

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

Anna Luchetta <sup>1\*</sup>, Giulio Catalano <sup>1</sup>, Carolina Cantoni <sup>1</sup> and Stefano Cozzi <sup>1</sup>  
<sup>1</sup> CNR ISMAR sede di Trieste - anna.luchetta@ts.ismar.cnr.it

## Abstract

$pH_T$  experimental data of good quality are still scarce in the Mediterranean as in the Adriatic 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 is surrounded 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 system parameters) 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  $\mu mol H^+/kg_{sw}$ ), at 25 °C, with a precision of  $\pm 0.001$  pH units. To our knowledge the dataset is the first collected with such a precision. The total alkalinity was experimentally determined (potentiometric titration, precision  $\pm 1.0 \mu mol/kg_{sw}$ ), 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 ( $fCO_2$ ,  $TCO_2$ ,  $H_2CO_3$ ,  $CO_3^{2-}$  and  $HCO_3^-$ , Revelle, calcium carbonate solubilities  $\Omega_{Ar}$ ,  $\Omega_{Ca}$ ) 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 ( $\sigma_t > 29.4 kg/m^3$ ), T/S properties are in agreement with those of NAdDW. It appeared also well ventilated (Apparent Oxygen Utilization mean value  $\sim 0 \mu M$ ), still rich of nutrients ( $1.00 < DIN < 7.00 \mu M$ ;  $1.20 < SiO_2 < 5.33 \mu M$ ), while the values of  $pH_T$  and all the other carbonate system parameters exhibited a very low variability within the water column ( $7.917 < pH_T < 7.973$   $pH_T$  units;  $290.0 < fCO_2 < 334.6 \mu atm$ , thus resulting much lower than the equilibrium value with atmospheric  $CO_2 = 398 \mu atm$ , mean value on measurements conducted on board). In the remaining part of the section pH and  $fCO_2$  values showed larger variabilities ( $fCO_2$  between 222.4 and 424.7  $\mu atm$ ; pH between 7.880 and 7.960) with the highest ( $fCO_2 > 400 \mu atm$ ) and lowest ( $pH_T < 7.880$   $pH_T$  units) values both at the bottom of the Meso Adriatic Pit, corresponding to AOU ( $> 65.0 \mu M$ ) and nutrients ( $SiO_2 > 6.0 \mu M$ ,  $DIN > 5.0 \mu M$ ) 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 ( $\sigma_t$  around 29.15-29.16  $kg/m^3$  down to 600 m) with a mean  $pH_T$  value of  $7.947 \pm 0.003$   $pH_T$  units homogeneously distributed from surface almost to the bottom. Total Alkalinity values varied between 2769 and 2613  $\mu MH^+/kg_{sw}$ , with a mean value of 2661  $\mu MH^+/kg_{sw}$ . The highest TA values were found in the northern part of the basin, due to the influence of highly 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:  $26.5 < \sigma_t < 29.45 kg/m^3$ ,  $13.0 < T < 21.0$  °C,  $37.250 < S < 38.800$  psu,  $7.850 < pH_T < 8.100$   $pH_T$  units;  $2674 < TA < 2598 \mu MH^+/kg_{sw}$ ;  $319.2 < fCO_2 < 810.4 \mu atm$ , as the nutrients and AOU concentrations did ( $0.05 < DIN < 7.73 \mu M$ ,  $0.59 < SiO_2 < 10.48 \mu M$ ). 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 ( $fCO_2 > 450 \mu atm$ ) there, such values were much higher than the equilibrium value (398  $\mu atm$ ) with atmospheric  $CO_2$ , thus indicating the whole northern basin was oversaturated with respect to atmospheric  $CO_2$ . Very low  $pH_T$  ( $< 7.888$   $pH_T$  units) and very high  $fCO_2$  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 ( $2674 < TA < 2598 \mu MH^+/kg_{sw}$ , mean value 2623  $\mu MH^+/kg_{sw}$ ) were 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.

## References

- 1 - Milliman J.D., Jetic L. and Sestini G., 1992. The Mediterranean Sea and Climate Change—An overview. In: Climatic Change and the Mediterranean. Jetic L., Milliman J.D. & G.Sestini (editors), 1992 Edward Arnold Publications. Kent.
- 2 - Yilmaz A. et al., 2008, Impacts of acidification on biological, chemical and physical systems in the Mediterranean and Black Seas. In: *CIESM Workshop Monographs* N° 36, F. Briand editor, CIESM, Monaco, 124 pp.
- 3 - MEDAR Group, 2002 MEDATLAS/2002 database. Mediterranean and Black Sea database of temperature salinity and bio-chemical parameters. Climatological Atlas. IFREMER Edition (4 Cd).
- 4 - Gacic M. et al. 2001. Adriatic Deep Water and Interaction with the Eastern Mediterranean Sea. In: Physical Oceanography of the Adriatic Sea. Past, Present and Future. B. Cushman-Roisin, M. Gacic, M.P. Poulain and A. Artegiani, eds, Kluwer Academic Publishers, The Netherlands, (pp. 67-109).
- 5 - Dickson, A.G., Sabine, C.L. and Christian, J.R. (Eds.) 2007. Guide to best practices for ocean  $CO_2$  measurements. PICES Special Publication 3, 191 pp.
- 6 - Lewis, E., and D. W. R. Wallace. 1998. Program Developed for  $CO_2$  System Calculations. ORNL/CDIAC-105. Carbon Dioxide Information Analysis Centre, Oak Ridge National Laboratory, U.S. Department of Energy, Oak Ridge, Tennessee.
- 7 - Luchetta A., Cantoni C. and Catalano G., 2009. New observations of  $CO_2$  induced acidification in the Northern Adriatic sea, over the last quarter century. *Chemistry and Ecology*. accepted.