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The response of the carbonate system to a green algal bloom during the post-bloom period in the southern Yellow Sea

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ABSTRACT

Since 2007, the green algal bloom occurred along the coast of Qingdao city every summer. In this study, we focused on how the carbonate system responded to the green algal bloom. Dissolved inorganic carbon (DIC), total alkalinity (TA) and pH were measured in two cruises during the green algal post-bloom period in summer 2008 in the southern Yellow Sea. Data showed that the average values of alkalinity calculated from DIC and pH were 2217 and 2241 μmol kg^{-1} during the first and second cruises, respectively. The alkalinity measured by Gran titration, however, was abnormal, with average values of 3333 and 3280 μmol kg^{-1}. The abnormal measured TA values were probably due to both direct contribution of organic matter and its side reaction in determining TA using Gran titration. Another significant phenomenon was an increase of DIC and a decrease of pH after the bloom. The changes of DIC and pH during the two cruises were +87 μmol kg^{-1} and −0.18, respectively. Normalized DIC and TA showed that DIC was not conserved after the bloom while TA could be still conserved. In contrast to green algal bloom period, during the post-bloom period, pCO_2 values were significantly raised in seawater, with average values of 596 and 981 μatm, resulting in CO_2 outgassing from seawater. These results showed that carbonate system in seawater could be greatly altered by green algal bloom.

1. Introduction

In the early summer of 2008, the coast of Qingdao city experienced a massive occurrence of green algae (Fig. 1). Large amounts of algae were washed up onto the shoreline, forming dense mats and fouling the air, inflicting heavy losses on the local tourism. However, this event was considered not forming locally (Liu et al., 2009; Sun et al., 2008). According to satellite data, the algae originated from the coast of Jiangsu Province, accumulated while moving into the middle of the Yellow Sea, and then drifted to the destination by the southeast monsoon (Liu et al., 2009). During its peak period, it was reported that an area of about 40,000 km^2 was affected and up to 1200 km^2 was covered by the green algae. According to the affected area and the amount of the biomass generated by the bloom, it was considered as one of the largest green tides observed ever in the world (Liu et al., 2009).

In recent decades, blooms of green algae along the coast and estuary are reported worldwide (e.g., Lougheed and Stevenson, 2004; Morand and Briand, 2009; Raffaelli et al., 1998), causing a series of environmental problems and economic loss. Numerous surveys have been conducted on the study of species identifications (e.g., Hiraoka et al., 2004; Leliaert et al., 2009), species abundance (e.g., Kamer et al., 2001; Lougheed and Stevenson, 2004), nutrients levels in the seawater and their effects on the blooms (e.g., Kamer et al., 2001; Teichberg et al., 2010). In this event, the algal that mainly responded to is within the morphological limits of the greenseed *Ulva prolifera* (*Enteromorpha prolifera*) (Lin et al., 2011). Thalli of this green algal are characterized by unattached, highly branched narrow tubes (Leliaert et al., 2009). Optical microscopic observation indicated that the thallus is tubular and hollow, consisting of one sheet of cells polygonal to squares in shape (Fu et al., 2008). There are multifarious patterns of reproduction of this green algal, including sexual, asexual and vegetative reproductions (Dan et al., 1997; Lin et al., 2008), and the most important way is asexual reproduction (Lin et al., 2008). Lab experiments showed that they could survive in a wide range of temperature, salinity, pH and irradiance conditions (Wang et al., 2007). It is one of the common seaweeds in the inter-tidal zone of ocean (Lin et al., 2008).

The occurrence of green tides reflects the coastal eutrophication and ecosystem changes in the region. When such a bloom occurs, the chemical environment in seawater, for example, the

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Fig. 1. Green algal bloom along the coast of Qingdao in June 2008 (photo from www.Qingdaonews.com).

dissolved oxygen (DO), dissolved inorganic carbon (DIC), total alkalinity (TA) and pH might be changed significantly. It is reported that during a massive phytoplankton bloom, pCO_2 in seawater can be significantly depleted (Coale et al., 1996). However, reports related to the carbonate system (DIC, TA, pH and pCO_2) in the green algal bloom are very limited (Dai et al., 2008). To the best of our knowledge, no studies have dealt with the change in CO_2 system during the post-bloom period. The objective of this paper is to investigate how the carbonate system responded to this green algal bloom during the post-bloom period and try to explain the large anomaly of measured TA after the bloom.

2. Material and methods

2.1. Study area

The study area is located in the southern Yellow Sea, which is a semi-enclosed marginal sea with an average depth of about 50 m. In its western region, the seawater is affected by the input of Lubei and Subei Coastal Waters along the Jiangsu Province all the year around (Lin et al., 2005); during summer, under the control of southeast monsoon, the water is also affected by Yangtze River input (Naimie et al., 2001). In the middle region during summer, there is a special water mass produced by winter cooling called the Yellow Sea Cold Water Mass, which is characterized by low temperature and rather stable salinity (Naimie et al., 2001; Su, 1998).

Two cruises were carried out on board R/V '*Dong Fang Hong* 2' during the post-bloom period in the southern Yellow Sea where relict algae could still be observed by eye at some stations. The first cruise was carried out from 22nd–25th, July 2008 with the stations marked as crosses. The second cruise was carried out from 05th–13th, August 2008 with the stations marked as circles. The study area and observation stations are shown in Fig. 2.

2.2. Sampling

During these two cruises, surface seawater for carbonate system analysis was collected by a 12 L Niskin bottle deployed on a Seabird 911+CTD rosette at each station. Similar to the sampling method for dissolved oxygen, after filling the seawater into 250 mL rigid polypropylene bottles, 200 μL of saturated $HgCl_2$ solution was added. Another 200–500 mL surface seawater was filtered by Whatman GF/F membranes. The filtrate was stored in glass vials at −20 °C for DOC analysis. Filter was collected and stored at −20 °C for chlorophyll *a* (Chl-*a*) analysis. All samples were taken to the home lab on shore and measured within several days.

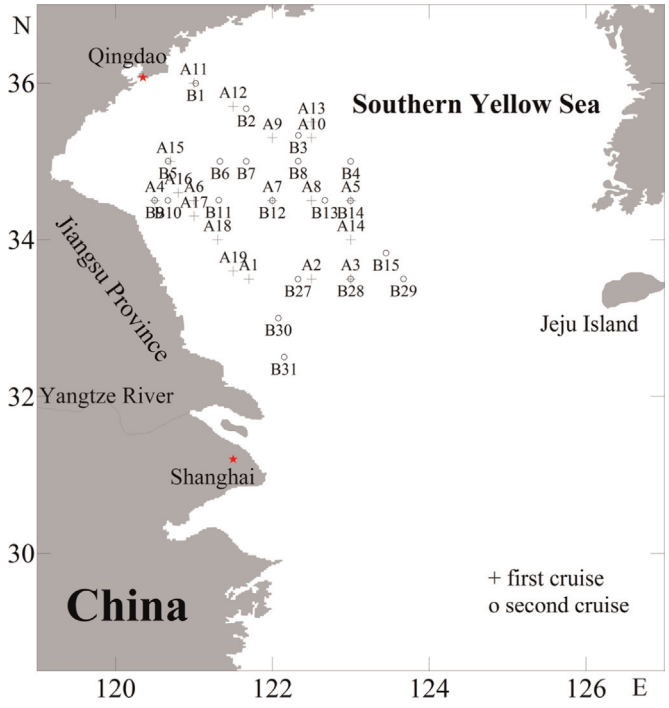

Fig. 2. Study area and sampling stations during the two cruises in the southern Yellow Sea.

2.3. Analytical methods

DIC was determined by using a DIC analyzer (AS-C3, Apollo SciTech Inc., Georgia, USA) (Cai and Wang, 1998). Seawater sample (0.5 mL) was acidified by addition of 0.5 mL 10% H_3PO_4. The extracted CO_2 gas was subsequently measured using a nondispersive infrared (NDIR) CO_2 detector (Li-COR, LI-6262) with a precision of 0.1%–0.2%. pH was measured under room temperature using a Ross Orion combination electrode and Fisher pH meter (AR15) on NBS scale (precision: 0.001). The measured pH values were then converted to in-situ conditions according to the formula $pH_{t2} = pH_{t1} + 0.0114 \times (t_1 - t_2)$ (Gieskes, 1969). TA was determined with 0.1 M HCl solution using Gran titration on a 25 mL sample by a Kloehn digital syringe pump (precision: 0.2%). TA was also calculated from DIC and pH using CO2SYS software (Pierrot et al., 2006) with the equilibrium constants from Mehrbach et al. (1973) refit by Dickson and Millero (1987), and $KHSO_4$ from Dickson (1990); the calculated TA has a precision of 2 μmol kg^{-1} (Grasshorf et al., 1999). The difference between measured TA and calculated one larger than 10 μmol kg^{-1} was considered to be TA anomaly in this study. pCO_2 was calculated form DIC and pH using the same parameters as those for TA calculation; the calcuated pCO_2 has a precision of 2.5 μatm (Grasshorf et al., 1999). DOC was measured by a high-temperature combustion method using a Shimadzu TOC-5000 Analyzer with an Al–Pt catalyst (Shimadzu Co., Japan). DOC concentration was calculated based on a calibration curve made from potassium hydrogen phthalate (Nacalai Tesque, Inc. Kyoto, Japan) (Spyres et al., 2000). The total DOC blank (including instrument blank and water blank) was < 5.0 μM C. The precision for DOC measurement was within 2.0%. Chl-*a* was fluorometrically measured with a Model F-4500 fluorescence spectrophotometer (Hitachi, Japan) after extraction in 90% acetone according to Parsons et al. (1984). Temperature and salinity were obtained from a Seabird 911+CTD.