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Effetcs of ocean acidification of winter dense waters in the Northern Adriatic Sea (NAdDW) on the calcium carbonate saturation states.

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The gradual process of ocean acidification (OA) has been well documented for surface waters of the world ocean at several open ocean sites (time series, rate $\sim$ 0.0018 pH units y^{-1}) over the last quarter century. In contrast, very little is known in the Mediterranean Sea, because of scarcity of good quality data, in spite of its importance as the high total alkalinity (A_T) is expected to help seawater to absorb more atmospheric CO_2(Touratièr and Goyet, 2010). Even more scarce data can be referred for the North Adriatic Sea, the northernmost sub-basin of the Mediterranean. This is a wide and shallow (depth<50 m) continental shelf region experiencing strong seasonal cycles. During severe winters it can be affected either by a pronounced cooling (down to 8 ˚C) of the water column, down to the bottom, and by episodes of strong dry and cold winds (Bora). Such conditions have the potential of enhancing the atmospheric CO_2 dissolution and forming very dense waters (Northern Adriatic Dense Waters, NAdDW). The meteorological and oceanographic conditions make this area potentially high sensitive to ocean acidification. This has been recently tested by means of a preliminary comparison between past and new data sets, spanning over the last 25 years (Luchetta et al., 2010). In both datasets NAdDW water bodies with comparable physical biogeochemical properties were selected; old pH data were converted into the "total scale" and the conversion was tested against reference samples. The comparison showed a pH_T drop of 0.064 μmoliH$^+$ Kg_{sw}^{-1} accompanied by an increase of pCO_2 = 110 μatm and shifts of carbonate system species (decrease of carbonate ion = 19.6 μmoli H^+ Kg_{sw}^{-1}, increase of bicarbonate ion = 126 μmoli H^+ $Kg_{sw}^{-1}$and TCO_2 = 110.3 μmoli H^+ Kg_{sw}^{-1}) which are all characteristic of the ocean acidification process. Several, different drivers of the pH_T decrease were taken into consideration: OA was inferred as the most probable.

In support of this hypothesis, the winter CO_2 fluxes in the Gulf of Trieste have been computed (Whaninkhof, 1992) from the carbonate system properties of the time series at PALOMA station. They are equivalent to 11.6, 11.1 and 11.9 mmol m^{-2} d^{-1}(February and March 2008; January 2009) fluxes into seawater.These values point out that the amount of CO_2 adsorbed during single events of Bora can be able to change significantly the carbon chemistry of the whole water column (25 m thick), determining pH decreases of 0.006, 0.005 and 0.011 pH_T units, respectively.

In the end, we present the computed calcium carbonate saturation states in NAdDW affected by acidification, as an example of its impact. The aragonite and calcite saturation states (Ω_{Ca}, Ω_{Ar}) have been shown to control the impact of OA on many marine calcifying organisms. Ω_{Ca} and Ω_{Ar} decreased of 0.46 and 0.31, respectively, between 1983 and 2008; equivalent to 8 % decrease. In 2008 their average values (Ω_{Ca}= 5.14, Ω_{Ar}= 3.41) were still well above the limit (Ω <1.0) under which the calcium carbonate dissolves, thus indicating a good environmental status for the dense waters of the N.A. Sea, however the decreasing tendency is evident. On the contrary, the Revelle factor increased of 0.72. This again suggests a trend to the weakening of buffering capacities in the dense waters, even in spite of an increase of A_T(= 75 μmoli H^+ Kg_{sw}^{-1}) observed over the same period. All these findings might be not negligible as the Adriatic dense waters can spread far from their source to the Ionian and Eastern Med basins, thus exporting the direct impact of lowered pH on biota.