DISTRIBUTIONS OF PH_T, TOTAL ALKALINITY AND CO_2 FUGACITY IN THE ADRIATIC SEA DURING THE SESAME CAMPAIGNS, WINTER AND LATE SUMMER 2008.

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Abstract

pH_T experimental data of good quality are still scarce in the Mediterranean as in theAdriatic Sea. Here are presented the results of two repeated surveys at basin scale, conducted within SESAME project, showing significant longitudinal and seasonal variabilities of the pH_T and other carbonate system parameters.

Keywords: Adriatic Sea, Carbon, Global Change, Ph

The rapid response of the Mediterranean basin to the climate change [1] can be particularly true for the CO_2 induced acidification of seawater; as a consequence the Mediterranean area would already present significant pH drops [2] however there's still lack of good quality experimental data, witnessing such an occurrence [3], in particular in the Eastern Mediterranean Sea. The Adriatic Sea can play a very crucial role for the entire Eastern Mediterranean basin: as it issurrounded by industrialized regions, releasing carbon dioxide to the atmosphere, and during winter water mass can be so cold that CO_2 solubility pump mechanism can efficiently work increasing the dissolved CO_2 amount pushing toward acidified conditions. In addition the basin is site of dense water formation, either on the northern shallow shelf [North Adriatic Deep Water (NAdDW), and by the deep Southern Adriatic Pit, Adriatic Deep Water (ADW). Adriatic dense waters after formation usually sink and outflow through the Otranto Strait sill (750 m), which controls the export to Ionian and Eastern Mediterranean Seas [4]. In this way Adriatic dense water masses have the possibility of sequestering acidified waters and spreading around through the Eastern Mediterranean impacting on biogeochemical cycles and ecosystems. We present and discuss two datasets (pH_T, TA and other carbonate systemparameters) gathered during the surveys conducted in the frame of the SESAME EU project and providing two seasonal snapshots (February and October 2008). **Methods** pH has been measured by the spectrophotometric method as described by Dickson [5], values are expressed on the total H^+ scale (pH_T, in µmol H^+/kg_{SW}), at 25 °C, with a precision of ± 0.001 pH units. To our knowledge the dataset is the first collected with such a precision. The total alkalinity was experimentally determined (potentiometric titration, precision ± 1.0 µm/kg_{sw}), as reported by Dickson, Certified Reference Material has been used. From the experimental determination, the in situ pH_T values and all the other parameters of the carbonate system (fCO_2, TCO_2, H_2CO_3, $CO_3^=$ and HCO_3^-, Revelle, calcium carbonate solubilities Ω_{Ar}, Ω_{Ca}) can be derived (by CO2SYS program [6] **Results and discussion** Our results indicate that in winter 2008 the North Adriatic shelf, being shallow and exposed to cold dry winds (Bora), was involved in a dense water formation event on meso scale. The water column was cold (8< T < 12 °C), well homogenized and dense (σ_t > 29.4 kg/m^3), T/S properties are in agreement with those of NAdDW. It appeared also well ventilated (Apparent Oxygen Utilization mean value ~ 0 µM), still rich of nutrients (1.00<DIN<7.00 µM; 1.20< SiO_2 <5.33 µM), while the values of pH_T and allthe other carbonate system parametersexhibited a very low variability within the water column (7.917 < pH_T <7.973 pH_T units; 290.0 <fCO_2<334.6 µatm, thus resulting much lower than the equilibrium value with atmospheric CO_2 =398 µatm, mean value on measurements conducted on board). In the remaining part of the section pHT and fCO_2 values showed larger variabilities (fCO_2 between 222.4 and 424.7 µatm; pH between 7.880 and 7.960) with the highest (fCO_2> 400 µatm) and lowest (pH_T <7.880 pH_T units) values both at the bottom of the Meso Adriatic Pit, corresponding to AOU (> 65.0 µM) and nutrients (SiO_2> 6.0 µM, DIN> 5.0 µM) maxima, thus suggesting the occurrence of an older water mass affected by remineralisation processes. Generally, NAdDW water mass flows southward and accumulates at the bottom of the Meso and Southern Adriatic pits (250 and 1250 m, respectively [4] as clearly indicated by density, higher than 29.3 and 29.2 respectively, at the bottom. For what concern the southern part of the section, in February 2008 a deep convection event was observed by the deepest stations, accompanied by deep mixing (σ_t around 29.15-29.16 kg/m^3 down to 600 m) with a mean pH_T value of 7.947 ± 0.003 pH_T units homogeneously distributed from surface almost to the bottom. Total Alkalinity values varied between 2769 and 2613 µMH^+/kg_{sw}, with a mean value of 2661 µMH^+/kg_{sw}. The highest TA values were found in the northern part of the basin, due to the influence of higly carbonatic rivers. At the beginning October '08 the situation appeared completely changed: vertical stratification of density, pH_T , TA and fCO_2, was widespread over the whole Adriatic basin. Density, T, S, pH_T,TA and fCO_2 varied over a much wider range than in February, as expected in late summer season: 26.5 < σ_t < 29.45 kg/m^3, 13.0 < T < 21.0 °C, 37.250 < S < 38.800 psu, 7.850 < pH_T < 8.100 pH_T units; 2674<TA<2598 µMH^+/kg_{sw}; 319.2< fCO2 < 810.4 µatm, as the nutrients and AOU concentrations did (0.05<DIN<7.73 µM , 0.59<SiO2<10.48 µM). The northern shallow shelf region exhibited much warmer water (T>15.0°C, even at the bottom,) with higher pH_T values (7.960<pH_T<8.050 pH_T units), due to the influence of primary production, the highest fCO_2 values have been observed ($fCO2$ >450 µatm) there, such values were much higher than the equilibrium value (398 µatm) with atmospheric CO_2, thus indicating the whole northern basin was oversaturated with respect to atmospheric CO_2. Very low pH_T (<7.888 pH_Tunits) and very high <$fCO2$ values were still recognizable at the bottom of both the Meso Adriatic Pit. pH_T values within the upper euphotic layer were everywhere distinctly higher (>7.960 pH_T units) than in winter, as expected in warmer waters dominated by production processes. Again total alkalinity values (2674<TA<2598 µMH^+/kg_{sw}, mean value 2623 µMH^+/kg_{sw}) where higher in the northern part of the basin because of the discharging river loads. Concluding, the comparison between the two surveys at basin scale evidenced high spatial (longitudinal/latitudinal) and seasonal variabilities of the marine carbonate system parameters, largely exceeding the precision of the analytical methods. From a comparison of pH_T values in the cold NAdDW water mass between 1983 and 2008, an acidification of 0.063 pH_T units turns out [7]. Such findings confirm that the Adriatic Sea is sensitive to the climate change and to atmospheric gas solubilisation (as CO_2) and should merit consideration in a discussion on the impacts of OA on the biogeochemistry of the marine carbonate system.

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