

## The carbonate system in the Gulf of Trieste: a two years time series at PALOMA station

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In the framework of VECTOR project (activity 6.2.2), pH, Total Alkalinity  $(A_T)$  and physical/chemical parameters were acquired on a monthly basis since January 2008, in the water column at the PALOMA site (Advanced Oceanic Laboratory PlatforM for the Adriatic sea, Gulf of Trieste, 25m depth).

The pH was measured by the spectrophotometric method (precision  $\pm$  0.003) and the results expressed on "total scale" at 25°C (pH<sub>T</sub>@25°C). A<sub>T</sub> was measured by potentiometric titration at 25°C (precision  $\pm$  3 µmol/kg) and the results were checked against sea water certified as reference material. The other parameters of the carbonate system (pCO<sub>2</sub>, DIC, CO<sub>3</sub><sup>=</sup>,  $\Omega$ Ar,  $\Omega$ Ca) were computed from pH, A<sub>T</sub>, salinity, temperature, SiO<sub>2</sub>, PO<sub>4</sub>.

To our knowledge this is the first time series of these parameters collected in the North Adriatic Sea. These data allowed an initial identification of roles played by biological ad physical factors in controlling the carbonate system dynamics and the pH annual cycle.

During the stratified period (April to September),  $CO_2$  uptake by primary producers in the upper layer (DO sat > 100 %, Fig 1) determined the highest annual values of pH<sub>T</sub>@25°C in both years (Fig 1). By contrast, remineralization processes generally prevailed in the deeper waters undersaturated of oxygen (DO down to 48%, Fig 1) and the minima annual values of pH<sub>T</sub>@25°C were reached.

From January to March of both years the water column was homogeneous and cold, reaching the lowest annual temperatures (down to 8.8 °C). The  $pH_T@25^{\circ}C$  values were generally low and constant and the oxygen saturation was around 100 %. These characteristics indicated that biological processes were playing a minor role in determining the observed values of  $pH_T@25^{\circ}C$  while physical factors as temperature induced  $CO_2$  solubilization were more important.  $A_T$  concentrations (median value 2633 µmol/kg) were higher than in open Mediterranean sea (~ 2600 µmol/Kg) due to the inflow of rivers with a carbonatic drainage basin.  $A_T$  variability was mainly modulated by riverine inputs with variable  $A_T$  concentrations and by the occurrence of strong remineralization processes in the bottom layer (Aug.- Nov. 2008, up to 2658 µmol/kg, S=37.5) as shown by the relationship with AOU.

The seasonal evolution of in situ  $pCO_2$  was deeply influenced by the variations of temperature that modulated not only CO<sub>2</sub> solubility but also the chemical equilibria between carbonate species. Despite the production processes in the upper water column during summer, pCO<sub>2</sub> values were higher than 400 µatm on the whole water column, from July to December 2008 and from August to October 2009. During these months the Gulf of Trieste was thus acting as a potential  $CO_2$  source. In contrast, from January to June of both years, pCO<sub>2</sub> values were always lower than 400 µatm and the Gulf was a  $CO_2$  sink (up to -19.0 mmol C m<sup>-2</sup>) d<sup>-1</sup>, on 14 Jan 2009) especially during high wind events. An exception to this trend were the high pCO<sub>2</sub> value (up to 606 µatm) observed in April 2009 and May 2008, in surface low salinity waters (S down to 27.6 psu), which were ascribed to the ventilation of CO2 from supersaturated riverine waters.

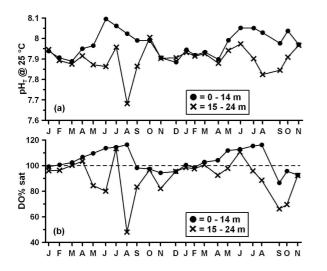


Fig.1 Averag	ge pH <sub>T</sub> @2	25°C (a	and and	oxygen	saturation
(b) values for the upper layer $(0 - 14 \text{ m})$ and for the					
lower layer	(15 - 2)	24 m)	from	January	2008 to
November	2009	at	PAI	LOMA	station.