DISSOLVED CARBON DIOXIDE, NUTRIENTS AND OXYGEN IN THE ADRIATIC SEA. A REGIONAL OBSERVING EFFORT.

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Abstract

The Adriatic Sea can be strongly affected by changes in climate and weather, it can play an important role in biological productivity and air-sea CO_2 fluxes,. In general the carbon cycling knowledge in these region is still limited., Regarding the atmospheric CO_2 sequestration mechanism, through the Continental Shelf Pump, the Adriatic Sea can play a very relevant role for the entire Eastern Mediterranean, since in winter is exposed to cold dry winds eventually producing dense waters (NAdDW and ADW), which are important contributors to the Eastern Mediterranean deep circulation. Here are presented the results (*fCO_2, AOU, dissolved inorganic nutrients*) of two repeated surveys on basin scale, and one short time series in the Gulf of Trieste, representative of the coastal environment.

The Mediterranean Sea is expected to have a rapid response to the climate variability because it is an area climatically complex with a deficient hydrological balance and high anthropogenic pressure ([1]. It can be regarded as very sensitive to the climate change, especially by the two northernmost areas where the winter cooling produces dense water (the Gulf of Lion and the Northern Adriatic Sea). In addition, increasing knowledge of the biogeochemistry of this basin has been reputed important, even on global scale, since this "semi-enclosed" sea can be considered as a model for many open-ocean processes, including carbon cycling [2].

Still within this frame, the Adriatic Sea can play a relevant role for entire Eastern Mediterranean Sea, since the combined effect of winter cooling and dry winds produce very dense water masses (NAdDW and ADW) [3, 4], which can be exported to whole Eastern Mediterranean basin through the Otranto Strait [5, 6], and since it is able to sustain one the most relevant primary production of region (Fonda Umani). These two processes (cold dense water formation and primary production) are basic for the atmospheric CO_2 sequestration mechanism through the Continental Shelf Pump, as proposed by Tsunogai [7]. The CSP requires that physical pump (high CO_2 solubility in cold seawater) and biological pump (primary production) work together for accelerating the absorption of atmospheric CO_2 on the continental shelf zone.

The shelf of the northern Adriatic basin, in particular, has been supposed to be able to play a major role on this mechanism since it is the widest of the Mediterranean basin and shallow.

Therefore data on dissolved CO_2 amount in the Adriatic Sea should provide very useful information for CSP studies and should be considered worthwhile to be carried out, at least by a few strategic sites where both dense water formation and intense primary production occur thus noticeably increasing the amount of carbon dioxide adsorbed in seawater. Another reason that makes worth these studies is dense water masses outflowing through the Otranto Strait and spreading in the Eastern Med, thus possibly exporting the absorbed in CO_2 deep and bottom layers.

Despite the importance of the subject and the increasing numbers of studies, there's still lack of good quality datasets regarding the inorganic carbon system in seawater over the region [8]. In situ fCO_2 values have been calculated, according to CO2SYS program [9], from experimental determinations of the pH_T (spectrophotometric method), and of the total alkalinity (potentiometric titration, precision of ± 1.0 µm/kg_{sw}), as reported by Dickson [10].

Results (fig. 1) from the two surveys at basin scale, carried out during 2008 in the VECTOR and SESAME projects, provided two seasonal snapshots of the dissolved CO_2 and other biogeochemical parameters (*Apparent Oxygen Utilization, AOU*). In winter (February) 2008 the water column was cooled, well mixed and ventilated down to the bottom (mean *AOU*=-4.1 µM), dense water mass (σ_t>29.3 kg/m^3) was occurring at sub basin scale which was rich of nutrients, *DIN* (1.00-7.00 µM) and *SiO_2* (1.20–5.33 µM), while intense primary production had not yet started). *fCO_2* values ranging from 222.4 to 334.6 µatm, from surface to the bottom over the whole area, resulted much lower than the equilibrium value with atmospheric *CO_2* (398 µatm, mean value on measurements conducted on board). Thus clearly indicating undersaturated conditions under which the northern Adriatic shelf region could act as a sink for. *CO_2* The dataset confirms, for the first time, that solubility pump was able to work and the first gear of the Continental Shelf Pump mechanism could be active in wintertime over such a wide area. In the remaining part of the section *fCO_2* values ranged between 222.4 and 424.7 µatm, with the highest values at the bottom of the Meso Adriatic Pit, corresponding to *AOU* (> 65 µM) and nutrients (*SiO_2*> 6.0 µM , *DIN*> 5.0 µM) maxima, indicating the occurrence of an older water mass affected by remineralisation processes.

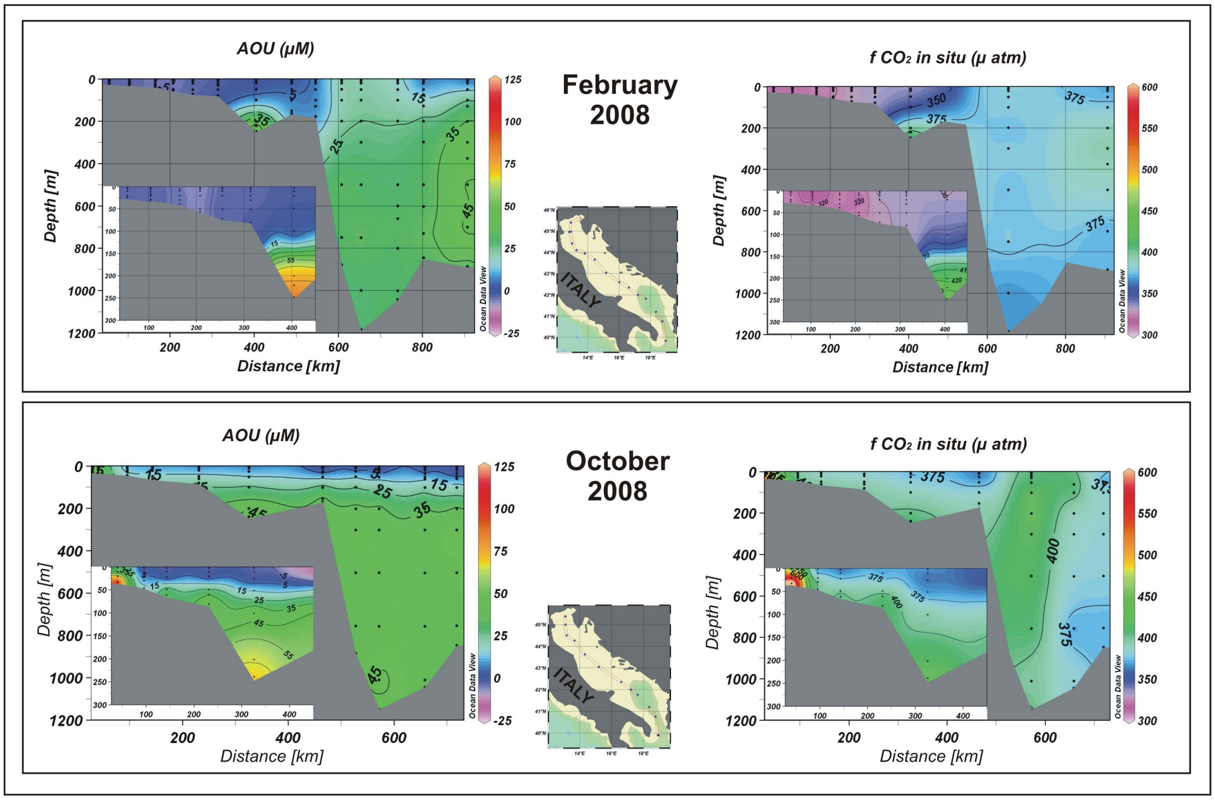

Figure 1 *Apparent Oxygen Utilization* and fCO_2 in the Adriatic Sea during the repeated surveys

In October 2008, the picture had completely changed: vertical stratification of density was widespread from the North to the South, as reported in Luchetta A., Cantoni C. and Celio M. (2010) Monitoring of pH In the Adriatic Sea. Results from a regional observing effort.In these proceedings (Annex). *Density, T* and *S* varied over a much wider range than in February: $26.5 < \sigma_t < 29.45$ kg/m^3, $13.0 < T < 21.0$ °C, $37.250 < sal < 38.800$ psu. 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 units) due to the influence of primary production, whereas lower pH_T values (<7.888 pH_T units, and lower than 7.920 pH_T units, as reported in Luchetta A., Cantoni C. and Celio M. (2010) Monitoring of pH In the Adriatic Sea. Results from a regional observing effort. In these proceedings. Annex) were still recognizable at the bottom of both the Meso and Southern Adriatic Pits. fCO_2 values too varied over a much wider range ($319.2 < fCO2 < 810.4$ µatm) as the *nutrients* and *AOU* concentrations did ($0.05 < DIN < 7.73$ µM , $0.59 < SiO2 < 10.48$ µM, *AOU*), as expected in late summer season. The maximum fCO_2 values have been observed in water masses of the northern Adriatic shelf. 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. The discrete linear correlation fCO_2/AOU (r^2= 0.7058), together with the good correlation fCO_2/pH_T (r^2= 0.9788), suggest the increase of dissolved CO_2 amount is related to the *pH* and to the biological processes (remineralisation of organic matter), on this base we suggest the Northern Adriatic basin in autumn function as a remiralisation basin

In conclusion, two completely different situations have been observed in the northern part of the Adriatic Sea, this suggest the basin worked differently depending on season: it functioned as sink for CO_2 during winter but as source during late summer through autumn. In contrast, over the remaining southern and deeper part of the section the situation remained quite constant in the two different seasons.

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 in a few key sites would be very useful for an observing network..

On this regard, we also report the first results of one time series carried out in the northernmost part of the Adriatic Sea (Gulf of Trieste), at the site of the mast PALOMA (Advanced Oceanic Laboratory PlatforM for the Adriatic Sea; middle of the gulf, 25 m of depth), Fig 2.

Since August 2008, CTD profiles, *dissolved oxygen* (Winkler method), *inorganic nutrients,* pH_T (spectrophotometric method) and *Total Alkalinity* were acquired, on monthly basis, at four depths, allowing the computation of all parameters of the carbonate system [9].

Data have shown a pronounced temporal variability of fCO_2 that was mainly determined by the complex interaction among seawater temperature, river loads and biological processes.

In August 2008, even if production processes dominated the surface layer (*Apparent Oxygen Utilization* = -41.2 µM), the highest water temperature (26.5°C) decreased carbon dioxide solubility (fCO_2) to 428 µatm. In September 2008, remineralization processes prevailed in the water column and surface fCO_2 reached values as high as 462 µatm, that lasted until December despite the decrease of seawater temperature (12.3°C). In both cases, the coastal waters of the gulf were potentially able to act as a source of CO_2, being the values of $fCO2$ in seawater exceeding the atmospheric pCO_2 (380 µatm; [10]).

From January 2009, the weak biological activity (*AOU* ≈ 0) coupledto a strong *temperature* decrease (9.8°C), lead to values of fCO_2 (~ 320 µatm) lower than the atmospheric pCO_2 (ΔpCO_2= -60 µatm), which might invert the CO_2 fluxes at the air/seawater interface.

This condition lasted until July 2009, because the increase in temperature was balanced by CO_2 uptake by primary production events, trigged by riverine nutrient supply. The high fCO_2 value recorded in April at surface (524 µatm) evidences the importance of direct riverine loads of dissolved $CO2$, that is probably determined by the presence of a large karstic area and karstic rivers (Timavo) flowing into the Gulf.

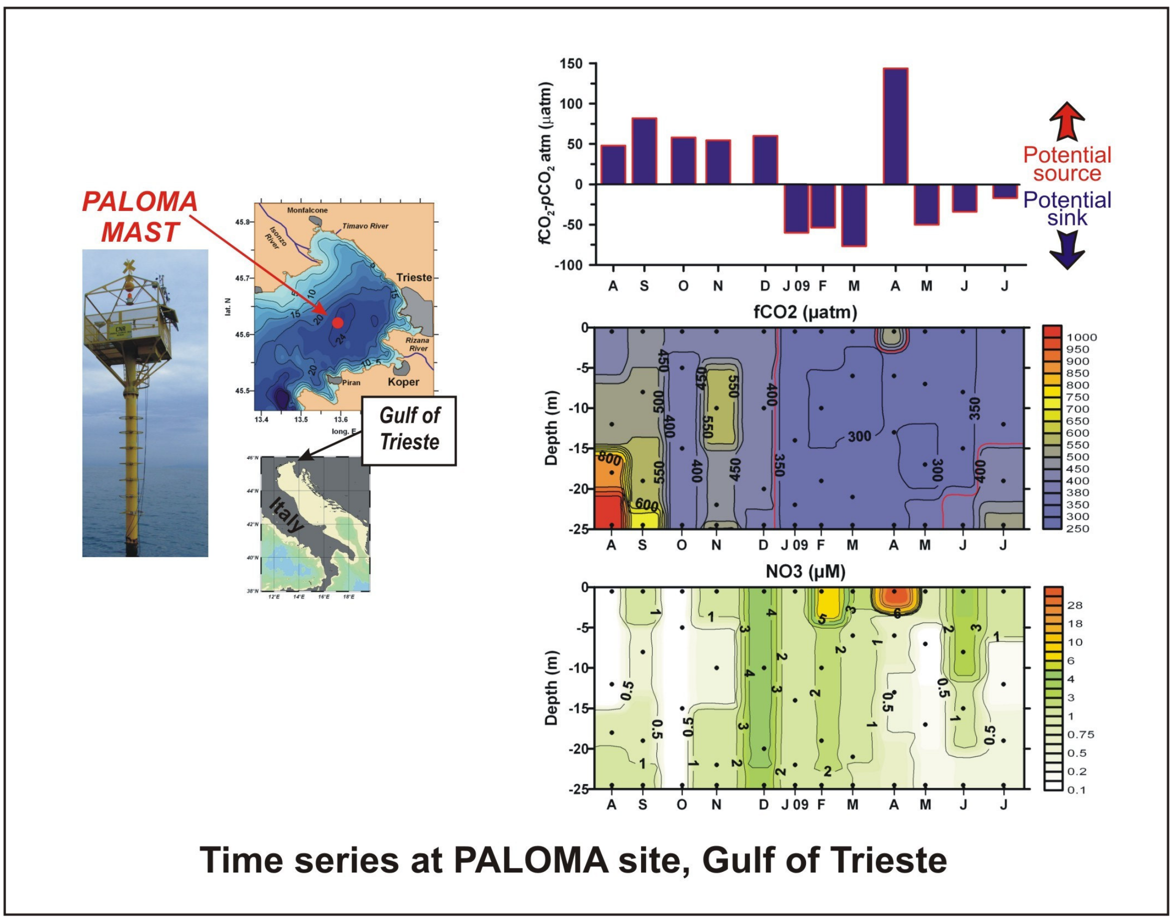

Figure 2 *Nitrate* and fCO_2 time series in the Gulf of Trieste

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