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Carbonate chemistry dynamics and biological processes along a river–sea gradient (Gulf of Trieste, northern Adriatic Sea)

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ABSTRACT

In this paper we investigated, for two years and with a bi-monthly frequency, how physical, chemical, and biological processes affect the marine carbonate system in a coastal area characterized by high alkalinity riverine discharge (Gulf of Trieste, northern Adriatic Sea, Mediterranean Sea).

By combining synoptic measurements of the carbonate system with *in situ* determinations of the primary production (^{14}C incorporation technique) and secondary prokaryotic carbon production (^{3}H-leucine incorporation) along a river–sea gradient, we showed that the conservative mixing between river endmember and off-shore waters was the main driver of the dissolved inorganic carbon (DIC) distribution and seasonal variation. However, during spring and summer seasons also the influence of biological uptake and release of DIC was significant. In the surface water of June 2012, the spreading and persistence of nutrient-rich freshwater stimulated the primary production (3.21 μg C L^{-1} h^{-1}) and net biological DIC decrease (−100 μmol kg^{-1}), reducing the dissolved CO_2 concentration and increasing the pH_T. Below the pycnocline of August 2012, instead, an elevated bacterial carbon production rate (0.92 μg C L^{-1} h^{-1}) was related with net DIC increase (92 μmol kg^{-1}), low dissolved oxygen concentration, and strong pH_T reduction, suggesting the predominance of bacterial heterotrophic respiration over primary production.

The flux of carbon dioxide estimated at the air–sea interface exerted a low influence on the seasonal variation of the carbonate system. A complex temporal and spatial dynamic of the air–sea CO_2 exchange was also detected, due to the combined effects of seawater temperature, river discharge, and water circulation. On annual scale the system was a sink of atmospheric CO_2. However, in summer and during elevated riverine discharges, the area close to the river's mouth acted as a source of carbon dioxide. Also the wind speed was crucial in controlling the air–sea CO_2 exchange, with strong Bora events (a typical ENE wind of the Gulf of Trieste) that drastically increased the absorption (−32.2 mmol m^{-2} day^{-1}) or the release (5.34 mmol m^{-2} day^{-1}) of carbon dioxide.

1. Introduction

Despite a small portion of the world ocean surface area (7%), the coastal regions are one of the most biogeochemically active environments in the biosphere and represent a crucial link between land, open ocean, and atmosphere (Borges et al., 2005; Gattuso et al., 1998; Liu et al., 2010). These areas are acknowledged to be a major component of global carbon cycles and budgets, but how physical, chemical, and biological processes affect the marine inorganic carbonate system and air–sea CO_2 exchange remains a huge challenge (Bauer et al., 2013; Chen et al., 2013). Inner shelf waters close to land tend to be sources of CO_2, by contrast mid- to outer-shelf are a sink of atmospheric carbon dioxide (Jiang et al., 2008). This general pattern reflects a balance between respiration of riverine organic matter and *in situ* autotrophic production stimulated by nutrient inputs, but can be greatly altered in large river plume environments and river-dominated margins (Huang et al., 2013). In these areas, the mechanisms influencing net uptake and release of CO_2 remain poorly understood because of limited research and highly variable contribution of freshwater input in terms of mixing and biological processing.

The Gulf of Trieste is a small shallow semi-enclosed basin in the northern part of the Adriatic Sea. The carbon cycle in this area is strongly affected by freshwater input (Cozzi et al., 2012), mainly from the Isonzo River, complex hydrodynamic (Malačič and Petelin, 2001), and atmospheric forcing including Bora wind (Boldrin et al., 2009). Also the biological processes play an important role and, despite the high variability, on a seasonal time scale the metabolic balance of the system usually shifts from net autotrophic status in winter–spring to net heterotrophic in summer–autumn (Fonda Umani et al., 2012).

Recent studies reported the Gulf of Trieste as an annual sink of atmospheric carbon dioxide (Cantoni et al., 2012; Ingrosso et al., 2015; Turk

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et al., 2013). They also showed that the strong Bora wind and the very low seawater temperature observed during dense water formation process can enhance the atmospheric CO_2 dissolution and consequently the ocean acidification process. This situation, however, could be not completely true. In the coastal areas changes of pH on long time scale result from a multitude of drivers, such as impacts from watershed, nutrient inputs, and changes in ecosystem trophic status (Duarte et al., 2013). In particular the Isonzo River in the Gulf of Trieste is a source of total alkalinity to the sea, due to a very high carbonate-weathering rate of its watershed (Szramek et al., 2007, 2011). This is a characteristic that differs from most of the world's rivers and, as reported by many studies relatively to similar ecosystems (Raymond and Cole, 2003; Raymond et al., 2008; Watanabe et al., 2009), an increase of total alkalinity export from river to the sea could increase the seawater buffer capacity and mitigate the effect of regional ocean acidification.

Taking into account the previous considerations, the sensibility of a coastal area to the ocean acidification remains unclear, therefore a better understanding of the factors that regulate the carbonate system seasonal variation is important to assess the future trend of ocean acidification process in a high CO_2 world. In order to fill these knowledge gaps, we examine the carbonate system dynamic in the Gulf of Trieste along a river–sea gradient, determining the different contributions of water mixing, air–sea CO_2 exchange, and biological processes. An estimation of biological uptake/release of dissolved inorganic carbon (DIC) from a carbonate system perspective was also attempted and compared with direct radioisotopic measurements of primary production and heterotrophic bacterial carbon production.

2. Materials and methods

2.1. Study area

The Gulf of Trieste is a small (~500 km^2) and shallow (maximum depth 25 m) semi-enclosed basin in the northeastern part of the Adriatic Sea (Fig. 1). In this area, fresh water inputs and atmospheric forcing greatly influence the seawater temperature, salinity, and water column stratification (Malačič and Petelin, 2001). Seawater temperature shows a seasonal oscillation from 8 °C (February) to 26 °C (August), whereas the salinity in the surface waters ranges between 24, in spring during high riverine discharge, and 38.3 (Celio et al., 2006). Typically, in winter the water column is well mixed, whereas during spring the freshwater input and surface heating lead to thermohaline stratification. The period between May and September is characterized by strong density gradients and the prevalence of respiration processes at the bottom layer, which determine low oxygen concentration and occasionally hypoxia events (Faganeli et al., 1985; Malej and Malačič, 1995). In autumn, convective and mechanical mixing, induced by water cooling and wind, disrupts the vertical stratification, oxygenates the bottom water and distributes the re-generated nutrients in the whole water column.

The main river of the Gulf is the Isonzo/Soča River from the north-west coast (Cozzi et al., 2012), which controls the salinity and nutrient concentration of the system with a highly variable outflow. On seasonal time scale, however, spring and autumn are generally characterized by the highest river discharges (due to snowmelt and rain respectively), while drought periods occur during winter and summer.

The trophic status of the Gulf depends also on prevailing circulation patterns and not only on the intensity of the Isonzo River discharge rate. The circulation of the Gulf is mainly cyclonic at the transitional and lower layer (10 m — bottom), while the surface layer (surface–5 m) is affected by wind conditions (Stravisi, 1983). There are mainly two dominant winds: the SE Scirocco and the ENE Bora (Stravisi, 1977, 1983). Bora-induced circulation is more frequent in autumn and in winter and it generates a cyclonic gyre at the surface layer, which quickly flows out of the Gulf the riverine waters. During Scirocco blowing, instead, an anticyclonic surface circulation favours the eastward spreading of nutrient-rich freshwaters, which increases primary production (Cantoni et al., 2003; Querin et al., 2006). The Gulf of Trieste is also under the influence of the Eastern Adriatic Current (EAC), a current flowing northwards along the Croatian coast and advecting warmer, saltier, and more oligotrophic waters coming from the Ionian Sea (Poulain and Cushman-Roisin, 2001). The ingression of EAC is more frequent in the cold seasons, when a cyclonic circulation is present, and it can favour oligotrophic conditions in the Gulf.

The phytoplankton annual cycle in the Gulf of Trieste is characterized by two blooms (Cabrini et al., 2012). The first one occurs during late winter–early spring and is typically due to a single diatom species. The second one arises in early autumn and it is characterized by a less intense density of three or more diatom species, usually of large cell size. In summer, the total phytoplankton abundance is generally low, due to the nutrient depletion, and the diatom-based phytoplankton community of the spring season is substituted by small phytoflagellates.

2.2. Sampling strategy and analytical procedures

Data were collected in the framework of the MedSeA (Mediterranean Sea Acidification in a changing climate) project. The sampling was carried out at four stations (Z1, Z2, Z3, Z4) along a transect from the Isonzo River mouth to the centre of the Gulf (Fig. 1), with a bimonthly frequency from March 2011 to February 2013. According to the main circulation of the gulf, the position of the four stations was selected to obtain a river–sea gradient along which the carbonate system dynamics and the influence of physical and biogeochemical processes were analysed.

Temperature (T) and salinity (S) profiles were obtained using a multiparametric SBE 19 Plus Seacat probe. The precision of measurements was ±0.005 °C for T and ±0.011 for S. Each station was sampled for chemical and biological analyses collecting 5 L Niskin bottles at the surface (0.5 m), at the bottom (Z1 = 4.5 m, Z2 = 13 m, Z3 = 18 m, Z4 = 23 m), and at one (for station Z3) and two (for station Z4) intermediate depths, selected in each cruise according to the T–S profile, in order to better characterize the different water masses.

The pH was measured following the spectrophotometric method (Dickson et al., 2007a) with the indicator dye m-cresol purple (Merck-105228). To avoid CO_2 gain or loss, unfiltered seawater samples were collected directly into quartz cuvettes with a 10 cm pathlength, leaving no head space. pH was always measured within a few hours from sampling and values are reported on total scale (pH_T). The analytical precision was estimated to be ±0.002 pH_T units, determined by replicates from the same Niskin bottle. Due to the use of an unpurified indicator, the results could present an error as large as 0.02 pH units (Liu et al., 2011; Yao et al., 2007). Data were then corrected with a batch-specific correction algorithm, obtained with a paired pH measurements between a purified indicator and the unpurified indicator in seawater samples of different pH values (over a range of 7.2–8.2), as described by Liu et al. (2011). The pH of freshwater samples was measured potentiometrically and the electrode was calibrated with standard NBS buffer solutions for pH 4.01, 7, and 9.

For the total alkalinity (A_T), samples were pre-filtered on glass-fibre filters (Whatman GF/F) into a 500 mL narrow-necked borosilicate glass bottle, to remove phytoplankton cells and particles of $CaCO_3$, derived from karstic watershed or calcifying organisms, which could artificially modify the A_T during titration (Bockmon and Dickson, 2014; Gattuso et al., 2010). Each bottle was poisoned with 100 μL of saturated mercuric chloride ($HgCl_2$) to halt biological activity, sealed with glass stoppers and stored at 4 °C in the dark until analysis. Total alkalinity was determined by potentiometric titration in an open cell (Dickson et al., 2007b) using a non-linear least squares approach. The HCl titrant solution (0.1 mol kg^{-1}) was prepared in NaCl background, to approximate the ionic strength of the samples, and calibrated against certified reference seawater (CRM, Batch #107, provided by A.G. Dickson, Scripps