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Physical and biological control of aragonite saturation in the coastal waters of southern South Korea under the influence of freshwater

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ABSTRACT

We investigated the aragonite saturation state (Ω_{arag}) during all four seasons in a coastal region of southern Korea that receives considerable freshwater input. The surface Ω_{arag} values were higher during productive seasons with enhanced freshwater influences, likely due to an increased net removal of dissolved inorganic carbon (DIC) from the water column (i.e., biological control). In addition, during the productive seasons, enhancement of Ω_{arag} was observed with decreasing salinity within a linear mixing zone present between river-influenced surface and saltier bottom waters. DIC appeared to be effectively sequestered from the warmer, less salty surface water by downward flux of organic matter, but not significantly affected by the relatively DIC-rich, cooler and saltier bottom waters under strong stratification conditions during these seasons (i.e., physical control). Low phytoplankton productivity and seasonal breakdown of the stratification caused reduced saturation in other seasons and made the study area a weak sink for atmospheric CO_2.

1. Introduction

The uptake of anthropogenic carbon dioxide (CO_2) by the ocean has a substantial impact on marine biogeochemistry by reducing the pH of seawater (Feely et al., 2008; Sabine et al., 2004). The surface pH (~8.2) has decreased by approximately 0.1 units since the preindustrial era (Caldeira and Wickett, 2003) and is expected to decrease by another 0.3–0.4 units by the end of this century, according to Intergovernmental Panel on Climate Change (IPCC) projections of future CO_2 emissions and subsequent absorption of anthropogenic CO_2 by the oceans (Doney et al., 2009; Orr et al., 2005). Induced by the absorption of anthropogenic CO_2, the reductions in pH and $CaCO_3$ saturation (defined as $[Ca^{2+}][CO_3^{2-}]/K_{sp}$, in which the denominator indicates the solubility product) lower the calcification rates of marine calcifying organisms (Doney et al., 2009; Gazeau et al., 2007; Orr et al., 2005; Jin and Gao, 2016; Zhan et al., 2016). In addition, adverse effects in the early development stages of these organisms were observed at higher CO_2 concentrations (Moulin et al., 2011; Gazeau et al., 2007; Guo et al., 2015).

An understanding of the impacts of ocean acidification is particularly important in coastal regions, which are critical habitats for many marine organisms highly vulnerable to reduced pH and $CaCO_3$ saturation. Coastal waters can be acidified by several factors, such as atmospheric CO_2 flux (Zeebe et al., 2008), eutrophication (Cai et al., 2011; Zhai et al., 2012; Zeng et al., 2015), the introduction of relatively acidic freshwater (Salisbury et al., 2008; Jiang et al., 2010), deposition of atmospheric pollutants (Doney et al., 2007), upwelling of CO_2-enriched deep water (Feely et al., 2008), and interaction between the water column and sediment (Santos et al., 2011). Indeed, recent studies showed that these acidification factors resulted in the undersaturation of aragonite (metastable $CaCO_3$) in coastal areas (Cai et al., 2011; Feely et al., 2010; D. Kim et al., 2013; Kim et al., 2014). All of these factors, except for the absorption of atmospheric CO_2, are directly associated with the introduction of new nutrients. These nutrients may facilitate biological drawdown of dissolved inorganic carbon (DIC) in seawater (thus increasing pH) and shift its $CaCO_3$ saturation to a higher state. Input of freshwater and upwelling of deep water also modify the physical state of the surface layer and the vertical structure of the water column. Thus, freshwater input associated with these physical, chemical, and biological changes may not always acidify coastal waters. Additionally, these effects may be subject to considerable seasonal variations; few studies have been conducted from this perspective.

This question led us to investigate the impact of freshwater input on the seawater carbonate system in a coastal area adjacent to Busan city,

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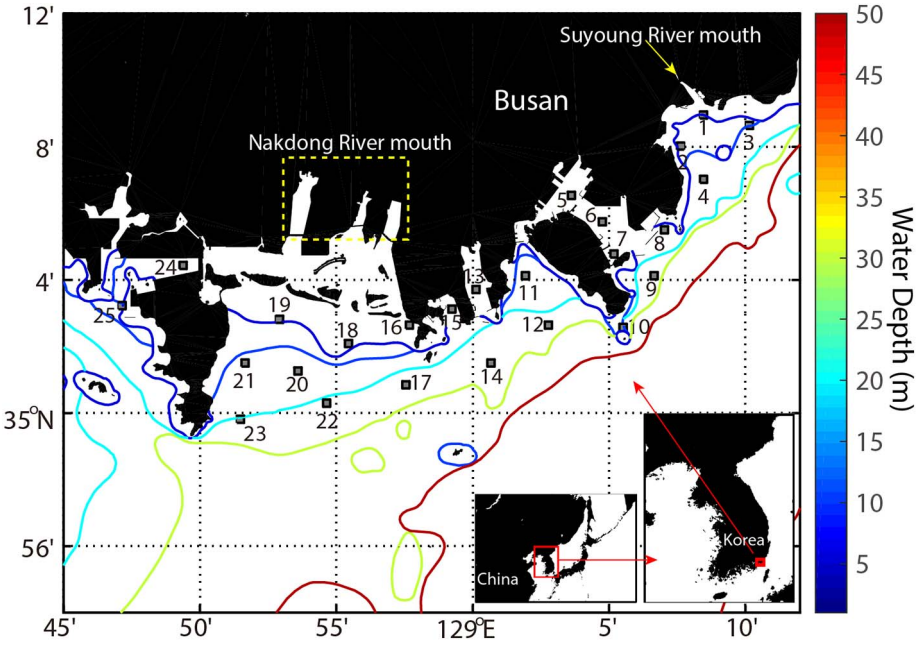

Fig. 1. Busan coastal area. The numbered gray squares indicate the stations included in this study. The contour lines on the sea correspond to bottom depths.

located in the southeastern part of the Korean Peninsula (hereinafter, referred to as the Busan coastal area; Fig. 1). This coastal system is significantly affected by freshwater input from the Nakdong River, the second-largest river in South Korea. In this study, we examined the responses of the aragonite saturation state (Ω_{arag}) to physical, chemical, and biological changes associated with freshwater inputs. These changes include strengthened water column stratification, dilution of seawater constituents, enhanced phytoplankton growth and subsequent bacterial remineralization, and air–sea gas exchange.

2. Study area and field survey

The water depth in the Busan coastal area ranges from 7 to 30 m, increasing seaward. The tide is semidiurnal, with a mean tidal range of 1.4 m (Lee et al., 1999). Busan, the largest city in the study area (and the second-largest city in South Korea), has a population of ~3.5 million. According to the National Water Resources Management Information System (WAMIS, www.wamis.go.kr), the Nakdong River with a watershed area of ~23,000 km^2 discharges approximately 6.8–11.3 × 10^9 m^3 of fresh water annually into the study area. Among the 25 stations sampled, Stations #16–#23 receive direct influence from the Nakdong River (hereinafter, direct influence zone; Fig. 1). The distance between the river mouth and Station #22 is approximately 9 km. The riverine freshwater plume generally extends to the northwest due to the dominant current flowing through the strait between Korea and Japan, diluting the effects of the Nakdong River on Stations #1–#15. The mean velocity of this current was estimated to be ~25 cm s^{-1} (Ito et al., 2014), which gives a surface water travel time of < 2 days (~30 km as a distance) from Station #22 to #1 via #10.

Field surveys were conducted along the Busan coast during all four seasons of 2013: winter (February 20), spring (May 7), summer (August 20), and autumn (November 12). Water samples were collected from the surface (~1 m below the surface) and bottom (~1 m above the bottom) using 5-L polyvinyl chloride Niskin sampling bottles (General Oceanics, Miami, FL, USA). Temperature (°C) and salinity (in practical salinity unit; PSU) were measured using a conductivity–temperature–depth sensor (Ocean Seven 319, Idronaut Co., Brugherio, Italy). At each station, dissolved oxygen (DO), chlorophyll-*a*, DIC, total alkalinity (TA), and nutrients were determined. Station #18 was not sampled at either depth during the May survey and surface water was not collected from station #8 in November.

3. Sampling and analytical procedures

DO was fixed immediately after seawater sampling using manganous sulfate/alkali-iodide solutions, and then measured within 24 h in the laboratory (Grasshoff et al., 2009). Nutrient samples were drawn from the Niskin bottles, filtered through 0.7-μm-pore GF/F filters, and stored frozen at −20 °C. The seawater samples for measuring DIC and TA were also collected from the Niskin bottles into precleaned 250-mL borosilicate bottles. These samples were poisoned by $HgCl_2$ to halt biological activity. For chlorophyll-*a* measurements, 1.0 L of seawater was immediately filtered onboard the research vessel through a 47-mm-diameter GF/F filter and then stored at −20 °C until further laboratory analysis.

DO was measured using the Winkler method (Grasshoff et al., 2009). Nutrient concentrations were determined using an autoanalyzer (model QuikChem AE, Lachat, Loveland, CO, USA) and calibrated using CSK Standard Solutions (Wako Pure Chemical Industries, Osaka, Japan). DIC was analyzed using a highly precise gas extraction/coulometric detection system (VINDTA; Marianda, Kiel, Germany), coupled with a CO_2 coulometer (model 5012; UIC Inc., Joliet, IL, USA). The analytical error for DIC measurement was < 3 μmol kg^{-1}. TA was measured by potentiometric titration using a Gran titration system (model AS-ALK2; Apollo SciTech, Bogart, GA, Inc.). Each sample was measured three times within a precision of 0.1%. Certified reference material provided by Andrew Dickson (Scripps Institution of Oceanography, San Diego, CA, USA) was used for calibration and accuracy assessment of DIC and TA measurements. Chlorophyll-*a* was measured using a Turner-designed fluorometer (Turner BioSystems, Sunnyvale, CA, USA), after extraction with 90% acetone, for 24 h in the dark.

Seawater pH (total scale), Ω_{arag} and partial pressure of CO_2 (pCO_2) were estimated from DIC and TA data using the CO2SYS software program (Lewis and Wallace, 1997). We used the carbonic acid dissociation constants of (Mehrbach et al., 1973), refitted by (Dickson and Millero, 1987), in the calculation. The solubility product of aragonite was calculated based on (Mucci, 1983). The uncertainty of Ω_{arag} was approximately ± 0.03, estimated based on uncertainties in the DIC and TA measurements and the thermodynamic constants.