Science

Carbon Dioxide Variability in the Gulf of Trieste: A New Coastal Carbon Time-series Station and EU/US Collaboration

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The importance of oceanographic time-series for understanding the processes controlling ocean carbon and biogeochemical cycles and the need for international collaboration in supporting and coordinating such efforts has recently been a topic of discussion at OCB workshops. A coastal time-series station VIDA has been launched in the Gulf of Trieste (GOT) in the northern Adriatic, with significant investment from the EU and Slovenia. It also benefits from international collaboration between the Marine **Biological Station Piran**, Slovenia and US scientists from the University of Montana and Columbia University. Their combined efforts are focused on inorganic carbon cycling in this unique coastal environment.

Coastal marine regions such as the GOT are strongly affected by changes in climate and weather, and play an important role in biological productivity and air-sea CO₂ fluxes. These regions serve as critical links between terrestrial and openocean carbon cycling, and potentially contribute large uncertainties to the estimate of anthropogenic CO₂ uptake based on the marine surface pCO_2 distribution. To date, in-depth studies of carbon cycling in coastal waters have been limited mostly to coastal transects that provide interesting 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



Figure 1. Schematic of the northern Adriatic Sea. The area of interest is a shallow, nearshore location with the time-series station VIDA. The system's hydrographic and meteorological conditions are strongly influenced by the proximity to land and rivers (marked in blue). Large inputs from rivers, such as the Soca (or Isonzo), and the isobaths showing the shallow depth of the Gulf of Trieste illustrate how the system may be significantly influenced by these regional environmental conditions. A moored CO_2 instrument is deployed at 3 m depth on the Piran buoy VIDA.

forcing in the atmosphere and ocean.

The GOT is a semi-enclosed Mediterranean basin situated in the northern part of the Adriatic Sea (Figure 1), reaching a maximum depth of ~25 m at its center. Though limited in size (~650 km²), 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 Gulf 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 CO₂ fluxes, no such studies have 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 (Figure 1). 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 (Figure 1) are comparatively small and have not been recognized as significant contributors to physical and

Science



Figure 2: <u>Piran Buoy VIDA</u> located at 45° 32' 55.68" N, 13° 33' 1.89" E anchored 2.28 km from shore.

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 m³ s⁻¹, and sometimes exceeds 1500 m³ 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 pCO₂ values (e.g., 200 ppm in the Amazon River Plume). To date, no data have been collected to examine riverine influences on CO₂ 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 annual average 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.

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. Time-series station VIDA (Figure 2) will advance global understanding of marine CO_2 cycling by providing 1) a valuable data set from an area where such information is currently unavailable; 2) new insights into

the environmental conditions controlling CO₂ dynamics in enclosed seas and coastal margins; and 3) information on coastal air-sea CO₂ fluxes under high-wind conditions.

The main objectives of this collaborative effort 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 CO₂; 2) Study temporal (diurnal, seasonal, and interannual) and spatial variability of air-sea CO₂ fluxes; 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 excess riverine input, eutrophication, phytoplankton blooms, net community metabolism, and high Bora wind events. Since we envision that additional chemical measurements (pH, alkalinity, 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.

Recently, a pilot 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 (Figure 3). Aqueous pCO_2 was measured with an autonomous sensor (SAMI-CO₂ Sunburst Sensors LLC). The measurements were performed at 3 m depth at 15-min



Figure 3: Time-series of wind speed (panel 1, top), SST (blue) and bottom temperature T_b (black) (panel 2), SSS (panel 3), and pCO_2 (panel 4, bottom) at the time-series station VIDA from April 1 – May 31, 2007.

Science



Figure 4: Daily flow rates for five northern Adriatic rivers (Timavo-Reka, Isonzo, Rizana, Dragonja, Po) and rainfall data from the meteorological station in Portoroz, Slovenia.

intervals. These measurements were combined with chlorophyll-a concentrations estimated from SeaWiFS ocean color and daily flow rates for rivers (Slovenian Environmental Agency (ARSO)) that influence the GOT (Isonzo, Rižana, Dragonja, Timavo-Reka, Po), as shown in Figure 1.

During the time period of our measurements (April 1-May 31, 2007), we observed primarily light winds with an average speed of 4.7 m s⁻¹, although there was a two-day period (April 5-6) marking stronger (>10 m s⁻¹) winds. The upper ocean evolved from a salinity-driven stratification in April to a temperature-driven stratification in May. The water pCO_2 ranged from 260-340 µatm, but dropped abruptly by ~60 µatm on April 2 and May 8, 2007, both of which coincided with reduced salinities. Eight-day mean Sea-WiFS chlorophyll-a data from VIDA's 2007 position (Piran) and the 3x3- and 5x5-pixel regions centered on the buoy location show an increase of 0.5 and 1.5 mg m⁻³ during the periods from April 2-10 and May 9-17, 2007 (data

not shown), respectively. This increase may be associated with increased river nutrient input and stratification.

Daily flow rates for the northern Adriatic rivers (Timavo-Reka, Isonzo, Rizana, and Po) and daily rainfall from a meteorological station in Portoroz, Slovenia are presented in Figure 4. All rivers except the Isonzo showed increased discharge between May 6-8, 2007 due primarily to a rain event on May 4. Although Po flow rates are significantly higher than other rivers, the satellite SST images indicate that the Po plume had not yet reached VIDA's location at the time of our observations. Our data suggest that the Timavo-Reka River, which drains a Karst terrain, was primarily responsible for the observed decrease in salinity, with smaller contributions from rivers Dragonja and Rizana. The average air-sea CO₂ flux during the April/ May study period indicated a sink of 4.9 mmol m⁻² d⁻¹, primarily driven by variations in wind speed.

Preliminary results indicate that: 1) The GOT was a sink for atmospheric

 CO_2 in late spring of 2007; 2) Aqueous pCO_2 was influenced by fresh water input from rivers and biological production associated with high nutrient input; and 3) Surface water pCO_2 showed a strong correlation with SST and a reasonable correlation with SSS during the presence of the river plume. Spatial surveys of air and water pCO_2 , salinity, temperature, dissolved oxygen, 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.

This is an exciting new collaboration to study the carbon cycle in the Mediterranean. The results of this study will be incorporated into the wider scope of the upcoming Mediterranean carbon cycle efforts within the FP 7 EU program and possibly the European Science Foundation (ESF) (both EU mechanisms that allow US participation) and related international programs and activities (i.e. SOLAS, IM-BER, and ESF- European Cooperation in Science and Technology (COST) activities). We look forward to interactions with the OCB community.

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