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Anthropogenic CO_2 in a dense water formation area of the Mediterranean Sea

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ABSTRACT

There is growing evidence that the on-going ocean acidification of the Mediterranean Sea could be favoured by its active overturning circulation. The areas of dense water formation are, indeed, preferential sites for atmospheric carbon dioxide absorption and through them the ocean acidification process can quickly propagate into the deep layers.

In this study we estimated the concentration of anthropogenic CO_2 (C_{ant}) in the dense water formation areas of the middle and southern Adriatic Sea. Using the composite tracer TrOCA (Tracer combining Oxygen, inorganic Carbon, and total Alkalinity) and carbonate chemistry data collected throughout March 2013, our results revealed that a massive amount of C_{ant} has invaded all the identified water masses. High C_{ant} concentration was detected at the bottom layer of the Pomo Pit (middle Adriatic, 96.8 ± 9.7 µmol kg^{-1}) and Southern Adriatic Pit (SAP, 85.2 ± 9.4 µmol kg^{-1}), associated respectively with the presence of North Adriatic Dense Water (NAdDW) and Adriatic Dense Water (AdDW). This anthropogenic contamination was clearly linked to the dense water formation events, which govern strong CO_2 flux from the atmosphere to the sea and the sinking of dense, CO_2-rich surface waters to the deep sea. However, a very high C_{ant} level (94.5 ± 12.5 µmol kg^{-1}) was also estimated at the intermediate layer, as a consequence of a recent vertical mixing that determined the physical and biogeochemical modification of the water of Levantine origin (i.e. Modified Levantine Intermediate Water, MLIW) and favoured the atmospheric CO_2 intrusion.

The penetration of C_{ant} in the Adriatic Sea determined a significant pH reduction since the pre-industrial era (− 0.139 ± 0.019 pH units on average). This estimation was very similar to the global Mediterranean Sea acidification, but it was again more pronounced at the bottom of the Pomo Pit, within the layer occupied by NAdDW (− 0.157 ± 0.018 pH units), and at the intermediate layer of the recently formed MLIW (− 0.143 ± 0.020 pH units). Our results indicate that the Adriatic Sea could potentially be one of the Mediterranean regions most affected by the ocean acidification and also demonstrate its active role in sequestering and storing C_{ant}.

1. Introduction

Since the beginning of the Industrial Revolution, approximately 28% of the total anthropogenic carbon dioxide emissions, released into the atmosphere mainly by fossil fuels burning and land use change, has been absorbed by the world's oceans (Sabine et al., 2004; McKinley et al., 2011; Le Quéré et al., 2015), and has led to a global reduction of the sea surface pH by 0.1 units (Caldeira and Wickett, 2003; Doney et al., 2009). This process is commonly known as “ocean acidification” and it represents one of the most serious threats facing the marine ecosystems in this century (Gattuso and Hansson, 2011).

The ocean acidification process is also occurring in the Mediterranean Sea (Touratier and Goyet, 2011). Though several attempts have been made to estimate the long-term trend of pH decrease in this basin, our understanding of the ocean acidification is still relatively unclear and contradicting observations of the pH decline have been reported. Some researchers estimated a pH reduction oscillating between − 0.055 and − 0.156 units with respect to the preindustrial levels (Hassoun et al., 2015). On the other hand, other works pointed out a pH change of the bottom waters ranging from −

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0.005 and – 0.06 pH units during the same period and concluded that the ocean acidification of the Mediterranean Sea is similar to the one of the global ocean (Flecha et al., 2015; Palmiéri et al., 2015). For the northwestern area Yao et al. (2016) revealed that the surface water pH decreased at a rate of 0.003 ± 0.001 pH units per year over the 1995–2011 time-period, Geri et al. (2014) predicted a decreasing rate of 0.002 ± 0.001 pH units yr^{-1} for the next fifty years and recently Kapsenberg et al. (2016) documented at the Point B time-series station a coastal ocean acidification rate of 0.0028 ± 0.0003 pH units yr^{-1}. These findings suggest that the ocean acidification trend in the Mediterranean Sea is slightly higher than those measured in other oceanic regions and that this basin represents one of the most sensitive areas in the world to CO_2 emission increase (Yao et al., 2016). Thanks to its warm and high alkalinity water masses, characterized thus by low Revelle Factor, and to the relatively short ventilation time of its deep layers, the Mediterranean Sea is able to absorb relatively more atmospheric CO_2 than the open ocean (Touratier and Goyet, 2009, 2011; Álvarez et al., 2014). This has a negative effect on some species (Maier et al., 2012; Cerrano et al., 2013; Meier et al., 2014), even if the high alkalinity concentration of the Mediterranean Sea makes its waters oversaturated with respect to calcium carbonate minerals (Schneider et al., 2007), and hence less prone than other oceanic regions to become "corrosive" (Feely et al., 2008; Bates et al., 2009).

On a global scale, the ocean overturning circulation has been recently recognized as the primary driver of the regulation in the oceanic CO_2 uptake (DeVries et al., 2017). In the same way, the Mediterranean Sea overturning circulation and the sites of dense water formation such as the Gulf of Lion, the Aegean Sea, and Adriatic Sea could play a very important role in the sequestration of anthropogenic CO_2 and the ocean acidification of the Mediterranean Sea (Krasakopoulou et al., 2009; Schneider et al., 2010; Touratier et al., 2016). The Northern Adriatic shelf is an efficient site for carbon sequestration during dense water formation events (Cantoni et al., 2012; Turk et al., 2013; Catalano et al., 2014; Ingrosso et al., 2016a). The winter cooling of the water column affects the solubility of CO_2 and governs the vertical transport of carbon into the deep layers (Cossarini et al., 2015) contributing to the ocean acidification of the Adriatic Sea. The first evidence of this process was provided by Luchetta et al. (2010), who quantified a reduction of 0.063 pH units in the dense waters between 1983 and 2008, corresponding to a mean acidification rate of 0.0025 pH units yr^{-1}. This study, however, did not take into account the anthropogenic CO_2 concentration (C_{ant}) of the Adriatic Sea, which is a key driver controlling the ocean acidification process. Indeed, in the Mediterranean Sea the C_{ant} absorption accounts for 73% of the observed long-term trend of pH reduction, followed by water temperature (about 30%, Yao et al., 2016). Several studies quantified the C_{ant} in the Mediterranean Sea (Touratier and Goyet, 2009, 2011; Rivaro et al., 2010; Schneider et al., 2010; Krasakopoulou et al., 2011; Hassoun et al., 2015; Palmiéri et al., 2015; Touratier et al., 2016), however few of these (Krasakopoulou et al., 2011; Hassoun et al., 2015) considered the Adriatic Sea.

Since C_{ant} cannot be measured directly, as it cannot be chemically discriminated from the bulk of dissolved inorganic carbon, different approaches for its indirect estimation have been developed (Millero, 2007; Sabine and Tanhua, 2010). All the proposed methods have various advantages as well as limitations, however, as highlighted by the inter-comparison exercise of Vàzquez-Rodríguez et al. (2009), five of the most recent methods to estimate the C_{ant} (ΔC^*, Gruber et al., 1996; C^0_{IPSL}, Lo Monaco et al., 2005; TTD, Waugh et al., 2006; TrOCA, Touratier et al., 2007; φC^0_T, Vàzquez-Rodríguez et al., 2009) gave a similar spatial distribution and magnitude between latitude 60°N–40°S.

The Tracer combining Oxygen, inorganic Carbon and total Alkalinity (TrOCA) approach, proposed by Touratier et al. (2007), is a carbon-based method that calculates the concentration of C_{ant} from potential temperature, dissolved oxygen, dissolved inorganic carbon, and total alkalinity without the need of further knowledge regarding the water mass properties or water mass age tracers. In the inter-comparison of Vàzquez-Rodríguez et al. (2009), the C_{ant} estimated with the TrOCA approach for the whole Atlantic Ocean was in the range of the inventories computed by the other methods. On the other hand, some works suggested that the TrOCA approach may overestimate C_{ant} (Huertas et al., 2009; Yool et al., 2010; Ríos et al., 2010). Touratier et al. (2012) strongly criticized these previous studies of using the TrOCA in inappropriate conditions (e.g. in the surface layer) or of using unrealistic outputs of a 3D model to validate the TrOCA method. Indeed, the TrOCA has been successfully applied to several world ocean regions (Atlantic Ocean, Touratier and Goyet, 2004; Touratier et al., 2005; Southern Ocean, Lo Monaco et al., 2005; Azouzi et al., 2009; Indian Ocean, Álvarez et al., 2009), to Mediterranean Sea (Touratier and Goyet, 2009, 2011; Rivaro et al., 2010; Krasakopoulou et al., 2011; Hassoun et al., 2015; Palmiéri et al., 2015), and recently also to the deep convection area of the western Mediterranean (Touratier et al., 2016). Taking into account all the previous considerations, the results obtained with the TrOCA approach provides similar spatial variations as other methods and in general they can be considered a reasonable upper limit of the real C_{ant}. Therefore, we choose to use the TrOCA method in the Adriatic Sea, considering only the waters deeper than 150 m.

Here, we present the carbonate system properties of the different water masses of the Middle and South Adriatic Sea. Data were collected through a survey carried out during March 2013. The purposes of the study are: (1) to quantify the distribution of the C_{ant} in the intermediate and the deep waters, (2) to estimate the role of deep waters in sequestering and storing the C_{ant}, and (3) to assess the pH reduction of the Adriatic Sea since pre-industrial era.

2. Material and methods

2.1. Study area

The Adriatic Sea, the most important site of dense water production in the East Mediterranean, is a semi-enclosed basin (~800 km long and ~200 km wide) located in the northern part of the Mediterranean. It communicates with the Ionian Sea through the Strait of Otranto (75 km wide, 800 m depth) and can be divided into three main subareas: the northern Adriatic, which includes the largest shelf area of the entire Mediterranean and is limited by the 100 m isobaths; the middle Adriatic, where maximum depths (~275 m) are encountered in a depression called Pomo Pit (known also as Jabuka Pit); and the southern Adriatic, between the Gargano Peninsula and the Strait of Otranto, where the maximum depth reaches about 1250 m in the Southern Adriatic Pit (SAP).

Different water masses can be distinguished in the Adriatic Sea. The Adriatic Surface Water (AdSW) is a relatively fresh and warm water mass, which originates from the Po River runoff. It flows southward along a narrow coastal layer of the western Italian shelf and exits through the Strait of Otranto. On the eastern side of the Strait, the inflow current is composed by the Ionian Surface Water (ISW), in the upper part of the water column, and by the Levantine Intermediate Water (LIW), which usually enters in the Adriatic at depths between 200 m and 600 m and it is characterized by salinity values between 38.75 and 39.0 (Vilibić and Orlić, 2001). The source of the LIW is the Levantine basin, from where its salinity, temperature, and dissolved oxygen decrease on the way to the Adriatic Sea.

The bottom layer of the SAP is occupied by the Adriatic Dense Water (AdDW), which represents the main component of dense waters for the whole Eastern Mediterranean basin (Schlitzer et al., 1991; Roether and Schlitzer, 1991). About 82% of this water mass is formed through winter convection in the southern Adriatic, within its quasi-permanent cyclonic circulation, while the remaining part has its origin on the northern Adriatic shelf and in the middle Adriatic (Ovchinnikov et al., 1985; Bignami et al., 1990; Malanotte-Rizzoli, 1991).