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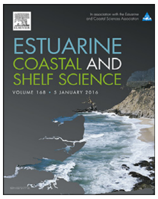

Drivers of the carbonate system seasonal variations in a Mediterranean gulf

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ABSTRACT

The effects of different physical and biogeochemical drivers on the carbonate system were investigated in a semi-enclosed coastal area characterized by high alkalinity riverine discharge (Gulf of Trieste, Northern Adriatic Sea, Mediterranean Sea). Our 2-year time-series showed that a large part of the seasonal carbonate chemistry variation was controlled by the large seasonal change of seawater temperature, though air-sea CO_2 exchange, biological activity (primary production-respiration), and riverine inputs also exerted a significant influence.

With the exception of summer, the Gulf of Trieste was a sink of atmospheric carbon dioxide, showing a very strong CO_2 fluxes from atmosphere into the sea (-16.10 mmol m^{-2} day^{-1}) during high wind speed event of north easterly Bora wind. The CO_2 influx was particularly evident in winter, when the biological activity was at minimum and the low seawater temperature enhanced CO_2 solubility. During spring, the drawdown of CO_2 by primary production overwhelmed the CO_2 physical pump, driving a significant decrease of dissolved inorganic carbon (DIC), [CO_2], and increase of $pH_{T25\ °C}$. In summer the primary production in surface waters occurred with the same intensity as respiration in the bottom layer, so the net biological effect on the carbonate system was very low and the further reduction of seawater CO_2 concentration observed was mainly due to carbon dioxide degassing induced by high seawater temperature. Finally, during autumn the respiration was the predominant process, which determined an overall increase of DIC, [CO_2], and decrease of $pH_{T25\ °C}$. This was particularly evident when the breakdown of summer stratification occurred and a large amount of CO_2, generated by respiration and segregated below the pycnocline, was released back to the whole water column. Local rivers also significantly affected the carbonate system by direct input of total alkalinity (A_T) coming from the chemical weathering of carbonate rocks, which dominate the river watershed. Our finding clearly demonstrates a high A_T concentration in low salinity surface waters (A_T max = 2742.8 μmol kg^{-1}) and a negative A_T-salinity correlation. As a result the Gulf of Trieste revealed a low Revelle factor (10.1) and one of the highest buffer capacities of the Mediterranean Sea ($\text{ß}_{DIC} = 0.31$ mmol kg^{-1}), which allows the system to store a significant amount of atmospheric CO_2 with a small decrease of seawater pH.

1. Introduction

The ocean currently absorbs approximately a quarter of the CO_2 added to the atmosphere from human activities each year, greatly reducing the impact of this greenhouse gas on climate (Sabine et al., 2004; Le Quéré et al., 2009, 2010; 2015; McKinley et al., 2011). However, the oceanic uptake of anthropogenic CO_2 also leads to a gradual acidification of the world's ocean, which is now a well known phenomena commonly referred to as "ocean acidification" (Caldeira and Wickett, 2003; Doney et al., 2009). Since the beginning of the industrial era, the ocean surface pH has decreased by 0.1 pH units and the global pH reduction actually ranges between -0.0014 and -0.0024 yr^{-1} (IPCC, 2013). In the NW Mediterranean Sea the ocean acidification process is also occurring

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(De Carlo et al., 2013) and the acidification rate has been estimated to be 0.003 pH units yr^{-1} (Geri et al., 2014).

The projections of ocean acidification in the coastal area, where paradoxically some of the most vulnerable taxa live, are still lacking and they are remarkably difficult to predict due to the great complexity of these ecosystems. Here, the CO_2 levels are regulated by different physical and biological drivers such as air-sea CO_2 exchanges, ecosystem metabolism, net community calcification rate, riverine inputs of carbonate weathering products, as well as hydrological features that determine the mixing between open ocean and coastal waters (Duarte et al., 2013). These processes can cause changes in pH from seasonal to decadal and longer timescales, enhancing or reducing the ocean acidification. For example, in temperate eutrophic waters with high degree of stratification and reduced ventilation in summer/autumn months (Melzner et al., 2012), the oxidation of organic matter in subsurface waters lowers dissolved oxygen concentrations, adds CO_2 to solution, reduces pH, and, over longer time scales, can exacerbate the ocean acidification process (Byrne et al., 2010; Cai et al., 2011). Conversely, an increase of total alkalinity export from river to the sea could increase the seawater buffer capacity and mitigate regionally the effect of ocean acidification (Raymond and Cole, 2003; Raymond et al., 2008; Watanabe et al., 2009).

The Northern Adriatic Sea (NAd), situated in the northernmost region of the Mediterranean Sea, receives freshwaters from many rivers and is subject to wide variations of temperature and salinity. Though oceanographic studies carried out in this area date back to the 18th century, long time series of chemical oceanography parameters began only in the 1970s and the carbonate chemistry observations were set up only recently (Turk et al., 2010).

Climatic and anthropogenic driven changes have occurred in the last decades in the NAd. An oligotrophication trend was observed by different authors (Solidoro et al., 2009; Mozetič et al., 2010; Giani et al., 2012), who ascribed this process to a reduction of annual river discharges and river-borne nutrient inputs. Moreover, Luchetta et al. (2010) have recently detected a pH decrease in the NAd, underlining the importance to follow also in this area the ocean acidification process.

The objective of the present work is to understand how physical and biogeochemical drivers could influence the seasonal cycles of marine carbonate system in a shallow Mediterranean gulf. Specifically, both the air-sea CO_2 exchanges and thermal/not-thermal contributions to the seasonality of the CO_2 system are quantified. We also investigate the buffer capacity of the area, which is affected by the products of carbonate mineral weathering coming from freshwater discharges of the local rivers.

2. Materials and methods

2.1. Study area

The Gulf of Trieste (Fig. 1) is a shallow semi-enclosed basin located in the northernmost part of the Adriatic Sea, with a maximum depth of 25 m and a surface area of about 600 km^2 (Malej et al., 1995). It is an example of a coastal region of freshwater influence (ROFI, Simpson, 1997), characterized by a high spatial and temporal variability of its physical, chemical, and biological properties. Four rivers discharge waters into the gulf: Isonzo, Timavo, Rižana, and Dragonja. The main freshwater input is through the Isonzo river from the north-west Italian coast (Cozzi et al., 2012), which is characterized by high discharges rate during spring and autumn, while drought periods occur in winter and summer. These discharges, due to the prevailing cyclonic circulation, affect mainly the north-western part of the gulf and only during the freshets in comitance with southerly winds the plume spread throughout the gulf (Querin et al., 2007).

The water column is subject to a strong variation in temperature, salinity, and vertical stratification during the year (Malačič and Petelin, 2001). Seawater temperature shows a seasonal cycle from winter minima of 6 °C to summer maxima of >29 °C (Cardin and Celio, 1997; Celio et al., 2006), whereas the salinity ranges from 33 to 38 (Malačič et al., 2006). During spring the freshwater input and surface heating cause the thermohaline stratification, which increases in strength during summer. In autumn and winter, convective and mechanical mixing, induced by water cooling and wind, disrupts the vertical stratification leading to a mostly homogeneous water column. Also in this period, strong Bora wind events, a regional ENE cold wind, cause the formation of dense waters, which are a fundamental component for the generation of North Adriatic Dense Water (Artegiani et al., 1997; Malačič and Petelin, 2001).

River watersheds along the Gulf of Trieste are composed mainly of carbonate rocks (e.g., limestone and dolomite) (Pleničar et al., 2009) and they have some of the highest carbonate-weathering in the world (Szramek et al., 2007, 2011). The riverine inputs then represent a very important source of inorganic carbon, which can significantly affect the marine carbonate system and the whole C cycle.

2.2. Sampling and analyses

The study was performed at the C1 station in the northeastern part of the Gulf of Trieste (45°42.05′N–13°42.60′E), a coastal time series station (bottom depth of 17.5 m) where a long term ecological monitoring has been in place since 1970 (http://nettuno.ogs.trieste.it/ilter/BIO/). The data presented here refer to the period of March 2011–February 2013. Discrete water samples were collected monthly with 5-L Niskin bottles at four depths (0.5, 5, 10, 15 m) in order to measure total alkalinity (A_T), pH, dissolved oxygen, and nutrients.

Depth profiles of salinity (Practical Salinity Scale of 1978) and temperature (°C) were determined using a Conductivity-Temperature-Depth/Pressure (CTD) recorders (Idronaut 316 and SBE 19 Plus Seacat probe).

For the total alkalinity, samples were pre-filtered on glass-fibre filters (Whatman GF/F) into a 500 mL narrow-necked borosilicate glass bottle. Filtration was performed to remove phytoplankton cells and particles of $CaCO_3$, derived from karstic watershed or calcifying organisms, which respectively can interact with HCl titrant solution and dissolve during measurements due to acid additions, producing a non-negligible error in the exact estimation of the A_T concentration (Gattuso et al., 2010; Hydes et al., 2010; Bockemon and Dickson, 2014). 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 (SOP 3b, Dickson et al., 2007) using a non-linear least squares approach. The titration procedure was performed with the titration unit Mettler Toledo G20 interfaced with a computer, using the data-acquisition software LabX. After titration the data were processed and A_T calculated with a computer program developed at OGS (Istituto Nazionale di Oceanografia e di Geofisica Sperimentale) similar to that listed in SOP 3 of DOE (1994) and adapted to work in association with the Mettler Toledo LabX software. 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 Institution of Oceanography, USA). Accuracy and precision of the A_T measurements on CRM were determined to be less than ±2.0 μmol kg^{-1}. Additionally,