Bruno et al., 2002) which are more likely at weak neap tides. Such undulatory processes enhance interfacial mixing and can inject deep, nutrient-rich water into the upper layer of Atlantic water. The upwelling inorganic nutrients are advected towards the Mediterranean Sea in the upper layer, and enhance the primary production in the Alboran Sea to the east of the Strait (Macías et al., 2007).

The present study aims to contribute to existing knowledge of the carbonate system in the Strait of Gibraltar, and in particular to evaluate the short-term temporal variability experienced on the tidal scale in the different sections over the length of the Strait. The main elements that must be taken into account in calculating the carbon exchange between the Atlantic Ocean and the Mediterranean Sea at the Strait have then been analysed.

2. Material and methods

Between 7 and 19 November 2003, nine stations were sampled for hydrology and water chemistry parameters (dissolved oxygen, total alkalinity (TA) and pH) in the Strait of Gibraltar, from on board the R/V *Mytillus*. Three stations were located at the western entrance to the Strait (St. D1–D3), one over the Camarinal Sill (St. D4), three at the Tarifa Narrows (St. D5–D7) and two fixed stations at the eastern entrance (A1 and A2). Seawater samples were collected at different depths of the water column using a CTD Rossete sampler with conventional Niskin bottles; a total of 230 discrete samples were taken. At each station (see Fig. 1), 5–6 depths were sampled, from the surface to 225–250 m. Additionally, four tidal samplings (3–12 h observation at each station) were performed at selected fixed stations over the Camarinal Sill (S1 and S2) and in the Eastern Section (A1 and A2). For each profile, CTDs were sampled at several depths down to 250–300 m every 15–30 min, and discrete samples for biogeochemical parameters were taken every 1–2 h.

The pH was measured with a glass combined electrode (Methrom) calibrated using the buffer Tris–Tris–HCl (ionic strength 0.7 M) on the Free pH Scale with an accuracy of ±0.003. The alkalinity computation was performed from the titration curve by means of the Gran Function and taking into account the correction for sulphate and fluoride interaction, using the constants proposed by Dickson (1990) and Dickson and Riley (1979), respectively. For the dissociation of dissolved inorganic carbon (DIC), the K_1 and K_2 acidity constants proposed by Lueker et al. (2000) in the Total pH Scale were selected. The method was validated with reference standards for TA obtained from A. Dickson (Scripps Institution of Oceanography, San Diego, USA) to an accuracy of $\pm 2\,\mu\text{mol kg}^{-1}$ for TA and a calculated error for DIC of $\pm 2.6\,\mu\text{mol kg}^{-1}$. The DIC accuracy represents the 2% of the differences in DIC concentration between the Atlantic and Mediterranean layers, and therefore it is adequate for the discussion of the results in this paper.

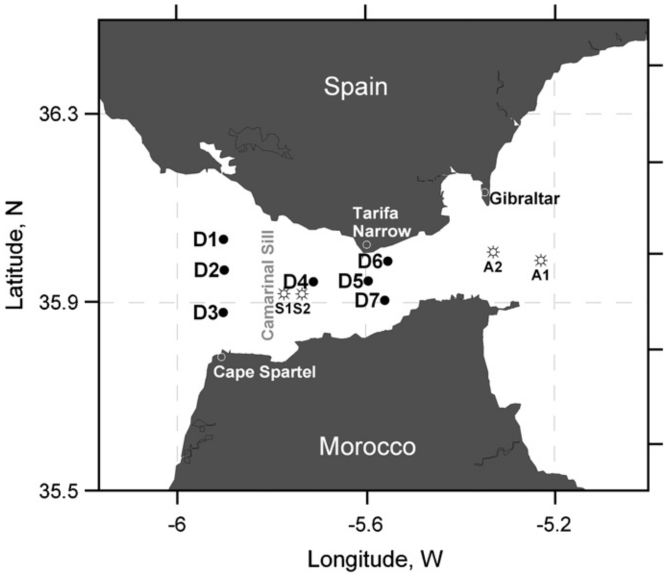

Fig. 1. Map of the Strait of Gibraltar showing the locations of the sampling stations. The fixed tidal stations (S1, S2, A1 and A2) are indicated as (☼) and the locations for the descriptive samplings (D1–D7) are indicated as (●).

The oxygen was fixed in a sealed flask and stored in darkness for 24 h, as described by the Winkler method, for later analysis by potentiometric titration with an accuracy of $3\,\mu\text{mol kg}^{-1}$ (Metrohm 670 Titroprocessor). The apparent oxygen utilization (AOU) is defined as the deviation of oxygen from an O_2 concentration in equilibrium with the atmosphere calculated from the Benson and Krause (1984) solubility equation. All the measurements for TA and oxygen were made on board within a maximum of 24 h after sampling. The estimation of the tidal current velocity has been made using the method of Alonso del Rosario et al. (2003).

3. Results and discussion

3.1. Spatial distribution

3.1.1. Hydrology

The normal regime in the Strait of Gibraltar consists of two superimposed flows; a shallow Atlantic inflow and a deeper Mediterranean outflow. The interface between these flows is characterised by a high salinity gradient and is subject to high spatial–temporal variability over the length of the Strait. Three different water masses participate in the circulation scheme (Gascard and Richez, 1985): the Mediterranean Outflow Water (MW) is cold and saline (temperature and salinity ranges, respectively, between 13.0–13.5 °C and 38.2–38.5), the Surface Atlantic Water (SAW) is warm and fresh (temperature and salinity ranges, respectively, between 19.0–20.0 °C and 36.4–36.2) and the North Atlantic Central Water (NACW; temperature and salinity ranges, respectively, between 13.5–14 °C and 35.6–36) is colder and fresher than SAW; the volume of the less abundant NACW is highly variable in time (as a function of the tidal phase) and along the Strait (Bray et al., 1995; Macías et al., 2006). The temperature/salinity diagram for the CTD profile obtained in this study at

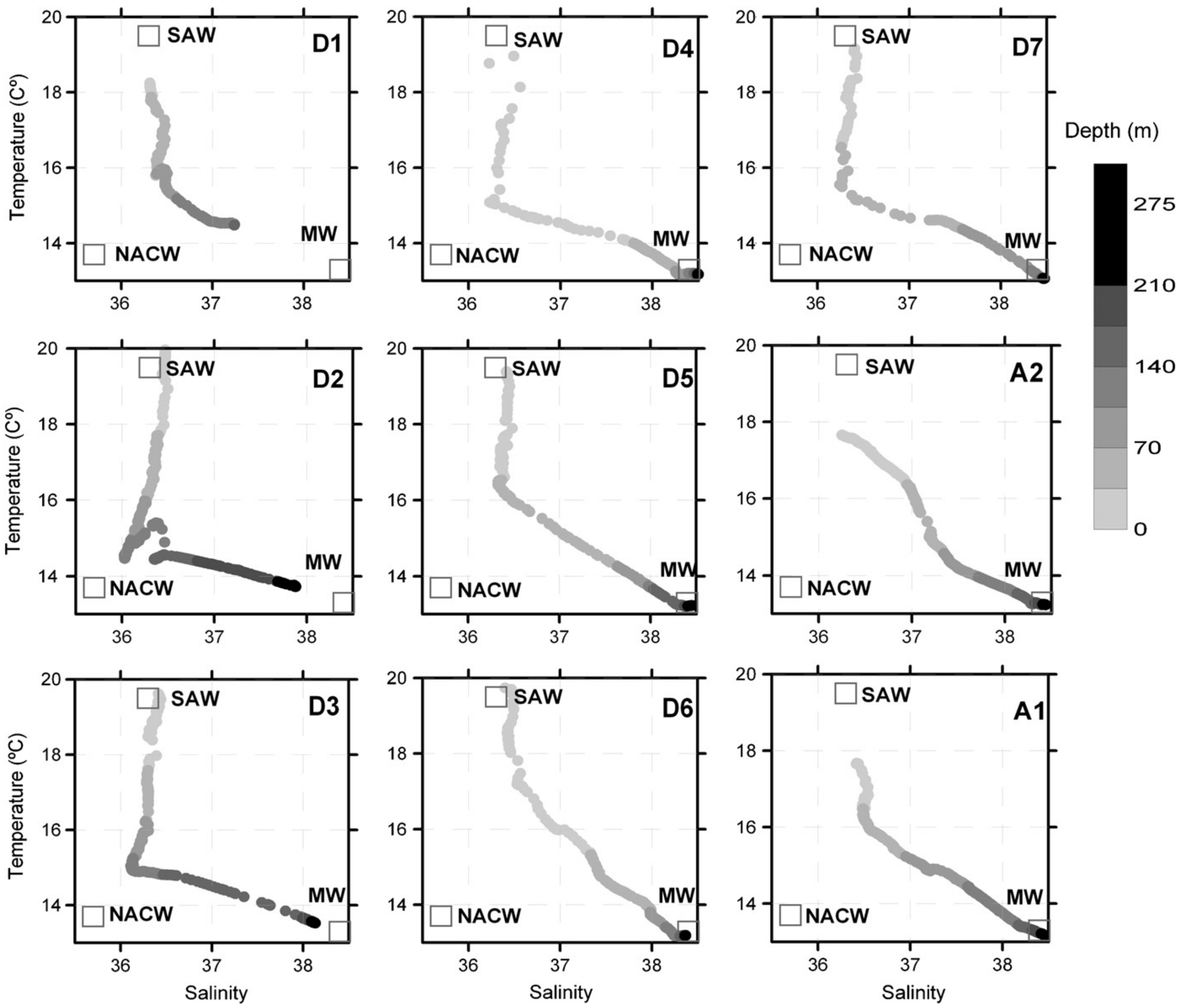

Fig. 2. Temperature/salinity diagrams for the different stations. Gray scale code indicates depth, with darker grey for deeper samples. Salinity and temperature characteristics for the three types of water masses are marked as SAW, MW and NACW.

stations from D1 to D7 (Fig. 2) allows the relative abundance of the different water masses to be discerned. Additionally, in each *T*/*S* diagram, the three types of water mass have been plotted following the characteristics proposed by Gascard and Richez (1985). A key feature that identifies the penetration of NACW through the Strait of Gibraltar is the appearance of a salinity minimum which separates SAW from the underlying mixture of Atlantic–Mediterranean Waters. The NACW signal is more significant in the southern (D3 and D7) than in the northern (D1 and D6) stations, and in the western (D1–D3) than in the eastern (D6–D7) stations. This is consistent with the previous characterization of water masses in the Strait of Gibraltar carried out by Bray et al. (1995), which shows a dramatic decrease in the NACW fraction eastward, and with the report of Gascard and Richez (1985), who observed that the injection of NACW into the Mediterranean Sea is highly influenced by the tides and the internal waves. The grey scale gradient in Fig. 2 reveals information about the east–west differences in the depth level of the different water masses. The *T*/*S* diagrams show how the NACW signal tends to appear preferentially to the south of the Strait, where the Atlantic–Mediterranean interface is deeper (García-Lafuente et al., 2000); the entry of the NACW over the Sill becomes easier in the south because of the geostrophic transport (Bray et al., 1995), whereas in the centre or north, it can only cross the Sill under maximum tidal forcing conditions, when the Atlantic layer is thicker and the interface occurs at a greater depth.

3.1.2. *Vertical and spatial patterns of TA, DIC and AOU*

Due to the high tidal variability that characterises the Strait of Gibraltar, the spatial distribution picture must be made up taking into consideration the tidal stage at the sampling time for each station. In spite of this tidal variability, the main vertical features of the DIC, pH_T (25) and AOU are evident in Fig. 3, which shows two vertical profiles for one eastern and one western station (D2 and D6) as examples of longitudinal differences. The average depth of the interface for both stations has also been indicated in Fig. 3. The Atlantic inflow water is characterised by lower TA and DIC content than the Mediterranean outflow water; in turn, the

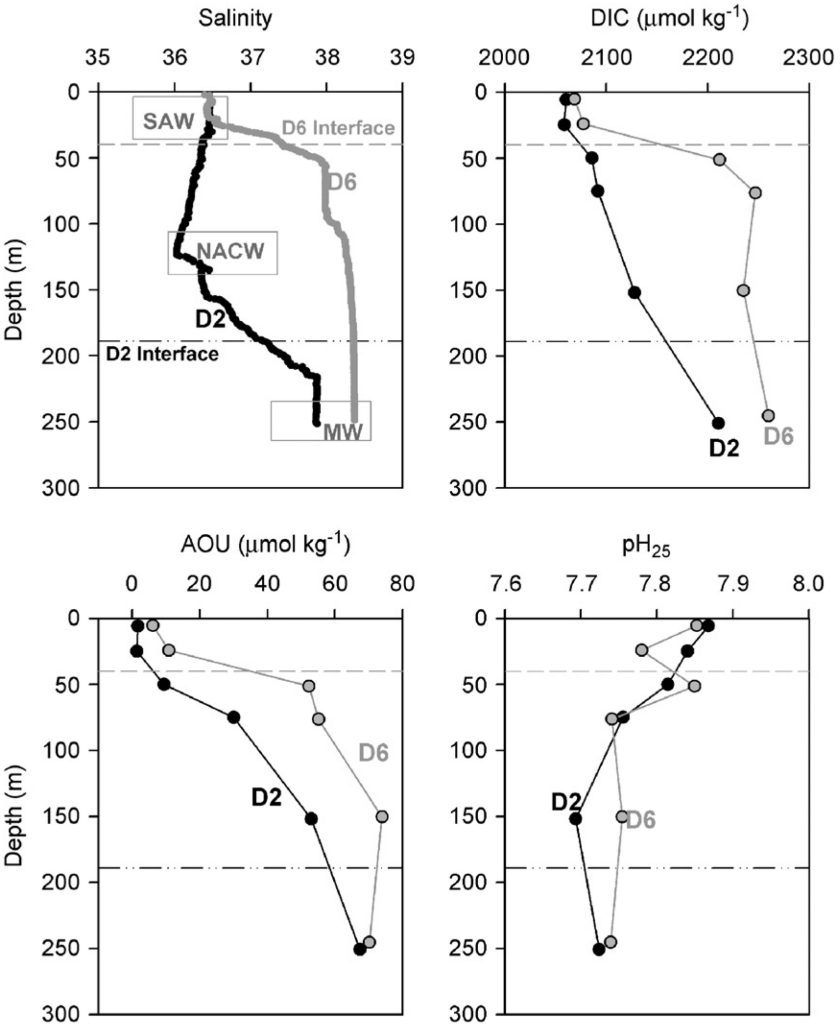

Fig. 3. Vertical distribution of salinity, DIC, AOU, and pH_T (25) along the Strait of Gibraltar for the stations D2 and D6 as an example. The horizontal lines indicate the interface location for each station. The presence of each water mass has been marked in the temperature and salinity profiles.

shape of the profile will depend on the interface thickness. Hence, the DIC and AOU values present a gradual increase down to the lower part of the interface and more homogeneous values for the deeper layer, following the salinity profile. In turn, the pH_T (25) values present a gradual decrease down to the interface and nearly constant values for the lower Mediterranean layer. DIC and AOU content of the different water masses present in the Strait of Gibraltar has been described previously in more detail by Santana-Casiano et al. (2002).

In order to study the effect of the tide on the variability of the physico-chemical spatial distribution, two descriptive samplings were performed on 11 and 17 November, each at different tidal amplitude and tidal phase, and both samplings were performed down to a depth of 250 m. For the prime sampling, the maximum current velocities were around 1.9 $m\,s^{-1}$, higher than the 1.4 $m\,s^{-1}$ that was recorded in the second grid. As well as the differences in tidal amplitude, the stations were sampled at different times in the tidal cycle (Table 1), i.e., the first grid was performed coinciding mainly with the outflowing and the second grid during the inflowing tide. Under these conditions, maximum interfacial mixing occurs during the sampling for the first grid. In addition to the descriptive sampling at these seven stations, the spatial description of the carbonate system obtained includes two profiles performed on the eastern side of the Strait (see Fig. 1) as part of the tidal sampling strategy (see Section 3.2). Table 1 shows the integrative average values for each of the three layers of water interacting in the Strait of Gibraltar. The horizontal distribution of the chemical parameters over the length of the Strait depends on the location of the interface layer. Although the actual thickness and characterization of properties of the interface must be defined in accordance with the halocline location and not with specific salinity values (Bray et al., 1995), the salinity values of 36.5 and 38 can be used to locate the upper and lower limits of the interface, adopting the same criterion as in previous studies such as those by Bryden et al. (1994) and Dafner et al. (2001a). As it was aforementioned, the vertical profiles for temperature and salinity show how the Atlantic layer and the interface are much deeper on the western side of the Strait (St. D1–D3) than on the eastern side (St. D5–D7, A1 and A2) and deeper to the north than to the south (Table 1). Based on the values shown in Table 1, it can be observed that the integrative DIC value found for the Atlantic layer ranged from 2064 $\mu mol\,kg^{-1}$ at D7 to the maximum of 2136 $\mu mol\,kg^{-1}$ at D1. The general distribution in the Atlantic layer on the western side shows higher DIC and AOU values, and lower pH_T (25), salinity and temperature values in the south compared with the north, except at station D1, with higher DIC and lower AOU values. Station D1 is subject to specific coastal hydrodynamics processes, continental inputs of inorganic carbon and nutrients that enhance the biological activity as previously described by Gómez et al. (2000). These north–south differences

Table 1
Chemical characteristics of the different water layers observed in the Strait of Gibraltar

Station[a]	Time[b]	Interface depth (m)	Atlantic layer					Interface layer[c]					Mediterranean layer				
			Salinity	Temperature	DIC (μmol kg^{-1})	AOU (μmol kg^{-1})	pH$_T$ (25)	Salinity	Temperature	DIC (μmol kg^{-1})	AOU (μmol kg^{-1})	pH$_T$ (25)	Salinity	Temperature	DIC (μmol kg^{-1})	AOU (μmol kg^{-1})	PH$_T$ (25)
D1_1	HW−4	98–141	36.39	16.92	2136	22	7.779	36.90	14.80	2154	44	7.750	–	–	–	–	–
D1_2	LW−2	86.5–141	36.35	17.07	2135	13	7.795	37.08	14.64	2137	31	7.782	–	–	–	–	–
D2_1	HW−3	156–251	36.29	16.43	2086	20	7.790	37.40	16.43	2171	61	7.707	–	–	–	–	–
D2_2	LW−1	144–203	36.29	16.83	2098	22	7.794	37.53	14.12	2188	46	7.733	38.16	13.47	2228	63	7.740
D3_1	HW−2	145–165	36.28	16.60	2117	30	7.780	37.13	14.37	2168	57	7.723	38.09	13.57	2203	67	7.727
D3_2	LW	182–227	36.28	16.77	2120	26	7.786	37.40	14.21	2199	61	7.740	38.25	13.44	2233	74	7.731
D4_1	HW	16–45	36.34	16.07	2125	20	7.794	37.34	14.27	2176	30	7.736	38.4	13.2	2254	77	7.710
D4_2	LW+1	107–151	36.33	16.73	2116	22	7.788	37.45	14.37	2171	51	7.730	38.3	13.26	2230	71	7.725
D5_1	HW+3	52–120	36.38	17.30	2085	16	7.841	37.69	14.16	2110	37	7.781	38.3	13.33	2215	72	7.701
D5_2	LW+3	92–151	36.37	17.69	2096	16	7.828	37.58	14.24	2180	46	7.768	38.23	15.28	2270	62	7.735
D6_1	HW+4	20–91	36.45	18.82	2073	9	7.815	37.63	14.59	2194	43	7.777	38.3	13.22	2247	66	7.743
D6_2	LW+5	101–127	36.37	17.52	2137	33	7.794	37.28	14.58	2226	59	7.756	38.42	13.19	2250	66	7.741
D7_1	HW+2	42–87	36.32	17.43	2117	11	7.847	37.50	14.38	2191	56	7.769	38.4	13.11	2224	67	7.766
D7_2	LW+4	44–138	36.30	17.06	2064	17	7.852	37.59	14.33	2135	49	7.769	38.24	13.25	2234	80	7.756
A1	HW	44–126	36.49	16.65	2106	16	7.807	37.24	14.92	2174	36	7.776	38.35	13.28	2237	48	7.771
A2	HW−2	12–128	36.34	17.55	2089	16	7.834	37.32	14.95	2189	58	7.757	38.29	13.33	2275	79	7.713
Average			36.35	17.09	2106	19.3	7.808	37.40	14.44	2172	48	7.753	38.29	13.46	2238	69	7.735

[a] The code 1 or 2 after the stations D1–D7 refers to the sampling date: "1" for the sampling carried out the 11 November 2003 and "2" for the sampling date 17 November 2003. Station A1 was sampled on 7 November 2003, and station A2 on 14 November 2003.

[b] HW, high water; HW+2, 2 h after HW; LW, low water.

[c] The upper and lower limits of the interface layer have been defined as between the salinity values 36.5 and 38, following Dafner et al. (2001b).

in concentrations can be explained by the greater presence of the NACW in the south, with higher DIC and AOU values than the SAW. In turn, no significant differences on DIC and AOU average values have been observed between different stages of the fortnightly tidal cycle in the upper Atlantic layer. To the east of the Sill, the northern part is warmer and saltier, but different patterns are found for DIC and AOU values for the different fortnightly tidal cycle stages. Thus, as mentioned already, the first grid sampling corresponded to a higher tidal coefficient, which causes the interface to be relatively shallow. This in turn results in the NACW being displaced to the south as it enters the Mediterranean and explains the higher AOU and DIC values found at station D7. Additionally, in the north, the nutrients and DIC are more bio-available as the interface rises, together with the enrichment of nutrients caused by vertical mixing at the Sill and the later eastward advection, enhancing the primary productivity and causing a lower AOU in this zone, compared with the second grid. For the sampling performed on 17 November (second grid), the pattern persists on the western side of the Sill, but a different situation is found in the east. The fortnightly tidal cycle results in a deeper interface just after the neap tide (Bryden et al., 1994). Such a circumstance favours the entry of the NACW to the north and central parts and explains the greater presence of the NACW on the eastern side, compared with the first grid. Moreover, because the upper layer on the eastern side is less fertile at neap tides, higher AOU values are found in this zone in the second grid. This is in agreement with the observation of Macías et al. (2006), who found that, in the eastern part, intense vertical mixing episodes at spring tides were more effective in enhancing primary production than the presence of the nutrient-enriched NACW.

These biochemical gradients are in accordance with the abundance of water masses over the length of the Strait observed by Bray et al. (1995), who described increases, from the westernmost to the easternmost sections, of 12% of the SAW and 5–10% of the MW in the upper layer, accompanied by a decrease of 20% of the NACW. Moreover, in the lower layer, the MW decreases from 95% to 83%, from east to west.

In summary, the average DIC and AOU values found in this study for the SAW are $2106 \pm 22\,\mu\mathrm{mol\,kg^{-1}}$ for DIC, and $19.3 \pm 6.5\,\mu\mathrm{mol\,kg^{-1}}$ for AOU; in the interface layer the values found are $2172 \pm 28\,\mu\mathrm{mol\,kg^{-1}}$ for DIC and $47.7 \pm 10.3\,\mu\mathrm{mol\,kg^{-1}}$ for AOU; and for the MW, $2238 \pm 20\,\mu\mathrm{mol\,kg^{-1}}$ and $68.6 \pm 8.3\,\mu\mathrm{mol\,kg^{-1}}$, respectively. These values are in accordance with previous literature on the carbonate system (Santana-Casiano et al., 2002; Dafner et al., 2001a) and for oxygen (Minas et al., 1991; Dafner et al., 2001b) available in the Strait of Gibraltar and in the Gulf of Cadiz (González-Dávila et al., 2003; Aït-Ameur and Goyet, 2006). It should be noted that the lower values for DIC in the MW compared to previous studies are due to sampling to a maximum depth of 250 m, where the Mediterranean Waters may be disturbed by the phenomenon of interface oscillations. In comparison with the relative homogeneous vertical concentration of DIC observed in the Mediterranean layer, previous studies performed in the Strait show a slight increase down to a depth of 300 m (Dafner et al., 2001a; Santana-Casiano et al., 2002).

3.2. *Tidal variability of DIC and AOU*

In order to obtain a better understanding of factors controlling the temporal variability of the inorganic carbon and oxygen, two fixed stations were sampled twice: one located at the main Sill (above St. D4) and the other at the easternmost section of the Strait (A1 and A2; see Fig. 1). The tidal cycle in the Strait is essentially semi-diurnal but the diurnal component is quite detectable (Gascard and Richez, 1985). The T/S diagram in Fig. 4 shows the composition of the water masses for each sampling. As noted previously, there is usually a relatively larger volume of the NACW at the Sill than in the eastern section. The tidal oscillation of the interface has a significant effect on the vertical distribution of DIC and AOU. Normally, the current flows eastward in the upper layer and westward in the lower layer, although they are considerably affected by the tidal cycle: at the Sill, especially at spring tide, the current flows from east to west, in the upper layer 5–6 h before high water (HW), and then flows in reverse, back to the east, 1–2 h before HW (Gascard and Richez, 1985). At the beginning of the high tide, the arrested internal waves generated as a consequence of the interaction of the tidal flow with the bottom elevation at the Sill are liberated and began to propagate towards the east (Bruno et al., 2002). These internal waves are expected to take 8–9 h to arrive to the easternmost stations A1 and A2, passing through this point at around HW−4. These phenomena are discernable in Fig. 4. At HW, the interface is at its shallowest depth over the Sill, where there is a noticeable increase in salinity from 25 to 150 m of depth, accompanied by higher DIC and AOU values. This upwelling of deeper and colder waters reaches the shallowest depth in the sampling performed on 13 November since the tidal coefficient is higher than for the sampling of 19 November; this also results in a shallower interface. At low water at the Sill ($\mathrm{LW} = \mathrm{HW} \pm 6$), the interface is at its deepest position, allowing the NACW to pass through the Sill at a depth of 75–150 m, identified by a minimum salinity value (<36.2). This presence of the NACW, identified by the minimum salinity ($S < 36.2$), is associated with an increase in AOU and DIC, to 40–45 $\mu\mathrm{mol\,kg^{-1}}$ and up to 2080–2100 $\mu\mathrm{mol\,kg^{-1}}$, respectively, at intermediate depths. The maximum velocity of current estimated is around 1.8 $\mathrm{m\,s^{-1}}$ on 13 November and 1.5 $\mathrm{m\,s^{-1}}$ on 19 November. The greater intensity of mixing leads to a higher vertical fluctuation of the isolines for salinity, DIC and AOU on 13 than on 19 November. The maximum interface thickness can be found at the Sill between HW−3 to HW+2 when the internal waves are expected to be arrested; this situation can be appreciated in the salinity, DIC and AOU values, especially on 13 November. The lower intensity of mixing at the Sill on 19 November is reflected in the weaker oscillation of the DIC and AOU isolines, and therefore lower DIC and AOU concentrations for the first 100 m of depth, due to less injection of deep water into the upper layer.

At the eastern entrance of the Strait, the interface is shallower at LW and begins to descending around HW−4 as a consequence of the passing of the internal wave liberated in the previous tidal cycle and the arrival of the undulatory disturbances, which lead to the undulations in the DIC and AOU isolines. The shallowness of the interface at LW explains the relatively high values for DIC (2130 $\mu\mathrm{mol\,kg^{-1}}$) and AOU (23.7 $\mu\mathrm{mol\,kg^{-1}}$) at 50 m. There is a significant difference in the AOU values between the first and the second samplings at the eastern station, and higher values are found for the entire water column for 7 compared with 14 November. Two different causes are plausible: the second sampling was performed during the night, without the irradiance needed for the primary producers, whereas the first sampling takes place during the day; second, the first sampling is performed during the spring tide but the second during the medium to neap tide. As previously mentioned, at spring tide the maximum vertical mixing rates at the Sill, as well as the enrichments in nutrients in the upper layer, are recorded (Macías et al., 2007). As a result, the advected nutrients from the Sill reach a more bio-available area, enhancing the primary productivity and causing a lower AOU in this zone. This coincides with the result obtained at the same station by Macías et al. (2006), who found maximum chlorophyll values related to the occurrence of the maximum mixing rates at the Sill. This chlorophyll maximum

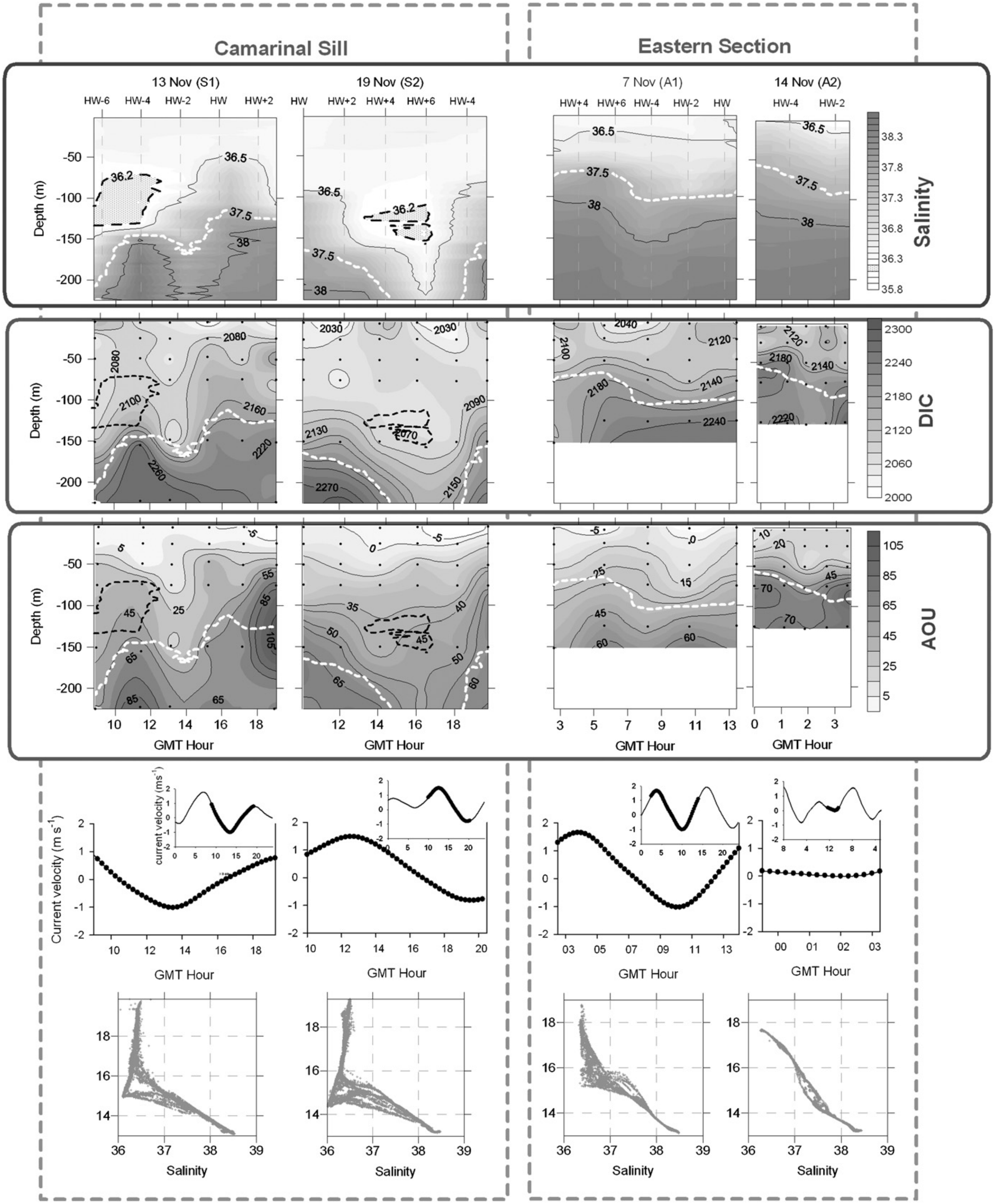

Fig. 4. Temporal evolution for salinity, DIC and AOU for the samplings performed at the Sill (13 and 19 November 2003) and eastern section (7 and 14 November 2003), *T*/*S* diagrams and current velocity prediction over the Camarinal Sill (m s^{-1}) during each sampling. The white dashed line indicates the average depth of the interface location. The continuous black lines in the salinity contours plots show the upper and lower limits of the interface defined by the salinity 36.5 and 38, respectively. The black dashed line marks the presence of the NACW.

could be related to the inputs of coastal water by suction action at the Sill during the outflowing of the Atlantic flow, and not to internal growth in the Strait. Several investigations (Gómez et al., 2001; Macías et al., 2006) have been performed at the eastern entrance of the Strait in order to gain a better understanding of the tidal variability on nutrients, their sources and the implication for the phytoplankton community. The main factors controlling the carbon and oxygen variability are the vertical oscillation of the interface as well as the intensity of the tidal mixing processes.

3.3. Relationship DIC and AOU versus salinity

Having assessed the tidal influence on the DIC and AOU values, in Section 3.2, the mixing diagrams of DIC, AOU and pH_T (25) versus salinity (Fig. 5) will be used in order to remove discrepancies due to tidal oscillations. For this analysis, the entire database available on the Strait of Gibraltar from the samplings performed during November, with a total of 183 samples, has been used. With the objective of obtaining a better characterization of the Atlantic and Mediterranean Water mixing, the NACW samples ($S<36.2$) have been disregarded. Fig. 5 shows a good linear correlation between DIC and salinity (S), a relationship which can be formulated precisely as $\text{DIC} = 86.96S-1079$ ($r^2 = 0.82$). This high degree of correlation applies to the entire water column sampled, but the Atlantic layer displays a higher variability for a narrower salinity range than the Interface and Mediterranean layers, due to the greater intensity of biological processes, as well as to the air–water exchange and coastal inputs. The DIC–S relationship obtained is similar to that in previous inorganic carbon studies performed in the Strait of Gibraltar during the CANIGO expeditions in September 1997 (Dafner et al., 2001a; Santana-Casiano et al., 2002) except for some slight differences in the fitting parameters; these differences can be explained because the previous formulation effectively disregarded the Atlantic layer by only taking into account salinities higher than 37. In order to study the sources of variability in the DIC values of surface water, Santana-Casiano et al. (2002) proposed a different formulation only for surface waters; this formulation gives values very close to those obtained in this study for the Atlantic layer.

As with DIC, the relationship of AOU vs. salinity shows a high linear correlation, which can be formulated as: $\text{AOU} = 33.62S-1213.1$ ($r^2 = 0.82$). This linear relationship is noteworthy since, even if the oxygen is subject to biological and gas exchange processes, these are much lower in magnitude and much slower for the endmembers than the Atlantic–Mediterranean Water mixing due to the short residence time of the water masses in the Strait of Gibraltar. This same explanation was put forward by Minas et al. (1991) for the oxygen–salinity relationship.

The decrease of pH_T (25) with salinity is related to the more acidic nature of the Mediterranean compared to Atlantic waters. This parameter shows a higher variability respect to DIC and AOU in the upper Atlantic layer (linear fit $\text{pH}_T\ (25) = -0.049S+9.63$; $r^2 = 0.65$). Similarly, Santana-Casiano et al. (2002) observed a higher temporal pH variability in surface waters compared to depth waters related to biological activity in the photic zone and tidal-induced mixing effects.

To assess the stoichiometric relationship between DIC and oxygen, the surplus DIC has been calculated, following DeGrandpre et al. (1997). The surplus DIC is defined as the difference between the observed DIC, and the DIC calculated from TA and the monthly average atmospheric CO_2 value for November; this last value corresponds to data measured at the Tenerife Atmospheric Observatory (Spain), taken from the World Data Centre for Greenhouse Gases (WDCGC/WMO) air sampling network (available at http://gaw.kishou.go.jp/wdcgg.html). The departure of the observed DIC from the DIC in equilibrium with the atmosphere enables the remineralization ratios with respect to oxygen to be assessed, and can be seen as the carbon analogy to the AOU. Although the relationship between AOU and surplus DIC (see Fig. 6) is very scattered ($r^2 = 0.36$), the plotted slope of 1.2 tracks the molar ratios for the western Mediterranean basin proposed by Bethoux et al. (2005), and is equal to $\Delta C:\Delta O_2 = 192:237 = 0.81$. Therefore, although it may be considered from the DIC and AOU mixing lines that most of the variability of these biochemical parameters is explained by the strong mixing processes taking

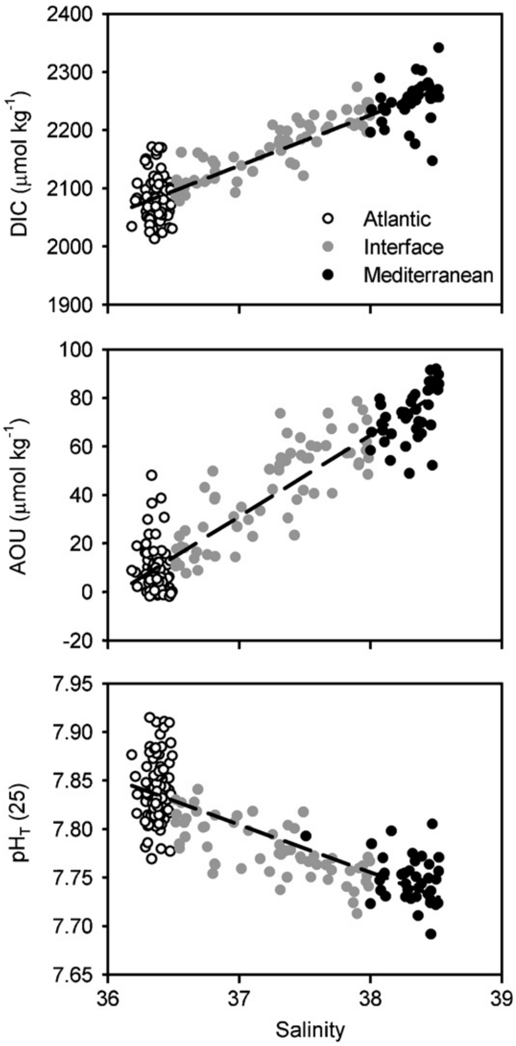

Fig. 5. Theoretical dilution line for DIC, AOU and pH_T (25) for the Atlantic, interface and Mediterranean layers. The linear regression line (black dashed line) has been drawn.

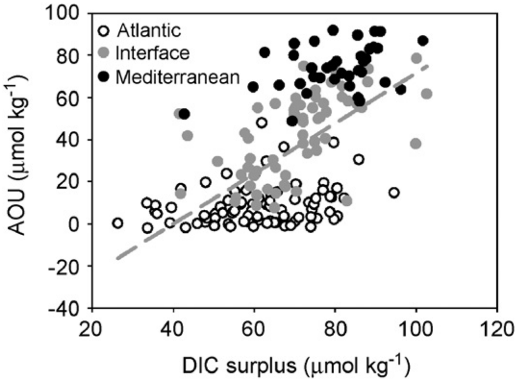

Fig. 6. AOU versus DIC surplus in the Strait of Gibraltar for the Atlantic, interface and Mediterranean layers. The linear regression line (black dashed line) taking into consideration the three layers has been drawn.

place in the Strait of Gibraltar, the value of the slope plotted for AOU vs. surplus DIC suggests that the main difference in DIC and AOU content between the Atlantic and Mediterranean Waters can be explained by the mineralization processes experienced by the MW during its cycle around the Mediterranean Sea basin and before its exits through the Strait of Gibraltar. The remineralization processes in the Mediterranean Water will be related to the residence time of the water in the Mediterranean, which is estimated to be around 50 years for the eastern deep waters and 15 years for the deep waters in the eastern basin (Bethoux et al., 2005). Unlike the MW, the AOU–DIC relationship for SAW will be affected by both the biological production as the gas exchange. In addition, the relatively invariable AOU values compare to the DIC surplus variability in the Atlantic layer suggest the existence of old biological production. This can be explained by the oxygen having sufficient time to return to near saturation whereas the CO_2 remains well above saturation.

3.4. *Inorganic carbon exchange in the Strait of Gibraltar*

The driving force of the exchange through the Strait of Gibraltar is the net loss of freshwater in the Mediterranean Sea, due to the excess of evaporation over precipitation and river runoff. Nevertheless, due to the complexity of the physical processes in this area, there is high variability over the average exchange from tidal to seasonal scale and depending on the position in the Strait, omission of interface movements, etc. It is this factor which is mainly responsible for the wide range of literature values for water fluxes and exchange of biogeochemical substances through the Strait of Gibraltar (Gómez, 2003). In this paper, the water fluxes are calculated using the budget proposed by Baschek et al. (2001) based on a tidal inverse model, estimating an average transport of 0.81 ± 0.07 Sv for the Atlantic inflow and -0.76 ± 0.07 for the Mediterranean outflow (positive flows are defined as those into the Mediterranean Sea). These numbers imply a net water flow of 0.05 Sv towards the Mediterranean. The water transport estimations by Baschek et al. (2001) fall within the range of those reported in studies by Bryden et al. (1994) and Tsimplis and Bryden (2000), but below the older estimation by Bethoux (1979) that did not take the interface layer into account in the water budgets. The inorganic carbon inflow and outflow will be calculated by multiplying the average concentration for each layer by its corresponding water transport. The estimates of the upper and lower layer volume transports thus depend on the choice of the separating isohaline. Baschek et al. (2001) define the isohaline 38.1 as the one that maximizes the transport in each layer. Therefore, in order to be consistent with the water volume transports used in this study, the DIC concentration has been averaged for waters above and below the isohaline 38.1. The average DIC concentration in the upper layer is 2118 and 2251 μmol kg^{-1} for the deep layer. Due to the shallowness of the sampling (down to 225 m depth) and in order to obtain a more realistic estimation of the transport in the Strait, the DIC values obtained in 2002 by Aït-Ameur and Goyet (2006) for the Mediterranean layer have been used (i.e., 2313 μmol kg^{-1}). The resulting estimate of transport yields a total Atlantic input of $(5.56 \pm 0.48) \times 10^{13}$ mol C yr^{-1} and a total Mediterranean output of $(5.70 \pm 0.5) \times 10^{13}$ mol C yr^{-1}; this produces a net DIC output to the Atlantic of 1.47×10^{12} mol C yr^{-1}. This quantity is subject to a high degree of uncertainty since the net transport represents only 1.3% of the total transport for the Atlantic or Mediterranean, but direct estimation of the net transport is difficult to achieve because of the great variability of the hydrodynamics environment, where the tidal currents produce flow fluctuation whose amplitude can be up to four times greater in magnitude than the time-averaged flow (García-Lafuente and Vargas Domínguez, 2003). If the small deviation due to the input from runoff and the loss by evaporation are ignored, the inflow and outflow are the same (0.81 ± 0.07 Sv vs. -0.76 ± 0.07 Sv). If both flows are assumed equal for the purpose of assessing uncertainty, then the net C flux is determined by the relative difference in the inflowing and outflowing waters. The relative difference is much more precisely known than the independent absolute concentration in each layer. Hence, it can be estimated that the uncertainty associated to the DIC (± 2.6 μmol kg^{-1}) measurements represents only the 3% of the total net DIC transport.

The net transport obtained in this study is very close to a recent estimation proposed by Aït-Ameur and Goyet (2006). Previous estimations in the literature for the inorganic carbon exchange at the Strait of Gibraltar results in a wide range of net DIC transport values, which vary from $3.8–4.9 \times 10^{12}$ mol C yr^{-1} (Dafner et al., 2001a) and 0.98×10^{12} mol C yr^{-1} Gómez (2003). The diversity of results found in the literature is due to the particular estimates made of DIC concentration for each layer, as well as to the values for water volume transport used.

With the object of calculating an average flux, it is worth noting the high variability of the water fluxes on different time scales. In order to asses this variability, Macías et al. (2007) developed a model that coupled hydrodynamic and biogeochemical factors to explore the effects of the strong advection and mixing processes on the biogeochemical exchange and on the pelagic community of the area. In this model, a third intermediate layer has been incorporated and this leads to a significant improvement in the estimation of biogeochemical budgets. The model calibration exercise, carried out for salinity values obtained from an extensive database, demonstrated the need to include mixing in any model for the Strait. Hence, the application of this model to the inorganic carbon database obtained in this study allows estimates to be made of the net amount of carbon in the outflowing layer that is introduced into the upper layer and therefore recirculated to the Mediterranean Sea. As a result, it has been estimated that, on average, 1.35% of the outflowing DIC is recirculated to the Mediterranean, varying between 2.6% at spring tides and 0.5% at neap tides. This means that, on average, a net DIC amount of 35.7 μmol kg^{-1} from the deep layer are being injected into the upper layer as a result of the mixing effects and transported again towards the Mediterranean Sea. This recirculation phenomenon by mixing means that the total Atlantic inflow is increased from 5.56×10^{13} to 5.64×10^{13} mol C yr^{-1}. Several direct and indirect estimations have been made for the nutrient recycling (Gómez et al., 2000; Dafner et al., 2003; Macías et al., 2007) to explain the upper layer fertilization in the Eastern Section of the Strait; this recirculation has been neglected until now for calculations of the carbon exchange in the Strait of Gibraltar.

Recent investigations (Ríos et al., 2001; Alvarez et al., 2005; Bethoux et al., 2005) have drawn attention to the role of the Mediterranean Sea on the sequestration of anthropogenic carbon. The Mediterranean Sea is one of the few areas around the global ocean where the formation of deep water is possible; this is then incorporated into deep water currents through its outflow at the Strait of Gibraltar (Bethoux et al., 2005). Using the database for oxygen, TA and DIC values, it is possible to estimate the anthropogenic carbon concentration in the Strait of Gibraltar by means of the TrOCA approach (Touratier and Goyet, 2004a, b), where the anthropogenic carbon (Cant) is calculated as

$$\mathrm{Cant} = \frac{\mathrm{TrCOA} - \mathrm{TrOCA}^0}{1.2},$$

where TrOCA is a semi-conservative tracer defined as

$$\mathrm{TrOCA} = \mathrm{O_2} + 1.2\mathrm{DIC} - 0.6\mathrm{TA}$$

and the tracer TrOCA^0 is defined as the preindustrial TrOCA. This preindustrial tracer was estimated using waters formed prior to the year 1800 (Touratier and Goyet, 2004b):

$$\mathrm{TrOCA}^0 = 1505.04\,e^{(-\theta/89.04)}$$

with θ being the potential temperature. The average anthropogenic carbon concentration in the Mediterranean Water obtained in this study is 65 μmol kg^{-1}, which represents 3% of the inorganic carbon transported to the Atlantic. Previous estimates vary in the approach used for its computation, and in the region of the study: values reported range from 50 μmol kg^{-1} (Ríos et al., 2001) in the eastern Atlantic region draw-down of the Central Atlantic Water plus Mediterranean Outflow Water, to 111 μmol kg^{-1} for the Mediterranean Outflow Water recently calculated by Aït-Ameur and Goyet (2006). Using the data obtained in our study for Cant and the water flux flowing out the Mediterranean Sea proposed by Baschek et al. (2001), it can be calculated the amount of Cant exported through the Strait of Gibraltar. The estimated Cant output is 50.8 kmol s^{-1} (1.6×10^{12} mol C yr^{-1}). This amount is in the same order of magnitude of the 88 ± 8 kmol s^{-1} (2.8×10^{12} mol C yr^{-1}) estimated by Alvarez et al. (2005) for the Cant exported northward with the MW into the North Atlantic. Once the Mediterranean Water cross the Strait of Gibraltar, part of this amount of Cant will be exported to the east by horizontal circulation (known as Meddies) and other part will travel northward and will be incorporated into the North Atlantic scheme circulation at intermediate levels. The percentage of each one as well as the temporal evolution of the Mediterranean outflow water are some of the question to resolve in order to achieve a better understanding of the anthropogenic uptake capacity by the ocean.

4. Conclusion

Given the key role of the Mediterranean Outflow in the global carbon budget, a better understanding is required of the carbonate system variability as the Outflow passes through the Strait of Gibraltar toward the Atlantic Ocean. The vertical distribution of the inorganic carbon and oxygen are highly dependent both on the position of the interface between the main water bodies interacting in the Strait, and on the intensity of the vertical mixing processes associated with the spring-neap tidal cycle. An increase in DIC and AOU with depth has been clearly identified, resulting from the larger carbon content budget of the Mediterranean Water as a consequence of the intense remineralization processes taking place in the Mediterranean basin (Dafner et al., 2001b; Bethoux et al., 2005). Tidal action causes the Strait to behave as a deep-water pulsating area, the intensity of which is a function of various fluctuation phenomena, such as the internal hydraulic jump and the arrested internal waves over the Camarinal Sill. As a consequence, the upwelling of deep water on the Camarinal Sill at high water causes an increase in the DIC and AOU in the upper water column; this water is subsequently advected to the eastern section and causes higher DIC and AOU concentrations in the eastern area. Although several authors (Gómez et al., 2000; Macías et al., 2006) have highlighted the effect of the nutrient input to the upper layer on the enhanced primary production of the eastern section, both the inorganic carbon pool and oxygen present a highly conservative behaviour, suggesting that hydrodynamics rather than biological processes are the main mechanisms involved in its variability. In any case, the high tidal variability on the inorganic carbon dynamics accounted in the Strait explains the difficulties for obtaining a accurate value for the average inorganic carbon and anthropogenic carbon exchange at the Strait of Gibraltar.

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