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Dense water flow and carbonate system in the southern Adriatic: A focus on the 2012 event☆

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ABSTRACT

The active deep overturning circulation of the Mediterranean is emerging as one of the most effective mechanisms in transporting the atmospheric imprint on the carbon cycle to the interior of the basin. There is growing evidence that sites of dense water formation over the continental shelf, such as the Northern Adriatic Sea, play a key role in this process. Nevertheless, little is known about the inorganic carbon chemistry of the Adriatic sea, and CO_2 absorption and its fate.

The winter of 2012 experienced peculiar meteorological conditions with an extended period of cold weather with strong winds that triggered, in February, a massive formation of an extremely cold and dense (potential density anomaly >30.00 kg m^{-3}) Northern Adriatic Dense Water (NAdDW) water mass. This event provided a unique opportunity to study this process at sub-basin scale taking into account CO_2 adsorption within the NAdDW source area (the Gulf of Trieste in the northern Adriatic), and its spreading over the shelf and into the Southern Adriatic Pit. The northern Adriatic and the Gulf of Trieste, during winter, act as a CO_2 sink. The average air-sea CO_2 flux of 60 mmol m^{-2} d^{-1} estimated during the exceptional 2012 event was at least 3 times higher than the flux measured in winter 2008 when dense water was produced through the same mechanism but under less extreme conditions. In winter 2012, absorbed CO_2 resulted in the decrease of pH_{T25} down to 7.907 (− 0.034 pH_T units) and the strong evaporation induced by wind-increased total alkalinity (TA) to 2673 (+ 16 μmol kg^{-1}).

Following its formation in the North, the NAdDW plume entering the Southern Adriatic, observed in March 2012, exhibited significantly modified values. The plume was characterized by colder temperature (~ 10 °C), lower pH_{T25} (7.947 pH_T units) and higher alkalinity (2635 μmol kg^{-1}) than the surrounding water masses along the western Adriatic shelf. However, the signal of atmospheric CO_2 enrichment was weaker than in the northern Adriatic source region, as well as positive apparent oxygen utilization (AOU) values (~ 20 μmol kg^{-1}) were recorded. This is suggestive of oxygen consumption in the water mass.

Observed changes in both physical and biogeochemical properties were similar to those observed in 2008, suggesting that mixing with Levantine Intermediate Waters (LIW) was the main driver modulating the changes of AOU and inorganic carbon chemistry in both winters. The rising of pH_{T25} and AOU due to the mixing indicates that NAdDW, at its origin, was richer in atmospheric CO_2 than the LIW was, thus confirming the relevance of the Northern Adriatic Sea for CO_2 adsorption.

The study provides the first characterization of inorganic carbon chemistry, including carbonate minerals saturation states (Ω_{Ar} and Ω_{Ca}), in the bottom waters both on the slope and along the expected pathways of dense water cascading in the Adriatic Sea. Therefore, it can represent a baseline to improve the knowledge on the acidification process and impacts as well as being useful for comparison with other benthic environments.

1. Introduction

Carbon dioxide (CO_2) emitted into the atmosphere by human activities has risen to unprecedented levels since the beginning of the industrial era (annual average of atmospheric CO_2 = 398 ppm at Mauna Loa observatory in 2014, URL: http://co2now.org/current-co2/co2-now/), thus leading to the unequivocal warming of both the atmosphere and the upper ocean (IPCC et al., 2013). The atmospheric CO_2 increase has occurred with pace and extension never experienced in the last 22,000

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years. However, only 45% of CO_2 emissions of the last 250 years has remained in the atmosphere, while about 25% was captured by land and forests and 30% was trapped by the oceans (Sabine et al., 2004), resulting in a decrease of pH and carbonate ion concentration in the upper ocean: a process known as Ocean Acidification.

The spatial and temporal variability of carbonate system is receiving growing attention in the current oceanographic research in the Mediterranean Sea. However, the knowledge of the spatial and temporal variability still suffers from the paucity of good quality data, preventing an adequate resolution at regional scale(Malanotte-Rizzoli et al., 2014).

The active deep overturning circulation of the Mediterranean is emerging as one of the most effective mechanisms in transporting the atmospheric imprint on the carbon cycle to the interior of the sea (Schneider et al., 2007; Krasakopoulou et al., 2011). At present, the carbon inventory in the water column for the Mediterranean is much higher than in the world ocean (Schneider et al., 2010; Lee et al., 2011) and this basin has been identified as an important area of anthropogenic carbon storage (Álvarez et al., 2005; Aït-Ameur and Goyet, 2006).

The relatively high alkalinity of the Mediterranean makes its water masses oversaturated with respect to calcium carbonate minerals (Schneider et al., 2007) and limits the formation of "corrosive" (undersaturated) waters, as observed in several other oceanic regions (Feely et al., 2008; Bates et al., 2009). On the other hand, a high alkalinity favours CO_2 adsorption, thus for a given increase in atmospheric CO_2 concentration, the Mediterranean Sea is expected to adsorb more CO_2 leading to a sharper pH decrease (Álvarez et al., 2014).

Despite the high alkalinity level, some recent studies highlighted the vulnerability to ocean acidification of some Mediterranean species, which include planktonic organisms (Meier et al., 2014) and corals (Maier et al., 2012; Cerrano et al., 2013).

Within this scenario, the most important sites of cold dense water formation on the northern shelves of the Mediterranean Sea, i.e. the Gulf of Lion, the northern Adriatic and the Aegean Sea, are emerging as preferential sites for CO_2 adsorption and transport into the abyssal layer of the basin.

The Adriatic Sea is commonly divided into three sub basins: the northern Adriatic, a continental shelf region with depth <100 m, the middle Adriatic including the Middle Adriatic Pit (270 m depth) and the southern Adriatic basin, extending from the Pelagosa Sill to the Otranto Strait, with a depression (the Southern Adriatic Pit) of about 1200 m (Fig. 1) (Gacic et al., 2001).

An important process in the northernmost area of the shelf (depth <60 m) is the formation of the Northern Adriatic Dense Water (NAdDW). This water mass is formed in winter, because of the cooling of the entire water column and of the evaporation caused by E-NE wind (named Bora). These two concomitant effects produce a dense water at a sub basin scale, which results to be the densest (potential density anomaly, $\sigma_\theta > 29.2$ kg m^{-3}) water mass in the Mediterranean Sea, with typical salinities >38.30 and temperatures <12.0 °C (Malanotte-Rizzoli, 1991; Artegiani et al., 1997). The process of formation of NAdDW is characterized by a high interannual variability since it is also preconditioned by periods of low freshwater discharge by the rivers at least 4–5 months before its generation (Vilibić and Supić, 2005).

Once formed, the NAdDW flows on the shelf as a subsurface buoyancy-driven current in near geostrophic equilibrium (Gacic et al., 2001). In the Middle Adriatic, NAdDW splits into two main branches.

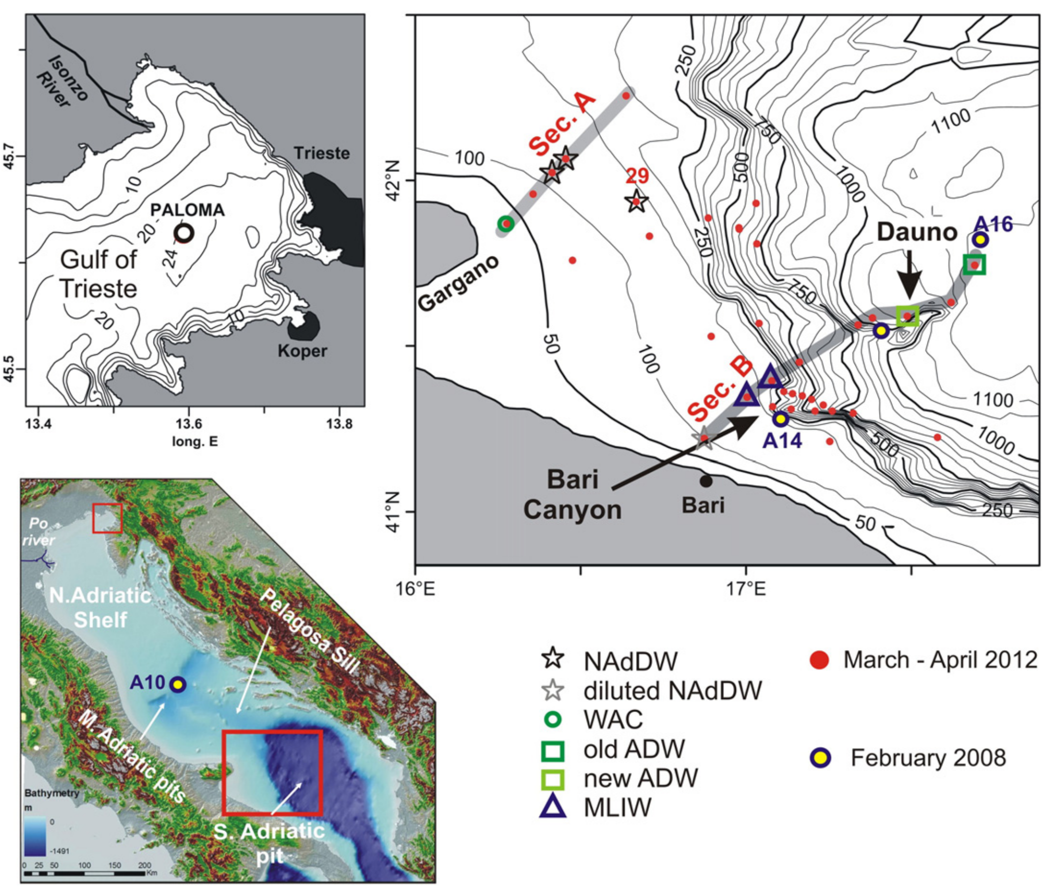

Fig. 1. Map of the Adriatic sea and the bathymetry of the two study area: the Gulf of Trieste with the PALOMA station and the western shelf of the southern Adriatic basin. Dots indicate the selected stations were nutrients and CO_2 measurements were taken: red dots stand for the ODW cruise (March 2012), blue and yellow for the February 2008 cruise. Sections (A and B) showed in Fig. 5 are indicated as grey lines; open symbols show where the core of different water masses was measured. The names of selected stations, not included in the sections, are also reported.