VARIABILITY IN NORTHERN ADRIATIC pCO_2

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ABSTRACT

Coastal marine regions such as the Northern Adriatic serve as a link between carbon cycling on land and the ocean interior and may play an important role in the global carbon cycle. Here we present the first measurements of water pCO_2 in the Northern Adriatic. pCO_2 was measured at the coastal oceanographic buoy VIDA, Slovenia using the SAMI-CO_2 sensor during four deployments in 2007 and 2008. pCO_2 measurements were combined with hydrological and biological observations to evaluate the processes that control inorganic carbon cycling in the region. The results indicate that during 2007 and 2008 the water was mostly under-saturated with respect to atmospheric CO_2. Although some of the interannual and seasonal variability in aqueous CO_2 can be explained with changes in sea surface temperature, our data also suggest a significant influence by fresh water input from rivers, biological production associated with high nutrient input, and Bora wind events.

1. INTRODUCTION

The Coastal marine regions such as the Gulf of Trieste (GOT) in the Northern Adriatic Sea are strongly affected by changes in climate and weather, and play an important role in biological productivity and air-sea CO_2 fluxes. These regions serve as critical links between terrestrial and open-ocean carbon cycling, and potentially contribute large uncertainties to the estimate of anthropogenic CO_2 uptake based on the marine surface pCO_2 distribution. To date, in-depth studies of carbon cycling in coastal waters have been primarily limited to coastal transects that provide important snapshots of carbon dynamics. The most comprehensive continental shelf CO_2 flux database currently available [1] does not include measurements from the coastal waters of the Mediterranean, and no CO_2 flux data are presently available from the northern Adriatic Sea. Limited data sets, coupled with the complexity of the coastal system, make it difficult to discern the processes governing carbon and nutrient dynamics and the response of these processes to physical forcing in the atmosphere and ocean.

The GOT is a semi-enclosed Mediterranean basin situated in the northern part of the Adriatic Sea (Fig. 1), reaching a maximum depth of ~25 m at its center. Though limited in size (~650 km^2), the GOT strongly influences the hydrographic properties of the Adriatic Sea [2]. The complex dynamics that characterize this area are collectively due to freshwater inputs from rivers, northward-flowing water masses along the eastern Adriatic coast, tidal dynamics, and atmospheric forcing. In particular, during Bora wind gales, wind speeds can exceed 30 m s^{-1}, producing a water outflow from the GOT at the surface, and an inflow at depth, along with strong vertical mixing [3]. Modeling studies have shown that Bora winds significantly affect heat fluxes [4], and while previous studies under high-wind conditions have shown increased air-water CO_2 fluxes, no investigations have yet been performed in the northern Adriatic.

The GOT area is also affected by riverine inputs that provide the basin with significant flows of freshwater and terrestrially derived nutrients. Freshwater enters the gulf mainly along the shallow northwestern coast, with the Isonzo River being the dominant source. Freshwater inputs from the karstic Timavo-Reka River and rivers along the southeastern coast such as the Dragonja and Rizana (Fig. 1) are comparatively small and have not been recognized as significant contributors to physical and biogeochemical processes in the GOT. The Po River on the western side of the northern Adriatic may influence the southern end of the GOT, depending on Bora winds and ambient stratification. Isonzo River discharge typically ranges from 90-130 m^3 s^{-1}, and sometimes exceeds 1500 m^3 s^{-1}. These exceptionally high flows often occur in spring during snowmelt and in the fall due to increased precipitation, and may cause a marked drop in surface salinities along the northern coastline. Previous work [5] has shown that river plumes not only reduce coastal salinity, but also introduce water with a lower inorganic carbon content, which results in lower pCO_2 values. To date, no data have been collected to examine riverine influences on CO_2 dynamics in the GOT.

Furthermore, the northern Adriatic is one of the most biologically productive regions in the Mediterranean [6]. Studies in the GOT have shown that seasonal plankton dynamics appear to be strongly related to Isonzo river runoff [7], and have also indicated that annual phytoplankton biomass is more closely tied to the excess freshwater discharge during the spring than to average annual discharge. This may be the same for dissolved inorganic carbon (DIC), but the effect of these blooms on the magnitude and distribution of CO_2 is unknown.

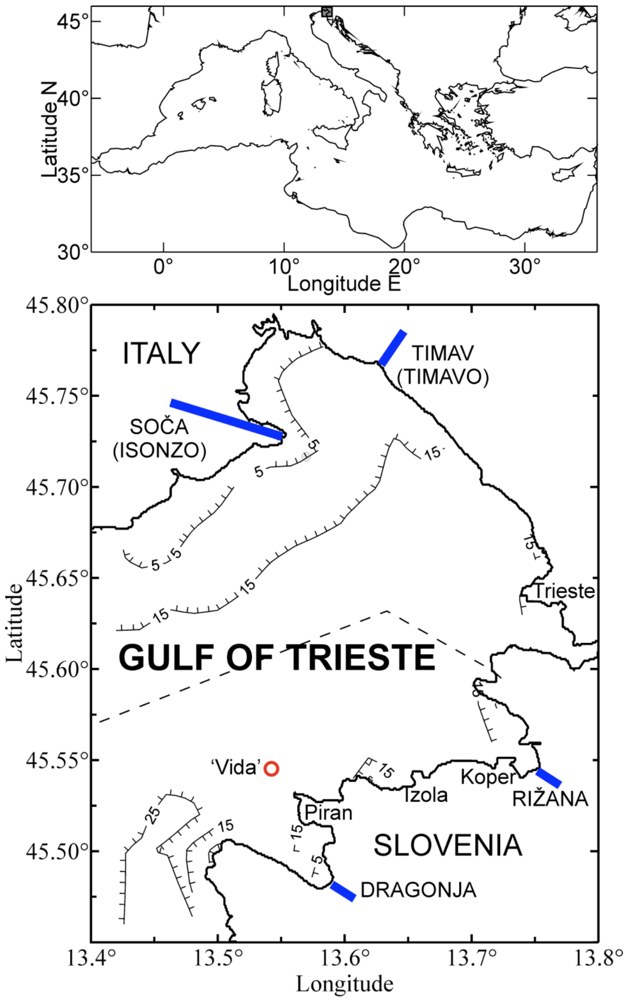

Figure 1. Schematic of the northern Adriatic Sea. The area of interest is a nearshore location with the time-series station VIDA located at 45° 32' N, 13° 33' E anchored 2.28 km from shore. The system's hydrographic and meteorological conditions are influenced by the proximity to land and rivers (blue). A CO_2 instrument is moored at 3-m depth on the MBS buoy VIDA.

The unique combination of environmental influences described above makes this region an excellent study site for air-sea interaction, and the relationship between biology and carbon chemistry. A coastal time-series station VIDA (www.mbss.org) has been launched in GOT, with significant investment from the EU and Slovenia. Time-series station VIDA will advance global understanding of coastal CO_2 cycling in enclosed basins by providing 1) a valuable data set from an area where such information is currently unavailable; 2) new insights into the environmental conditions controlling CO_2 dynamics in enclosed seas and coastal margins; and 3) information on coastal air-sea CO_2 fluxes under high-wind conditions.

The main objectives of this study are to collect and utilize the first measurements of CO_2 in the GOT to: 1) determine whether the Gulf of Trieste in the northern Adriatic Sea is a sink or source of atmospheric CO_2; 2) study temporal (seasonal, and interannual) variability; and 3) identify and quantify the biological and physical controls of air-sea carbon dynamics in coastal waters of the northern Adriatic Sea over this range of scales. Specifically, we will consider the effects of riverine input, eutrophication, phytoplankton blooms, and high Bora wind events. Since we envision that additional chemical measurements (pH, alkalinity, and DIC) will be obtained from VIDA in the future, we will also study the impacts of anthropogenic CO_2 and ocean acidification on marine biogeochemistry and ecosystems in the northern Adriatic.

2. METHODS AND DATA

Recently, a study was conducted with time-series measurements of air temperature (T_a), sea surface temperature (SST), sea surface salinity (SSS), bottom temperature (T_b), wind speed and currents, and aqueous pCO_2 from VIDA (Fig. 2). Aqueous pCO_2 was measured with an autonomous sensor (SAMI-CO_2 Sunburst Sensors, LLC) during four separate deployments in 2007 and 2008. The measurements were performed at 3 m depth at 30-min intervals. These measurements were combined with chlorophyll-a concentrations estimated from SeaWiFS ocean color and daily flow rates for nearby rivers (Slovenian Environmental Agency (ARSO)) that influence the GOT (Isonzo, Rižana, Dragonja, Timavo-Reka, Po).

3. RESULTS AND DISCUSSION

Water pCO_2 measurements (Fig. 2) show a seasonal cycle with highest values in the summer (reaching maximum of 500 µtm in 2008) and lower values in the spring and fall (minimum of 200 µatm in spring of 2008). The pCO_2 cycle is primarily a function of the SST pattern which also depicts lowest values in the spring (~10^{0}C), and reaching ~ 25^{0}C in the summer, which is then followed by fall cooling. This observation suggests that the seasonal changes of $pCO2$ are largely affected by the SST change. Most of the time, with exception of summer of 2008, surface waters of GOT were undersaturated with respect to the atmosphere, and thus the GOT is a net sink of carbon dioxide on an annual scale.

There are some significant differences in water pCO_2

values between 2007 and 2008 at times and interannual consistency at other times. For example, in the Spring of 2007, pCO_2 was significantly higher (~50 µatm) than during the same period in 2008 (Figure 2). SST was also significantly higher (~2^{0}C), which indicates that difference in SST was primarily responsible for the higher values of pCO_2 in the spring time. On the contrary, we observe lower pCO_2 in late summer (~100 uatm) and fall of 2007 compared to 2008. While SST in the late summer shows similar values in both years, late fall of 2008 was ~1^{0}C warmer than 2007. The difference in pCO_2 between the two years can not be explained by water temperature alone.

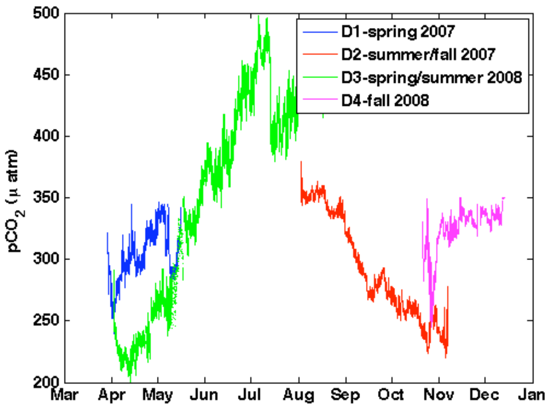

Figure 2. Water pCO_2 during four SAMI-CO_2 deployments (D1-blue, D2-red, D3-green, D4-cyan) at coastal buoy VIDA in 2007 and 2008.

The general seasonal and interannual cycle in the GOT is significantly perturbed by episodic environmental conditions lasting between a few days to a couple of weeks, when of pCO_2 vary of order 20 to >100 µatm (Figure 2). The physical measurements from VIDA in combination with observations of discharge by rivers entering the GOT, and SeaWiFS chlorophyll-a concentrations indicate that during these events, factors other than just SST (such as river input, wind events, and phytoplankton blooms) are responsible for variability of water pCO_2.

Spatial surveys of air and water pCO_2, S, T, DO, pH, total alkalinity (Talk), and DIC will be performed to study changes in seawater chemistry and potential impacts of coastal acidification on marine biogeochemistry and ecosystems. Modeling efforts are also coming together to further examine these processes in the northern Adriatic.

4. ACKNOWLEDGEMENT

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5. REFERENCES

1. Cai, W.-J., Dai, M. & Wang, Y. (2006). Air-sea exchange of carbon dioxide in ocean margins: A province-based synthesis, *Geophys. Res. Lett.*, **33**, L12603, doi:10.1029/2006GL026219.

2. Cardin, V. & Celio, M. (1997). Cluster analysis as a statistical method for identification of the water bodies present in the Gulf of Trieste (Northern Adriatic Sea). *Boll. Geofis. Teor. Appl.*, **38**, 119-135.

3. Mosetti, F. & Mosetti, P. (1990). Measurements on wind driven circulation in the North Adriatic Sea. *Boll. Oceanol. Teor. Applic.*, **8**, 251-261.

4. Malačič, V. & Petelin, B. (2006). Numerical modeling of the winter circulation of the Gulf of Trieste (northern Adriatic), *Acta Adriat.,* **47** (Suppl.), 207-217.

5. Körtzinger, A. (2003). A significant CO_2 sink in the tropical Atlantic Ocean associated with the Amazon River plume, *Geophys. Res. Lett.*, ***30***(24), 2287, doi:10.1029/2003GL018841.

6. Fonda Umani, S., Milani, L., D. Borme, D., de Olazabal, A., Parlato, S., Precali, R., Kraus, R., Lucic,D., Njire, J., Totti, C., Romagnoli, T., Pompei, M. & Cangini, M. (2005). Inter annual variations of planktonic food webs in the northern Adriatic Sea, *Science of the Total Environment*, **353**, 218–231.

7. Mozetic, P., Turk, V. & Malej, A. (1998). Nutrient-enrichment effect on plankton composition. *Ann, Ser. hist. nat.*, **13**, 31-42.