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The contribution of low temperature and biological activities to the CO_2 sink in Jiaozhou Bay during winter

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ABSTRACT

In some mid-latitude coastal oceans in winter, in addition to the decrease in sea surface partial pressure of carbon dioxide (pCO_2) caused by cooling, strong primary production always occurs and consumes CO_2. Therefore, the consumption of CO_2 by primary production may be the main reason for the appearance and strengthening of a CO_2 sink in such regions during winter. In our study, field survey results and analysis before and after a significant cold wave during the winter of 2016 in Jiaozhou Bay (JZB) showed that JZB acted as a CO_2 sink due to the decrease in sea surface temperature (SST) and a phytoplankton bloom. Besides, with the decreasing SST during the cold wave, the primary production was also greatly enhanced. The estimated pCO_2 reductions between the cruises caused by the thermal and non-thermal processes were 31 μatm (~6–62 μatm) and 38 μatm (~27–63 μatm), respectively. The pCO_2 reduction calculated by the dissolved inorganic carbon (DIC) change caused by biological activities was 39 μatm (~30–60 μatm), and this value was very close to the pCO_2 reduction caused by non-thermal processes. The results clearly indicated that biological activities and decreasing SST were the main factors leading to the CO_2 sink in JZB during winter. The pCO_2 reduction caused by biological activities was greater than that caused by the SST change in most areas except the north-western area, where the opposite was observed.

1. Introduction

Determining the strength of sources and sinks for atmospheric CO_2 in coastal oceans has attracted considerable attention in recent years (Borges, 2011; Cai, 2011; Gruber, 2015). It is estimated that coastal oceans account for 10–20% of the CO_2 absorbed by world oceans (Chen et al., 2013; Wanninkhof et al., 2013; Laruelle et al., 2014). However, due to the highly dynamic biogeochemical processes in coastal oceans, the estimates of air-sea CO_2 fluxes still have large uncertainties. Therefore, it is necessary to develop a comprehensive and deeper understanding of the controlling mechanisms of coastal CO_2 system.

The decrease in seawater temperature in winter increases the solubility of CO_2 in seawater, resulting in a decrease in the sea surface partial pressure of CO_2 (pCO_2). In most of the world's mid-latitude oceans, seasonal water temperature variation from summer to winter accounts for > 50% of the seasonal sea surface pCO_2 changes (Takahashi et al., 2002). Many studies in mid-latitude oceans, such as those undertaken in the Bermuda Atlantic, the North Sea, the Gulf of Cádiz in Spain, and the northern Yellow Sea in China, have all demonstrated that low water temperature was the main reason for the low sea surface pCO_2 during winter and sometimes even transformed a CO_2 source to a sink (Bates, 2001; Schiettecatte et al., 2007; Ribas-Ribas et al., 2011; Xue et al., 2012). However, in some mid-latitude coastal oceans, under the coupled influence of vertical mixing, terrestrial input and other processes, strong primary production always occurs and consumes CO_2 in winter. For instance, based on the data collected over five years (from 1998 to 2003) in the region off the Otaru coast in Hokkaido, Japan, Sakamoto et al. (2008) reported that the concentrations of nutrients reached a peak in winter due to vertical mixing and continuous respiration since autumn. High nutrients concentrations promoted the phytoplankton bloom and the entire sea served as a strong CO_2 sink in February when the water temperature was at its lowest (2 °C). Their results showed that the contribution ratio of the primary production to the seasonal variation in the fugacity of CO_2 in the seawater (fCO_{2sea}) was 35% in winter, higher than that of low water temperatures (25.2%). Moreover, in the Loire estuary, increased river discharge in winter promoted the vertical stratification of seawater and provided large amounts of nutrients. These conditions led to a phytoplankton bloom consisting mainly of diatoms; the bloom caused the sea surface pCO_2 to rapidly decrease to an undersaturated state (Guillaud

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et al., 2008; Bozec et al., 2012). The authors pointed out that low seawater temperatures (7.5 to 11.1 °C) and the phytoplankton bloom jointly transformed the plume of the estuary from a CO_2 source in autumn to a sink in winter. Therefore, in addition to low temperatures, biological activity is also an important cause of the CO_2 sink development in coastal oceans during winter.

Many studies have reported high levels of primary production in winter in mid-latitude coastal oceans. For example, in the Bahía Blanca Estuary of Argentina (Popovich et al., 2008), the occurrence of a winter bloom increased the chlorophyll *a* (Chl *a*) concentration to the annual maximum value (44 μg L^{-1}). In Massachusetts Bay and Narragansett Bay in North America (Keller et al., 2001; Oviatt et al., 2002), phytoplankton biomass started accumulating in December to January and reached the highest level in February to early April. In the coastal regions of northern China, the Chl *a* concentrations in the northern Yellow Sea showed a bimodal pattern with peaks in summer and winter (Liu et al., 2011). Additionally, in the coastal regions of the Bohai Sea, the Chl *a* concentrations in winter were higher than in summer, especially in the Laizhou Bay where the Chl *a* concentrations in winter were three times as high as in summer (Zhao et al., 2004). Although the winter phytoplankton bloom is relatively common in mid-latitude coastal oceans, insufficient attention has been paid to its influence on the CO_2 source/sink structure.

Jiaozhou Bay (JZB) is a typical semi-enclosed bay in northern China (35°18′–36°18′N, 120°04′–120°23′E). It is located in the mid-latitude region and adjacent to downtown Qingdao, which has a population of 4.9 million. Due to increasing urbanization, JZB is characterized by high levels of respiration and primary production (Wang and Wang, 2011). Studies of primary production in JZB over nearly 20 years have shown that the population of phytoplankton exhibited a clear bimodal pattern with peaks in summer and winter (Wu et al., 2005; Wang and Wang, 2011; Sun et al., 2011a). In summer, high values of Chl *a* always appeared in the western area affected by discharge from the Dagu River, whereas in winter, the high values often appeared in the north-eastern area close to the industrial district (Wang et al., 2015). To investigate the carbon system in JZB, Zhang et al. (2012) conducted one cruise in autumn and another in winter. Their results indicated that the intense respiration in autumn made the entire bay act as a CO_2 source. In contrast, in winter, due to the phytoplankton bloom, the entire bay transformed into a CO_2 sink, and high values of Chl *a* and the strongest CO_2 sink both appeared in the north-eastern area. Recently, Li et al. (2017) discussed the main controlling mechanisms of sea surface pCO_2 in JZB during summer. They proposed that the increasing terrestrial input resulting from heavy rain stimulated the rapid growth of phytoplankton in JZB. Especially in the western area, the mechanism controlling the sea surface pCO_2 shifted from calcium carbonate ($CaCO_3$) precipitation to strong primary production, and the sea area transformed from a CO_2 source to a sink. In conclusion, the formation of CO_2 sinks in winter and summer in JZB coincided well with the bimodal pattern of phytoplankton and the high Chl *a* regions in these two seasons.

In this paper, according to field survey data collected before and after a significant cold wave in the winter of 2016, we analysed the contributions of cooling and primary production to the CO_2 sink in JZB and the main mechanisms controlling sea surface pCO_2. We hope that our study aids understanding of the controlling mechanisms of sea surface pCO_2 and the CO_2 source/sink features during winter in mid-latitude coastal oceans.

2. Study area and methods

2.1. Study area

JZB is located off the southern shores of the Shandong Peninsula (Fig. 1). The city of Qingdao encloses the bay on three sides and seawater exchange occurs only through the southern part of the bay. JZB covers a water area of 340 km^2. The average water depth is 7 m, and the maximum depth is 66.9 m. JZB is mainly affected by the East Asian Monsoon, which features a north-west wind in winter and a south-east wind in summer (Li et al., 2006). The tidal system is regular semi-diurnal with an average tidal range of 2.8 m. The tides create strong vertical mixing, which contributes to homogeneous vertical profiles of seawater temperature and salinity, except in areas significantly affected by runoff in summer (Chen et al., 1999). The rivers flowing into JZB include the Dagu River, Licun River, Haibo River, Loushan River, and others. They have almost no natural runoff except during the period after heavy rains in summer. A wastewater treatment plant (WWTP) is located beside each of the major estuaries along the eastern coast. These WWTPs – the Licun River WWTP, Haibo River WWTP and Loushan River WWTP – have designed treatment capacities of 250,000, 160,000, and 100,000 m^3 d^{-1}, respectively. Therefore, the estuaries have already become conduits for wastewater (Gao et al., 2008). The average water residence time in JZB is 52 days (Liu et al., 2004).

2.2. Cruise sampling and laboratory sample processing

The basic data were collected during winter on 21 January and 26 January 2016 at 29 stations (Fig. 1). The cruise survey began from station 1 and ended at station W10 (see route map). During the cruise on 26 January, due to the influence of cold weather, some parts of the western area in JZB were frozen, and stations 9, 11, 12, and W5 were not sampled. All seawater samples were collected from the sea surface at a depth of approximately 1.5 m because of the homogeneous vertical profiles in the JZB water column (Chen et al., 1999). Sea surface temperature (SST) and salinity (SSS), oxygen saturation level (DO%) and sea surface pCO_2 data were collected continuously. Discrete water samples were collected into 5 l Niskin bottles for later analysis of dissolved inorganic carbon (DIC), total alkalinity (TA), and Chl *a*.

SST and SSS were automatically recorded each second and averaged over 1 min using an SBE 45 Micro TSG (Sea-Bird Inc., Bellevue, WA, USA), with a nominal precision of 0.002 °C for temperature and 0.005 for salinity. The DO% was measured with a YSI-5000 oxygen analyser (YSI Corporation, Yellow Spring, OH, USA), which was calibrated using the Winkler titration method (nominal precision: 0.1%). The sea surface pCO_2 was measured with a G2131-i Analyzer (PICAROO, USA) using wavelength-scanned cavity ring-down spectroscopy (WS-CRDS) with a nominal precision of < 50 ppbv over 5 min intervals.

DIC and TA samples need filtration treatment to avoid the effect of the particulate matter in coastal oceans (Li et al., 2017). The DIC samples were directly collected from the Niskin bottle using a syringe and filtered through a 0.45 μm disposable syringe filter to avoid exchange with the air. TA samples were filtered through cellulose acetate membranes (0.45 μm) using a borosilicate glass filter. The DIC and TA samples were all poisoned with saturated mercury chloride (final concentration: *c.* 0.02% by volume) and preserved at 4 °C (Li et al., 2017). The DIC values were determined by acid extraction with a DIC analyser (AS-C2, Apollo SciTech, USA), and sample variation between duplicates was < 0.1%. The TA values were determined by Gran titration using a Total Alkalinity Titrator (AS-ALK2, Apollo SciTech, USA). The concentration of HCl solution used in the titration was calibrated against Certified Reference Materials (CRMs) from Scripps Institution of Oceanography. The TA measurement precision was within 0.1%.

Samples for Chl *a* measurements were filtered through GF/F glass fibre membranes (0.7 μm; Whatman, Maidstone, UK) at pressures below 0.04 MPa. Then, 0.5 to 1 ml saturated magnesium carbonate was added to the membranes after filtration, and the samples were preserved at −20 °C. Before analysis, the samples were extracted with 90% acetone for 24 h and centrifuged for 10 min (4000 rpm); then, the supernatant fluid was analysed using a fluorescence spectrophotometer (F4500, Hitachi Co, Tokyo, Japan).