Marine Chemistry 121 (2010) 236–245

Contents lists available at ScienceDirect

Marine Chemistry

journal homepage: www.elsevier.com/locate/marchem

Distributions of carbonate properties along the water column in the Mediterranean Sea: Spatial and temporal variations

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ARTICLE INFO

Article history:
Received 28 May 2009
Received in revised form 8 April 2010
Accepted 21 May 2010
Available online 27 May 2010

Keywords:
Total alkalinity
pH
Anthropogenic CO_2
Mediterranean Sea
Southern Tyrrhenian Sea

ABSTRACT

Surface and water column measurements of the total alkalinity and the pH were recorded in the Mediterranean Sea and in the Southern Tyrrhenian Sea from May–June 2007 and from November 2006 and February 2008, respectively. The measurements were conducted within the framework of the Italian VECTOR Research Project activities.

The total alkalinity was measured using a potentiometric titration with an open cell system. The pH was also determined using a potentiometric method, with a combination of glass/reference electrode with an NTC temperature sensor. The total alkalinity varied linearly with the salinity in the Mediterranean Sea and the measure ranged between 2431 and 2638 μmol kg^{-1}, with the lowest values in the upper layer of the westernmost data stations (2431–2439 μmol kg^{-1}). This pattern resulted from the influence of less salty water with low-alkalinity intruding from the nearby Atlantic waters. With respect to the seasonal variation, the data collected in the Southern Tyrrhenian Sea did not have any statistically significant differences for the alkalinity parameter in the water column layers. The measured pH exhibited high and variable values in the surface layer and an increasing gradient from the western to the eastern Mediterranean data collection stations, particularly at intermediate depths around 300–500 m. The minimum pH and the maximum of the total alkalinity were commonly found at mid-depth in correspondence of the core of Levantine Intermediate Water.

The pCO_2 values were calculated from the direct measurements of the alkalinity and the pH. During the summer of 2007, the pCO_2 in the surface water of the Mediterranean was, on average, above the equilibrium with the atmospheric pCO_2, thus implying that the CO_2 was escaping the sea. Seasonal measurements at the VTM station in the Southern Tyrrhenian Sea indicated that the pCO_2 surface values ranged from 323 to 430 ppm, with the lowest values in February 2007 and 2008, when the VTM station represented a sink for the atmospheric CO_2. The Tracer combining Oxygen, inorganic Carbon and total Alkalinity (TrOCA) was used to estimate the distribution of the anthropogenic CO_2. The results show that the entire water column has already been invaded by the anthropogenic CO_2 throughout the Mediterranean Sea. Generally, the concentrations of the anthropogenic CO_2 in the intermediate and deep layers were higher than those measured in the Atlantic waters.

1. Introduction

The Mediterranean Sea represents 0.8% of the global oceanic surface. The Sicily Channel divides the Mediterranean into the Western and Eastern basin, but its structure is overall much more complex. There are many sub basins throughout that are connected by means of variable depth channels, inputs of fresh water areas and dense water formations or upwelling areas.

The role of the Mediterranean Sea in the global carbon cycle has been a subject of interest for a number of years. Nevertheless, little is known, for instance, about its role as a source or a sink for the atmospheric CO_2. This lack of knowledge is due to the generally poor sampling of the Mediterranean for the parameters that are essential to understanding the carbonate system, in particular, the pH, the total alkalinity (A_T), the total inorganic carbon (C_T) and the partial pressure of CO_2 (pCO_2). The limited published measurements originate from the western Mediterranean (Millero et al., 1979), in particular from the DYFAMED site in the Ligurian Sea (Bégovic and Copin-Montégut, 2002; Copin-Montégut and Bégovic, 2002; Marty, 2002; Copin-Montégut et al., 2004; Touratier and Goyet, 2009), the Gulf of Cadiz (Aït-Ameur and Goyet, 2006), the Alboran Sea (Copin-Montégut, 1993), the Catalan Balearic Sea (Delgado and Estrada, 1994) and the Gibraltar region (Santana-Casiano et al., 2002; Sempere et al., 2003). These measurements indicate that the Mediterranean Sea acts as a sink of organic carbon and a source of inorganic carbon to the Atlantic Ocean (Dafner et al., 2001). Some pH and A_T data are also available for the eastern basin and can be found in the MEDAR/MEDATLAS database (2002, http://www.ifremer.fr).

Basin-scale estimates of the CO_2 air–sea flux in the Mediterranean have only been produced indirectly as the residual after all others variables in the carbon budget have been determined. However, there is a large uncertainty concerning the magnitude and the direction of this flux.

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doi:10.1016/j.marchem.2010.05.003

The C_T, A_T and carbon dioxide fugacity (fCO_2) mixed-layer fields were reconstructed for the Mediterranean Sea, from the 1960s to the 1990s, using the MEDAR/MEDATLAS database (Louanchi et al., 2009). The results showed that the Mediterranean Sea transformed from a net CO_2 source for the atmosphere during the 1960s (0.62 Tg C $year^{-1}$) to a net CO_2 sink during the 1990s (21.98 Tg C $year^{-1}$) following a balance between decadal temperature anomalies and primary production. Moreover, the upper ocean carbon dynamics of the entire Mediterranean Sea were simulated for the period from 1998 to 2004 with an array of 1D coupled physical–biogeochemical models (D'Ortenzio et al., 2008). The C_T and the A_T vertical profiles were derived from the MEDAR/MEDATLAS climatological salinity profiles using the relationships derived by Copin-Montégut and Bégovic (2002), while the atmospheric pCO_2 was derived from the monthly measurements of the CO_2 concentration at the Lampedusa Island station (Chamard et al., 2003). The results show that, over the study period, the Mediterranean Sea is close to equilibrium with the atmosphere, acting as a slight sink for the atmospheric CO_2.

The properties of the carbonate system in natural waters can be characterized by measuring the pH, the A_T, the C_T and the pCO_2, which is the partial pressure of CO_2 in wet (100% water-saturated) air that is at equilibrium with the sample, and it is proportional to the dissolved CO_2 similar to the fCO_2. The fugacity is about 0.3% to 0.4% lower than the partial pressure over the range of interest, due to the non ideality of CO_2. The A_T and the C_T are independent of the temperature and the pressure, while the fCO_2, the pCO_2 and the pH are not. The knowledge of any two of these parameters, along with the temperature, salinity, pressure, the concentrations of other constituents of the seawater, and the relevant equilibrium constants, allows for the determination of the other two parameters.

In 2006–2008 the Italian VECTOR (VulnErability of the Italian coastal area and marine Ecosystems to **C**limatic changes and Their rOle in the Mediterranean caRbon cycles) Project was carried out. One of the general objectives of the WP 8 Carpel within the work project was to study the role that the pelagic regions in the Mediterranean Sea have in the carbon cycle.

A branch of the WP8 Carpel was carried out at the basin scale cruise in the Mediterranean Sea, while another branch was devoted to the study of the Southern Tyrrhenian, which plays an important role in the circulation of water in the Mediterranean Sea, because several water masses cross this basin in spite of its marginal position (Budillon et al., 2009). Unfortunately, at present, the effects of the physical processes on the biogeochemical parameters are poorly understood due to a lack of adequate investigation. Most studies have focused on the distribution of nutrients and photosynthetic pigments (Ribera d'Alcalà et al., 2009; Decembrini et al., 2009).

In this paper, we present the A_T and the pH data that were collected in the framework of the WP8 Carpel-VECTOR Project activities. We examine the spatial variability of the A_T and the pH in the Mediterranean Sea and the seasonal variability of these parameters in the Southern Tyrrhenian Sea. In particular, this study provides, for the first time, a seasonal reporting with regard to the carbonate parameters in the Southern Tyrrhenian Sea.

Moreover, we calculate the pCO_2 from the A_T and the pH data to evaluate its Mediterranean basin scale surface distribution over the investigated period.

Finally, we estimate the distribution of the anthropogenic CO_2 using the TrOCA approach (Touratier et al., 2007).

2. Methods

2.1. Sample collection

From 28 May to 27 June 2007 the R/V *Universitatis* (owned by the Italian Consortium of University for the Marine Sciences — CoNISMa) and the R/V *Urania* (owned by the Italian National Council for the Research — CNR) occupied a cruise track (TRANSMED cruise) extending from the Atlantic Ocean to the Eastern Mediterranean Sea. Ten stations (1 Atlantic and 9 Mediterranean) were occupied to describe the hydrology and the biogeochemical parameters of the water column (Fig. 1a). A total of 150 seawater samples was collected for the pH and the A_T measurements. Some of the samples taken by the Atlantic station were lost due to collection and storage inconveniences.

Five multidisciplinary cruises were completed between November 2006 and February 2008 (November 2006; February, April and July 2007 and February 2008) in the Southern Tyrrhenian Sea. A total of 317 seawater samples was collected at the VTM fixed station (39°30′ N, 13°30′E) and along a transect extending from the Gulf of Naples to the VTM station (Fig. 1b). The VTM station corresponds to station V2, which was sampled during the TRANSMED cruise.

Conductivity temperature depth (CTD) casts were performed using a Sea Bird Electronics SBE 911*plus* probe with double temperature, conductivity fluorescence and oxygen sensors that was flushed at a constant rate. The CTD was coupled to a Carousel water sampler SBE 32.

The water samples that were used for the pH and the A_T analyses were collected from 12 L Niskin bottles in a 500-mL borosilicate glass bottles, using standard operating procedures described in the DOE, 2007 handbook (DOE, 2007). These water samples were poisoned with saturated $HgCl_2$ solution to stop biological activity from altering the carbon distributions in the sample containers before analysis. Samples were stored in dark, cold (+4 °C) conditions and analyzed at the Department of Chemistry and Industrial Chemistry at the University of Genoa.

2.2. A_T and pH measurements

The A_T (μmol kg^{-1} seawater) was measured using a potentiometric titration system with a Metrohm 806 Exchange Unit and a 702 SM Titrino dosimat following the methods described in the DOE, 2007 handbook (DOE, 2007).

Each sample (165 g of seawater) was placed in an open cell where it was titrated with a solution of hydrochloric acid in a two-stage titration. The sample, maintained at constant temperature (25 ± 0.1 °C) by a thermostated water bath, was first acidified to a pH between 3.5 and 4.0 with a single aliquot of titrant (~3.7 mL of HCl 0.1 M), then stirred for 10 min to allow for the escape of the CO_2 that was evolved. The titration continued until a pH of about 3.0 had been reached. The ionic strength of the hydrochloric acid solution was adjusted with NaCl in order to be similar to that of the samples (salinity range 35–39.4). The progress of the titration was monitored using a pH glass electrode/reference electrode cell, and the total alkalinity was computed from the titrant volume and e.m.f. measurements using a non-linear least-squares approach similar to that proposed in the DOE, 1994 handbook (DOE, 1994).

The pH was determined using a potentiometric method that employed a combination glass/reference electrode with an NTC temperature sensor. The total hydrogen ion concentration measurements were expressed in the pH scale ($[H^+]$ as moles per kilogram of seawater, pH_T). The TRIS buffer used to standardize the pH electrode was prepared according to the DOE, 2007 handbook (DOE, 2007). The salinity of the TRIS buffer was 38. Both the TRIS buffer and the seawater samples were brought to the same temperature (25 ± 0.1 °C) using a thermostated water bath before the measurements were conducted.

The reference material certified for the A_T and the C_T (Batch #79, provided by A.G. Dickson, Scripps Institution of Oceanography, USA) was analyzed twice a week. The accuracy of the A_T measure was ±4 μmol kg^{-1} and the standard deviation ±2 μmol kg^{-1}. The calculated pH_T value of this material ranged between 7.893 and 7.919 depending on the constants values used. The precision of the pH measurement was ±0.007 units.

2.3. pCO_2 calculation

Since direct measurements of the pCO_2 had not been carried out, we used the A_T and the pH to calculate this parameter. For this