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Distribution and transport of natural and anthropogenic CO_2 in the Gulf of Cádiz

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Abstract

During the 2002 SEMANE cruise (16–22 July), we sampled seawater for total alkalinity (TA) and total inorganic carbon (TCO_2) measurements. In this area six water masses are clearly identified by their different chemical properties: (1) Spanish Coastal Water (SCW), (2) North Atlantic Surface Water (NASW), (3) North Atlantic Central Water (NACW), (4) North Atlantic Deep Water (NADW), (5) Lower Deep Water (LDW), and (6) Mediterranean Water (MW). TA and TCO_2 concentrations were higher in the Mediterranean Sea than in the Atlantic Ocean. At this time period, the surface water of the Gulf of Cádiz was acting as a slight source of CO_2 for the atmosphere with a net CO_2 flux of $18.6 \pm 4\,\mathrm{mmol\,m^{-2}\,day^{-1}}$.

The Mediterranean Sea is a significant CO_2 source for the Atlantic Ocean. The net export of inorganic carbon from the Mediterranean Sea to the Atlantic Ocean, ranges from 0.02 to $0.07\,\mathrm{pg\,C\,yr^{-1}}$ and strongly depends upon the water masses transport. As expected, the Mediterranean Sea contains higher concentrations of anthropogenic carbon than the Atlantic Ocean waters. The estimated input of anthropogenic carbon from the outflowing Mediterranean Sea waters to the Gulf of Cádiz ranges from 0.032 to $0.066\,\mathrm{pg\,C\,yr^{-1}}$. This anthropogenic CO_2 transport into the Atlantic Ocean represents up to 4.8% of the TCO_2 outflowing from the Mediterranean Sea through the Gibraltar Strait.

This study shows that the Mediterranean Sea is a significant source of anthropogenic carbon to the Atlantic Ocean and that the complex circulation in the Gulf of Cádiz facilitates the sequestration of this anthropogenic carbon below the mixed-layer depth, thus illustrating the importance of the contribution of the Mediterranean Sea in the sequestration and storage of anthropogenic carbon into the ocean.

Keywords: Anthropogenic carbon; Gulf of Cádiz; TCO_2 transport; Mediterranean Sea

1. Introduction

It has long been recognized that the oceans represent a sink of carbon dioxide for the atmosphere, absorbing about 30–40% of the anthropogenic carbon released into the atmosphere (Brewer, 1978; Chen and Millero, 1979; Siegenthaler and Sarmiento, 1993; Feely et al., 2001; Sarmiento and Gruber, 2002; Takahashi et al., 2002). However, little is known about the role of the marginal seas (like the Mediterranean Sea) and of the continental shelves in the global carbon cycle. In the shelf area, the processes that affect the CO_2 system (phytoplankton activity, atmosphere–ocean exchange,

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deep water formation) are complex and further submitted to river discharge and tidal forcing.

The Gulf of Cádiz is a domain of considerable interest since it connects the Mediterranean Sea with the Atlantic open ocean and receives the outflowing Mediterranean seawater through the Gibraltar Strait. It therefore plays an important role in the North Atlantic circulation and climate in general (Reid, 1979; Price and O'Neil-Baringer, 1994; Mauritzen et al., 2001). The physical processes of these areas are well documented (Madelaine, 1970; Ambar et al., 1976; Lacombe and Richez, 1982; Bryden et al., 1994; Carton et al., 2002). However, studies of carbon exchange through the Gibraltar Strait and their impact on the Eastern North Atlantic Ocean are relatively scarce (Parrilla et al., 2002). Only few biogeochemical studies have been done in this area (Minas et al., 1991; Minas and Minas, 1993; Echevarria et al., 2002), especially for the CO_2 system (Dafner et al., 2001; Santana-Casiano et al., 2002; González-Dávila et al., 2003).

In response to the increased interest in the global carbon cycle and climate change, measurements of total alkalinity (TA) and total dissolved inorganic carbon (TCO_2) were included into the SEMANE (Sortie des Eaux Méditerranéennes en Atlantique Nord Est) project conducted in the Gulf of Cádiz in July 2002.

In this paper, we present new TA and total dissolved inorganic carbon (TCO_2) data in this area. We then estimate the role of the Gulf of Cádiz as a source of CO_2 during this period. We further present an estimate of the inorganic carbon transport through the Strait of Gibraltar as well as the repartition of the natural and anthropogenic carbon in the Mediterranean outflowing waters.

2. Materials and methods

2.1. Sampling strategy

From July 16 to 22, 2002, during the SEMANE cruise on the R.V. Thalassa, 3 stations were sampled for the hydrology and water chemistry parameters (salinity, dissolved oxygen, nutrients and CFCs). One hundred and eighty discrete seawater samples also were collected at 22 of these stations for TA and TCO_2 measurements. They were collected throughout the water column using a CTD Rosette sampler with conventional Niskin bottles, along three sections (Fig. 1A and B): a North–South (N–S) section (33.5–37°N), from the Moroccan coast to the Spanish coast, an East–West (E–W) section from the entrance of the Strait of Gibraltar to 7.5°W, and a N–S section at the entrance of the Strait. Temperature and salinity continuous profiles were obtained from the CTD-O_2 Neil-Brown Mark III.

For TA and TCO_2 measurements, seawater was collected into 500-ml standard borosilicate glass screw cap bottles following the procedure described in the DOE Handbook (DOE, 1994). The samples were poisoned with 100 µl of saturated mercuric chloride solution, stored in the dark at a temperature of 4 °C and then analyzed at the University of Perpignan, BDSI Laboratory (Biophysique et Dynamique des Systèmes Integrés).

2.2. Measurements

TA and TCO_2 measurements were performed using a potentiometric method as described in the DOE handbook of methods for CO_2 analysis (DOE, 1994). Titrations of seawater samples were performed in a closed cell maintained at constant temperature (25 ± 0.1 °C) by a thermostated water bath. The ionic strength of the hydrochloric acid solution (0.1 N) used for the titrations was adjusted with NaCl in order to be similar to that of the samples (salinity ranged from 35 to 38.2). The hydrochloric acid solution was added with an automatic burette (ABU 901, radiometer). The burette and the pH-meter were interfaced with a computer using data-acquisition software. TA and TCO_2 were estimated using a non-linear least-squares approach similar to that used by Dickson (1981). The accuracy of the titration system (2 µmol kg^{-1} for both TA and TCO_2 measurements) was determined using Certified Reference Materials (CRMs, batch 35, provided by A. G. Dickson, Scripps Institution of Oceanography). The precision of the measurements, evaluated by duplicate analyses, was estimated to be 3 and 2 µmol kg^{-1} for TA and TCO_2, respectively. These accuracies and precisions are similar to those described in the DOE handbook of methods for CO_2 analysis (DOE, 1994).

3. Results and discussion

3.1. Hydrology in the Gulf of Cádiz

A classical model of water exchange at the Strait of Gibraltar suggests that two main water masses