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Acidification of the Mediterranean Sea from anthropogenic carbon penetration

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ABSTRACT

This study presents an estimation of the anthropogenic CO_2 (C_{ANT}) concentrations and acidification ($\Delta pH = pH_{2013} - pH_{pre\text{-}industrial}$) in the Mediterranean Sea, based upon hydrographic and carbonate chemistry data collected during the May 2013 MedSeA cruise. The concentrations of C_{ANT} were calculated using the composite tracer TrOCA. The C_{ANT} distribution shows that the most invaded waters (>60 μmol kg^{-1}) are those of the intermediate and deep layers in the Alboran, Liguro- and Algero-Provencal Sub-basins in the Western basin, and in the Adriatic Sub-basin in the Eastern basin. Whereas the areas containing the lowest C_{ANT} concentrations are the deep layers of the Eastern basin, especially those of the Ionian Sub-basin, and those of the northern Tyrrhenian Sub-basin in the Western basin. The acidification level in the Mediterranean Sea reflects the excessive increase of atmospheric CO_2 and therefore the invasion of the sea by C_{ANT}. This acidification varies between -0.055 and -0.156 pH unit and it indicates that all Mediterranean Sea waters are already acidified, especially those of the Western basin where ΔpH is rarely less than -0.1 pH unit. Both C_{ANT} concentrations and acidification levels are closely linked to the presence and history of the different water masses in the intermediate and deep layers of the Mediterranean basins. Despite the high acidification levels, both Mediterranean basins are still highly supersaturated in calcium carbonate minerals.

1. Introduction

The Mediterranean Sea is a land-locked relatively small marine ecosystem that represents approximately 0.8% of the world's ocean surface area (EEA, 2002; UNEP/MAP-Plan Bleu, 2009). It is connected to the Atlantic Ocean via the Strait of Gibraltar; it receives surface Atlantic waters (AW) flowing Eastwards and exports intermediate waters to the Atlantic contributing thus to the global overturning circulation (Bergamasco and Malanotte-Rizzoli, 2010). The Mediterranean Sea is considered a small-scale ocean with high environmental variability and steep physicochemical gradients within a relatively limited region (Béthoux et al., 1999). The circulation is characterized by the presence of sub-basin gyres, intense mesoscale activity and a strong seasonal variability related to highly variable atmospheric forcing strongly affected by orographic constraints (Malanotte-Rizzoli et al., 1997; Millot, 1999).

The Mediterranean Sea is very special in terms of CO_2 dynamics, global carbon cycle and anthropogenic CO_2 drawdown and storage. Its waters are characterized by high alkalinity (~2600 μmol kg^{-1}; Schneider et al., 2007; Hassoun et al. 2015b) compared to other oceans. In addition, the Mediterranean waters are slightly more basic (less than a quarter of a pH unit) than the Atlantic waters at corresponding depths (Millero et al., 1979; CARINA project data collection—version 1.2, http://odv.awi.de/en/data/ocean/carina_bottle_data/). Thus, through the simple acid-base reaction, CO_2 is attracted more easily in a slightly more basic seawater than in a slightly less basic seawater. Moreover, its warm and high alkalinity waters, characterized thus by low Revelle factor, are prone to absorb CO_2 from the atmosphere and be transported to the interior by the active overturning circulation (Álvarez, 2011). The anthropogenic CO_2 inventory for the Mediterranean has been estimated to be 1.7 PgC, thus indicating that this marginal sea has higher C_{ANT} concentrations than the global average, mainly determined by the surprisingly high anthropogenic carbon content of the Eastern Mediterranean Sea (Sabine and Tanhua, 2010; Schneider et al., 2010).

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However the role of marginal seas (like the Mediterranean) as a sink of atmospheric CO_2 has been understudied because they have been considered to play a minor role in absorbing and storing anthropogenic CO_2 due to their small surface area (Lee et al., 2011). Several scientists from various research institutes have recently measured the carbonate system properties (pH; total alkalinity, A_T; total dissolved inorganic carbon, C_T; and partial pressure of CO_2, pCO_2) in the Mediterranean Sea. The majority of these studies have been performed in the Western Mediterranean basin (Alekin, 1972; Millero et al., 1979; Copin-Montégut, 1993; Bégovic and Copin-Montégut, 2002; Copin-Montégut and Bégovic, 2002; Copin-Montégut et al., 2004; De Carlo et al., 2013), in the Catalano-Balearic region (Delgado and Estrada, 1994), in the Strait of Gibraltar and the Gulf of Cadiz (Dafner et al., 2001; Santana-Casiano et al., 2002; Huertas et al., 2006; De la Paz et al., 2008; De la Paz et al., 2009; Ribas-Ribas et al., 2011). Whereas fewer ones have been achieved in the other Mediterranean Sea areas: Sicily strait (Chernyakova, 1976); Eastern basin (Schneider et al., 2007; Pujo-Pay et al., 2011). Moreover, few attempts have been dedicated to estimate the C_{ANT} penetration in the Mediterranean and the C_{ANT} exchanges with the Atlantic (Aït-Ameur and Goyet, 2006; Huertas et al., 2009; Flecha et al., 2012). Data attained in the Strait of Gibraltar and the Gulf of Cadiz by the abovementioned studies have indicated that a net export of total inorganic carbon occurs from the Mediterranean to the Atlantic, while there have been contradicting results about the sign of the net C_{ANT} that is exchanged between both basins with the exchange being markedly sensitive to the interface definition between the inflowing and the outflowing water bodies and the method considered for C_{ANT} estimation. However, the role of the Mediterranean outflowing waters as an important contributor of the North Atlantic C_{ANT} inventories has been well recognized (Ríos et al., 2001; Álvarez et al., 2005; Aït-Ameur and Goyet, 2006; Huertas et al., 2009; Flecha et al., 2012). To date, studies devoted to the estimation of the C_{ANT} in the Eastern basin are still very scarce (Schneider et al., 2010; Rivaro et al., 2010; Krasakopoulou et al., 2011).

In order to quantify the ocean capacity to sequester C_{ANT} as well as the increase of acidification, the C_{ANT} should be accurately known. Since anthropogenic CO_2 cannot be measured directly, as it cannot be chemically discriminated from the bulk of dissolved inorganic carbon, several independent approaches for its indirect estimation have been developed. Using a common and a high quality dataset available for the Atlantic, the Antarctic, and the Arctic Oceans, Vázquez-Rodríguez et al. (2009) performed an inter-comparison exercise of the C_{ANT} concentrations estimated by the five most recent models (ΔC^*, Gruber et al., 1996; C^0_{IPSL}, Lo Monaco et al., 2005; TTD, Waugh et al., 2006; TrOCA, Touratier et al., 2007; and the φC^0_T, Vázquez-Rodríguez et al., 2009). They concluded that all methods give similar spatial distributions and magnitude of C_{ANT} between latitude 60°N–40°S, and that some differences are found among the methods in the Southern Ocean and the Nordic Seas. The C_{ANT} total inventories computed with the TrOCA approach for the whole Atlantic Ocean is 51 PgC; this clearly shows that this approach does not over- or underestimate C_{ANT} since it is well in the range of the inventories computed by the four other methods (from 47 to 67 PgC). Several studies have estimated the C_{ANT} using the TrOCA approach in the Mediterranean Sea (Touratier and Goyet, 2011), in the Otranto Strait (Krasakopoulou et al., 2011), in the Bay of Biscay (Castaño-Carrera et al., 2012) and in the Iberian Sub-basin (Fajar et al., 2012). The differences between the C_{ANT} estimations from the φC^0_T method and those from the TrOCA method are very small (-0.77 ± 4.4 μmol kg^{-1}, $n=301$), and both C_{ANT} estimates present the same spatial variations (Castaño-Carrera et al., 2012). Thus, these recent comparisons testify that the TrOCA method provides similar spatial variations as other models and a reasonable upper limit of C_{ANT} estimates (within the uncertainty of the results). Therefore, here this simple and accurate method is chosen to estimate the C_{ANT}.

Although there are already some quantifications of the C_{ANT} in the Mediterranean Sea and some estimations of the acidification evolution in its waters (Touratier and Goyet, 2009; Rivaro et al., 2010; Schneider et al., 2010; Touratier and Goyet 2011; Palmiéri et al., 2015), there is still a lack of data to get a complete picture of the evolution of the C_{ANT} and the acidification in this semi-enclosed sea. Thus, the present study has the following objectives: (1) to quantify the C_{ANT} and to examine its trends in the Mediterranean Sea based on the new data of the MedSeA (Mediterranean Sea Acidification In A Changing Climate) cruise collected during May 2013; (2) to characterize the different Mediterranean water masses based on the C_{ANT}, and (3) to assess the acidification state of the Mediterranean waters.

1.1. *Oceanographic features of the Mediterranean Sea*

At the Strait of Gibraltar, the AW inflows at the surface layer of the Mediterranean Sea. This water mass flows Eastwards at shallow depth into the Tyrrhenian Sub-basin, then into the Eastern Mediterranean basin via the Strait of Sicily. The salinity of the AW increases along its pathway from 36.5 to >38 due to net evaporation and is then described as Modified Atlantic Water (MAW; Wüst, 1961). The surface water in the Western Mediterranean basin is supplied by less dense AW through the Strait of Gibraltar (Stöven and Tanhua, 2014).

The heat loss of the MAW during winter time along with evaporation leads to a sufficient increase of density to form the Levantine Intermediate Water (LIW) in the Eastern Mediterranean basin (Wüst, 1961; Brasseur et al., 1996). The main volume of the LIW flows back Westwards over the shallow sill between Sicily and Tunisia entering the Tyrrhenian Sub-basin along the continental slope of Italy forming a maximum-salinity layer in a few hundred meters depth (Wüst, 1961). Moreover, the mid-depth waters are also fed by the warm and saline waters (Cretan Intermediate Waters, CIW) formed in the Aegean Sub-basin. These waters outflow through the Western Cretan Straits and circulate in the major part of the intermediate layers of the Ionian Sub-basin. The LIW is a dominant water mass which circulates through both the Eastern and Western basins and is the principal component of the efflux from Gibraltar to the Atlantic Ocean (Roether et al., 1998) with weak contribution of other Mediterranean deep waters [Tyrrhenian Deep Waters (TDW) and Western Mediterranean Deep Waters (WMDW)].

The Mediterranean Sea is a site for deep water mass formation processes. These processes take place in both the Eastern and Western basins; the deep water renewal time has been estimated to be 20–40 years in the Western basin (Stratford et al., 1998) and about 100 years in the Eastern basin (Roether et al., 1996; Stratford and Williams, 1997; Stratford et al., 1998). In the Eastern basin, parts of the LIW enter the Adriatic Sub-basin via the Strait of Otranto, where it serves as an initial source of the $EMDW_{Adr}$ (Stöven and Tanhua, 2014). The formation of $EMDW_{Adr}$ in the Adriatic Sub-basin is based on interactions between the LIW and water masses coming from its northern part as well as the natural preconditioning factors, e.g. wind stress and heat loss (Artegiani et al., 1996a, b; Astraldi et al., 1999; Lascaratos et al., 1999). The $EMDW_{Adr}$ flows then over the sill of Otranto into the Ionian Sub-basin intruding the bottom layer and thus representing a main source of the Eastern Mediterranean Deep Water (EMDW) (Schlitzer et al., 1991; Roether and Schlitzer, 1991). However, in the 1990s, the “engine” of the closed thermohaline cell switched to the Aegean Sub-basin (Bergamasco and Malanotte-Rizzoli,