MONITORING PH OF SEAWATER IN THE ADRIATIC SEA. RESULTS FROM A REGIONAL OBSERVING EFFORT.

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Abstract

Ocean acidification in the Mediterranean Sea is expected to have a rapid response to the climate change, being its hydrological balance deficient and anthropogenic forcing high. So the basin can be regarded as a key site very sensitive to the climate variability, especially in dense cold water formation areas. In this frame, the Adriatic Sea can play a very relevant role for the entire Eastern Mediterranean Sea, since in winter is exposed to cold dry winds eventually producing dense waters (NAdDW, ADW), which are important contributors to the Eastern Mediterranean deep circulation. Here are presented results of two repeated surveys, on mesoscale, and those of two short timeseries, one representative of a coastal environment and the other of open sea. Preliminary results, based on spectrophotometric analysis of pH (total scale, precision of ± 0.001 pH_T units), indicate the two times series reflect dynamics and processes of their respective environments.

The Mediterranean Sea is expected to have a rapid response to the climate variability as it is an area climatically complex with a deficient hydrological balance and high anthropogenic pressure [1]. On global scale, the basin can be regarded as very sensitive to the climate variability [2], especially by the two northernmost areas where dense water formation occurs: the Gulf of Lion and the Northern Adriatic Sea. This can be particularly true for CO_2 induced acidification process, which depends on both CO_2 atmospheric levels and CO_2 solubility in seawater (which increase with the decreasing sea surface temperature).

Within this frame, the Adriatic Sea can play a crucial role for the entire Eastern Mediterranean Sea: it is actually surrounded by industrialized regions, releasing carbon dioxide to the atmosphere, while during winter water mass can be so cold that CO_2 solubility pump mechanism can efficiently work increasing the dissolved CO_2 amount and 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 [3]. In this way Adriatic dense water masses have the possibility of sequestering acidified waters and spreading around through the Eastern Mediterranean. Recently, an acidification of 0.063 pH_T units (μmol H^+/Kg_{sw}, at 25 °C) over the last 25 years has been observed in the dense, cold waters (NAdDW) formed in Northern Adriatic Sea [4].

The Adriatic Sea has been considered the dominant source region of dense waters for the Eastern Med until the occurrence of the Eastern Mediterranean Transient [5], in the end of 1980's, which abruptly changed the deep circulation pattern. However, at present time, the deep circulation scheme seems to have switched back to pre-Transient conditions.

For such reasons monitoring the *pH* of seawater of the Adriatic Sea should provide very useful data for ocean acidification studies and should be considered worthwhile to be carried out, at least by a few strategic sites where dense water formation occurs.

Despite the increasing numbers of studies on ocean acidification, there's still lack of good quality *pH* data over the whole Adriatic region [6]. We present and briefly discuss pH_T data gathered over the basin during two surveys (in February and October 2008). All of the values have been measured by the spectrophotometric method as described by Dickson [7], and are expressed on the total H^+ scale (pH_T, inμmol 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 over the whole basin. Since also the *Total Alkalinity* (*TA*) has been measured, the pH_T values in situ and all the other parameters of the carbonate system (fCO_2, TCO_2 *Revelle*, Ω_{Ar}, Ω_{Ca}) can be derived using CO2SYS program [8].

Results from the two surveys at basin scale, conducted during 2008 in the frame of VECTOR and SESAME projects, are reported in fig. 1 and show that in winter the North Adriatic shelf was involved in a dense water formation process being shallow and exposed to cold dry winds (Bora), as reported in the past [9, 10]. The water column was actually cold (8< T < 12 °C), quite homogeneous (well mixed), dense (σ_t > 29.4 kg/m³) and ventilated (*Apparent Oxygen Utilization, AOU,* mean value ~ 0 μM) from surface to the bottom, at meso scale. The dense water mater mass had *T/S* properties in agreement with those of NAdDW (among the densest of the Mediterranean Sea [11]. The pH_T values were also homogeneously distributed in the water column, ranging between 7.917 and 7.973 pH_T units, with a mean value of 7.946 ± 0.012 in the dense water mass (NAdDW). Such a homogeneous distribution over an extend area mirrored the winter time conditions found, where *pH* values were driven by the CO_2 solubility in seawater and intense biological processes had not yet started (as indicated by *AOU*). Generally, NAdDW water mass flows southward and accumulates at the bottom of the Meso and Southern Adriatic pits (250 and 1250 m, respectively [3, 12] as clearly indicated in fig.1 by *density*, red and orange spots, higher than 29.3 and 29.2 respectively, at the bottom. The dense waters of the Meso Adriatic pit exhibited pH_T values lower (<7.880 pH_T units, green spot) than those on the northern shelf since the water mass was older (*AOU* higher than 65.0 μM) and remineralisation processes had time to work decreasing the *pH*.

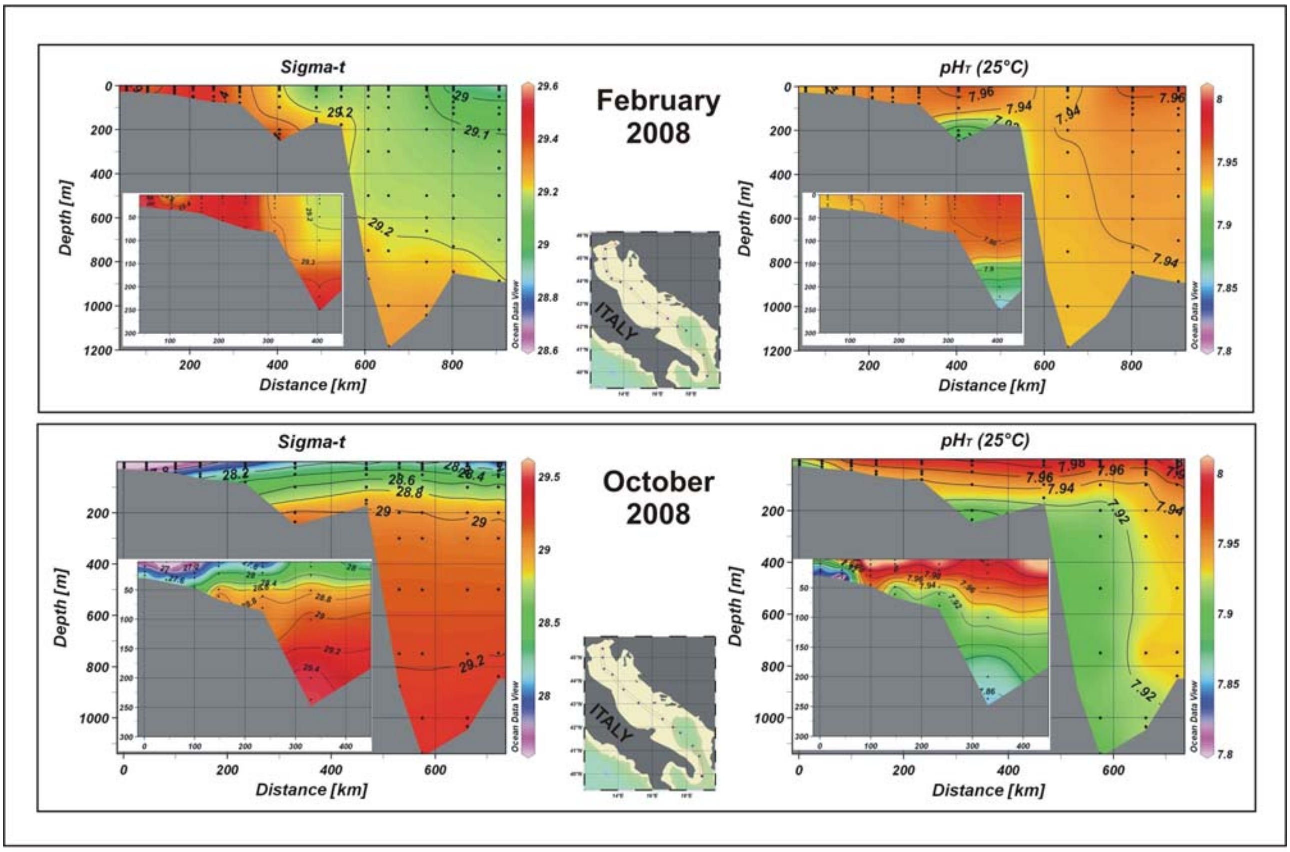

Figure 1 *Density* and *pH* of the Adriatic Sea during the repeated surveys

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, yellow-green, in fig.1) with mean pH_T value of 7.947 ± 0.003 pH_T units homogeneously distributed from surface almost to the bottom. This was confirmed by observations carried out during the seasonal time series at the deep station AM1 (fig. 2, vertical profiles in January and February 08 are homogeneous from surface to 600 m) and results in agreement to what reported in literature for the area, which known to be dominated by a quasi-permanent cyclonic circulation that intensifies in autumn creating the conditions for the production of dense and oxygenated deep waters during winter deep convection events [13].

At the beginning October '08 the situation appeared completely changed: vertical stratification of density and pH_T values was widespread over the whole Adriatic basin, from the North to the South. *Density, T, S* and pH_T varied over a much wider range than in February: $26.5 < \sigma_t < 29.45$ kg/m^3, $13.0 < T < 21.0$ °C, $37.250 < S < 38.800$ psu, $7.850 < pH_T < 8.100$ pH_T units. The northern shallow shelf region exhibited much warmer water (*T*>15.0°C, even at the bottom,) with higher pH_T values (between 7.960 and 8.050 pH_T

units, orange-red spots in fig. 1) due to the influence of primary production, whereas lower pH_T values (<7.888 pH_T units, blu spot, and lower than 7.920 pH_T units, green spot in fig. 1) were still recognizable at the bottom of both the Meso and Southern Adriatic Pits. pH_T values within the upper euphotic layer were everywhere distinctly higher (>7.960 pH_T units) than in February, as expected in warmer waters dominated by production processes.

Concluding, the comparison between the two surveys pointed out high spatial and seasonal variability of *pH*, exceeding the precision of analytical method, which is related either to the circulation pattern, to the CO_2 solubility pump and to the biological processes affecting water masses (primary production, increasing pH_T values, and respiration of organic matter, lowering them). This confirms the Adriatic Sea is sensitive to climate change and to atmospheric gas solubilisation (as CO_2). Therefore the acquisition of time series, at least by a few key sites such as those where deep water formation occurs in winter, would be very useful for an observing network on ocean acidification.

On this concern, we report (fig. 2) the new preliminary results of two time series, recently started, by two key areas: the Gulf of Trieste (very shallow, the northernmost of the Mediterranean Sea) representative of a coastal environment and the Southern Adriatic Pit (1250 m deep, site of deep convection locally originating dense waters and site of accumulation and/ or transformation of NAdDW) representative of an open sea environment.

Since January 2008 pH_T (spectrophotometric method), *TA* and the mayor biogeochemical and physical parameters were acquired on monthly basis on the whole water column at the coastal site PALOMA (centre of the Gulf, 25m deep, close to the mast PALOMA - Advanced Oceanic Laboratory PlatforM for the Adriatic sea, 45° 37 N, 13° 34 E). First results evidenced a complex time evolution of pH_T, mainly driven by the combined effect of strong changes in both temperature and production/ remineralisation processes. During winter pH_T values were generally low (7.868-7.958, avg 7.920) and homogeneous owing to the increased CO_2 solubility driven by the low water *temperature* (down to 8.0°C) and to the absence of intense production processes. During spring and summer pH_T was highly variable and mainly driven by the biological processes: the highest values (up to 8.120, June 2008) were reached in the upper layer during high production events (*AOU*= -34 µM) and the lowest values (down to 7.648, August 2008) in the bottom layer during biomass remineralisation (*AOU*= 142 µM)

During Jan-March 2008 the oceanographic properties (average σ_t = 29.35 Kg/m^3, T = 8.84 °C) and pH_T values (7.907 ± 0.028) of site PALOMA, indicating dense water formation, fit well to the general North Adriatic Sea conditions over the same period. In summer, small scale biological processes prevailed in determining pH_T values both in PALOMA site and in the North Adriatic, depicting a more complex situation. In conclusion, from such preliminary data the site located in the centre of the Gulf of Trieste results to be a good indicator not only of coastal dynamics/ processes but also of sub-basin wide (North Adriatic Sea) processes and dynamics.

In the southern Adriatic Pit, five seasonal datasets (from September 2007 to October 2008) have been gathered by the station AM1 (1250 m deep, located at 41° 50 N and 17° 45. E), within VECTOR and SESAME projects, for assessing both the vertical distributions and the seasonal variations of pH_T .

Time series reported fig. 2 show pH_T varies with depth and season, within one layer. More interestingly it fits well to the main processes affecting water masses: i.e. the deep convection event of February '08 is witnessed by the homogeneous profiles of *density* (29.1<σ_t<29.2 kg/m^3) down to 600-800 m, accompanied by similar constant vertical profiles of pH_T (7.915 <*pH*<7.925 pH_T units). In surface waters (0-100 m), pH_T exhibit the widest variations, between 7.888 and 8.057 pH_T units, with a clear correlation with the vertical stratification of water column (σ_t profiles) and to the season: the lowest values (7.888-7.940) were observed below 50 m depth through summer and autumn (probably due to remineralisation of organic matter), still quite low values in winter (7.950-7.970, in January and February 2008) whereas the highest were found in late spring through late summer (>8.000 pH_T units in September 07, June 08, October 08), primarily due to biological processes occurring there because of the vertical injection of nutrients in the euphotic zone after winter convection [14].

Below 100 m, the pH_T decreased and varied between 7.889 and 7.959 pH_T units, with the minimum generally located between 150 and 300 m (Levantine Intermediate Water, LIW), also in this case the difference between winter and summer autumn conditions appears clear. Below 300 m, pH_T values increase again up to values between 7.920-7.941 pH_T units in the deep/bottom waters. In the deep layers, below 500 m, a seasonal trend can be still observed, with decreasing values from autumn - winter (September 07, January-February 08) to the next summer-autumn 08 (June and October 08). The seasonal trend in the intermediate and deep layers could be explained either by remineralisation processes of organic matter or by advection of slightly different water masses, due to the gradual strengthening of cyclonic circulation, toward autumn [13], sucking water masses from the South. This aspect will be afforded in next future studies.

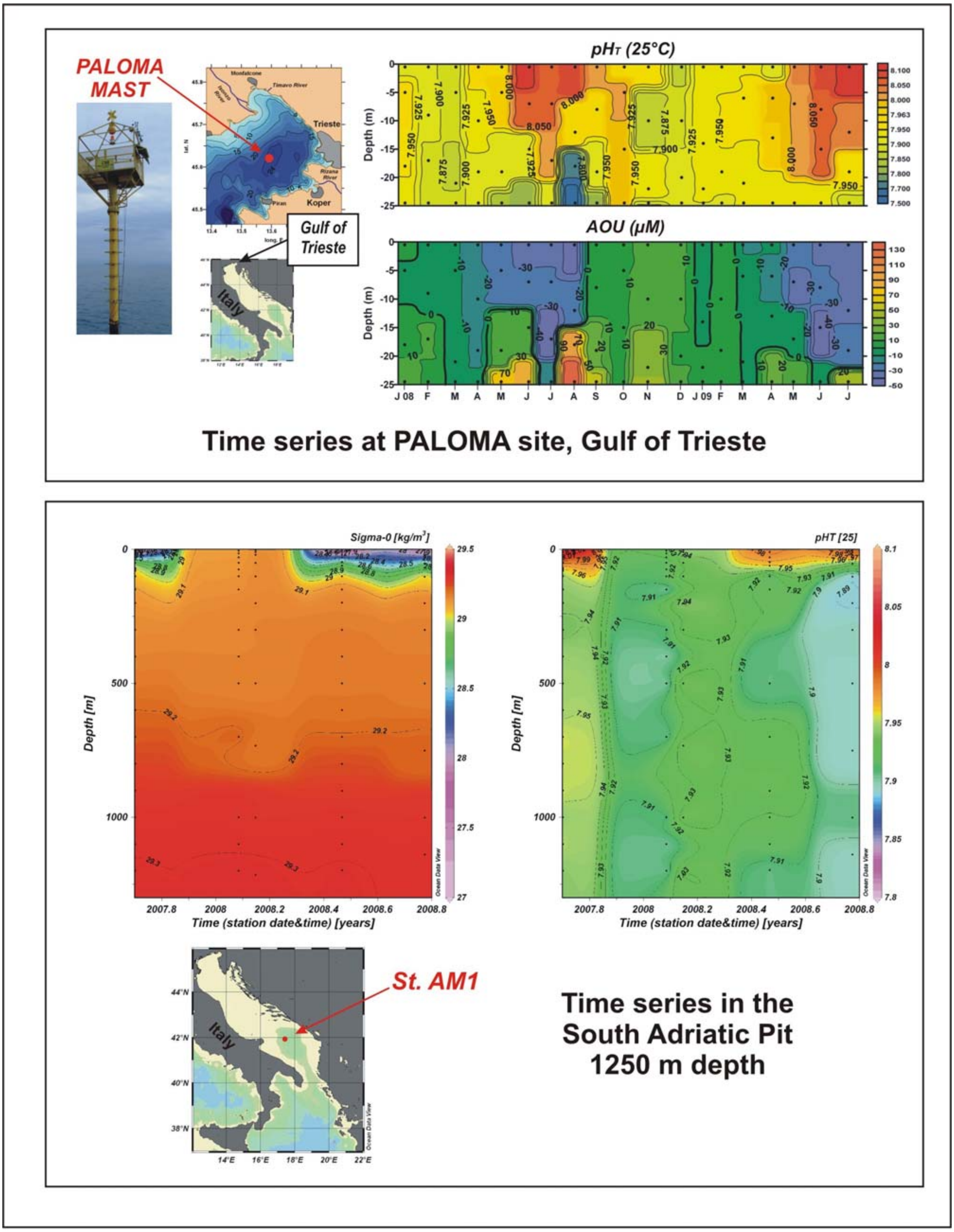

Figure 2 Time series of *density* and *pH* by the two key areas of the Adriatic Sea

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