



Tidal-induced inorganic carbon dynamics in the Strait of Gibraltar

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ARTICLE INFO

Article history:

Received 31 July 2007

Received in revised form

18 April 2008

Accepted 30 April 2008

Available online 10 May 2008

Keywords:

Inorganic carbon

AOU

Tidal mixing

Carbon exchange

Strait of Gibraltar

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.

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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 CO₂ 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 CO₂ (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 *Mytilus*. 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

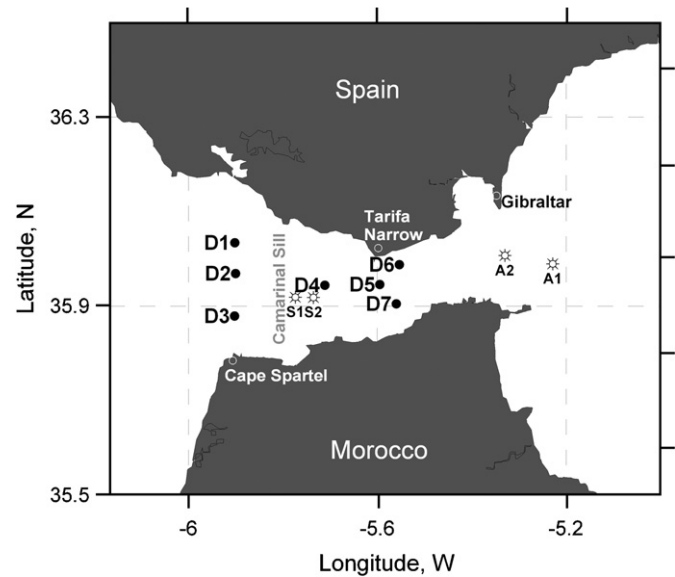


Fig. 1. Map of the Strait of Gibraltar showing the locations of the sampling stations. The fixed tidal stations (S1, S2, A1 and A2) are indicated as (⊠) and the locations for the descriptive samplings (D1–D7) are indicated as (●).

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.

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 $13.0\text{--}13.5^\circ\text{C}$ and $38.2\text{--}38.5$), the Surface Atlantic Water (SAW) is warm and fresh (temperature and salinity ranges, respectively, between $19.0\text{--}20.0^\circ\text{C}$ and $36.4\text{--}36.2$) and the North Atlantic Central Water (NACW; temperature and salinity ranges, respectively, between $13.5\text{--}14^\circ\text{C}$ and $35.6\text{--}36$) 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

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