CARBONATE SYSTEM DYNAMICS IN THE GULF OF TRIESTE (NORTH ADRIATIC SEA)

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Abstract
We present first results of a study started in January 2008 and focused on the analysis of the variability of carbonate system in the Gulf of Trieste (N. Adriatic Sea). Total alkalinity, pH, and mayor physical and biogeochemical parameters were measured at PALOMA station (centre of the Gulf). We evidenced the role of direct inorganic carbon riverine inputs, sea water temperature and production / regeneration processes as mayor drivers of the observed carbonate system variability during the studied period.
Keywords: Adriatic Sea, Ph, Coastal Systems, Carbon

Introduction
The Gulf of Trieste (Adriatic Sea) is the Northernmost area of the Mediterranean which, as other sub-tropical continental shelf areas, experiences a strong seasonal cycle. Here, the pronounced cooling of the coastal waters during winter (7-8°C) and the mixing due to Bora wind events increases the solubility of CO_2 in water, permitting its potential sequestration in the denser bottom waters by the mechanism of the physical carbon pump. In summer, the warming of surface waters (28°C) and the scarce circulation may invert the flux of CO_2 with the atmosphere, particularly during period of low primary production. Because of the low inertia of this shallow coastal ecosystem compared to the deep sea and of its pronounced seasonal cycle, the Gulf of Trieste is thought to be highly sensitive toward the climate changes and the global atmospheric CO_2 rising. For this reason, the increase of CO_2 dissolved in seawater and the consequent decrease of pH might lead in this area to earlier changes of the marine environment due to ocean acidification than elsewhere.
We present first results of a study started in January 2008 and focused on the analysis of the variability of carbonate system in the Gulf of Trieste with respect to riverine inputs, sea water temperature and production / regeneration processes.

Methods
Since January 2008, pH, Total Alkalinity (TA) and physical/chemical parameters were acquired on monthly basis, on the whole water column at the site PALOMA (centre of the Gulf, 25m depth, close to the dynamic pylon PALOMA – Advanced Oceanic Laboratory PlatforM for the Adriatic sea). pH have been measured by the spectrophotometric method [1,2] with a precision of ± 0.001 and the results were expressed on "total scale" in $\mu molH^+/Kg_{SW}$ at 25°C (pH_T@25°C). TA has been measured by potentiometric titration at 25° C (precision ± 2 µmol/kg) and the results were controlled with sea water certified as reference material (supplied by dr. A.G. Dickson). The other parameters of the carbonate system (pCO_2, pCO_2@15C°, DIC, Revelle factor, "Omega"Ar, "Omega"Ca) were computed from pH, TA, salinity, temperature, SiO_2, PO_4 with the "CO2sys" program. To our knowledge this is the first time serie of this set of parameters collected in the N. Adriatic Sea.

Results and Discussion
From October to March, the water column was homogeneous and well ventilated. pH_T@25°C was generally low and constant (avg 7.920), because of the increased CO_2 solubility caused by the low water temperature (down to 8.0°C) and by the exceeding respiration compared to primary production. During the stratified period of both years (April – Sept.), the combined effect of high temperature and CO_2 assimilation in the upper waters determined the highest values of pH_T@25°C (Tab 1). In contrast, the remineralization processes in the bottom layer (Apparent Oxigen Utilization – AOU = 142 µM) prevailed on the effect due to the high water temperature (18.9°C) determining the lowest values of pH_T@25°C observed during the whole time series (Tab 1).
TA concentrations (Tab 1) were higher than in open Mediterranean sea (~ 2600 µmol/Kg [3]) due to the inflow of rivers with a carbonatic drainage basin. TA variability was mainly modulated by riverine inputs with variable TA concentrations and by the occurrence of strong remineralization processes in the bottom layer (Aug.- Nov. 2008, up to 2693 µmol/kg) as shown by the relationship with AOU.
The seasonal evolution of in situ pCO_2 was deeply influenced by the variations of temperature. Despite the production processes in the upper water column, the effect of temperature increased pCO_2 at values higher than 400 µatm on the whole water column, from August to December 2008. In contrast, its values were always lower than 350 µatm from January to June 2009. If we assume an average value of 380 µatm for atmospheric CO_2 concentrations, the Gulf of Trieste was supersaturated from August to December 2008, acting as a potential source of CO_2 for the atmosphere; on the contrary surface waters were undersaturated from January to June 2009 acting as a potential CO_2 sink.
An exception to this trend was the high pCO_2 value (523 µatm) observed in April 2009, in surface low salinity waters (S=27.6), which was ascribed to the ventilation of CO_2 from supersaturated riverine waters.
The superficial pCO_2@15C° values were compared with those reported from other European coastal zones [4]. From the relatively few data collected, pCO_2@15°C presented a clear seasonal cycle with lower values in summer (258 µatm) and higher in winter (495 µatm) wiht an amplitude of 236 µatm. This cycle was more similar to what reported for the North Sea coastal zones than to the olygothrophic coastal site studied in the western Mediterranean.
Despite the high alkalinity, the pronounced variability of Revelle factor and of "Omega" Ca and Ar evidence the overall weak buffering capacity of carbonate system in the Gulf of Trieste.

Tab. 1. Average values and variability of carbonate system parameters at PALOMA station on an annual cycle: Aug08-Juy09.

	pH_T (25°C)	TA (25°C) µmol/Kg	pCO_2 µatm	pCO_2 (15°C) µatm	DIC µmol/Kg	ΩCa	Ω Ar	Rev.
Avg	7.947	2652	418	406	2365	4.96	3.20	10.91
Med	7.946	2647	381	394	2352	4.86	3.11	10.82
Max	8.109	2859	1047	895	2651	6.67	4.37	14.88
Min	7.648	2624	291	258	2281	2.76	1.79	9.24

References
1 - R.H. Byrne and J.A. Breland, 1989. High precision multi-wavelenght pH determination in seawater using cresol red. *Deep-Sea Res.*, 36: 803-810.
2 - A.G. Dickson, C.L. Sabine and J.R. Christian (Ed), 2007.Guide to best practices for ocean CO_2 measurements. Sop 6b. PICES Special Publication 3, pp 191.
3 - A. Schneider, D.W.R. Wallace, A. Körtzinger, 2007.Alkalinity of the Mediterranean Sea. *Geophys. Res. Lett*., 34: L15608.
4 - A.V. Borges, L.-S. Schiettecatte, G. Abril, B. Delille, F. Gazeau., 2006. Carbon dioxide in European coastal waters. Estuarine, *Coast. Shelf Sci*., 70: 375-387.