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Aragonite saturation state and dynamic mechanism in the southern Yellow Sea, China

Xuemei Xu [a,b], Kunpeng Zang [b], Cheng Huo [b], Nan Zheng [b], Huade Zhao [b], Juying Wang [b,*], Bing Sun [a,**]

[a] College of Environment Science and Engineering, Dalian Maritime University, Dalian 116026, China
[b] Key Laboratory for Ecological Environment in Coastal Areas (State Oceanic Administration), National Marine Environmental Monitoring Center, Dalian 116023, China

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ABSTRACT

Based upon surveys conducted in November 2012 and June 2013, the distribution and dynamics of aragonite saturation state (Ω_{arag}) were investigated in the southern Yellow Sea (SYS) of China. In summer, surface water Ω_{arag} ranged from 2.1–3.8 and enhanced biological production fueled by Changjiang River freshwater input increased Ω_{arag} to 3.8 in the southern SYS. However, subsurface water Ω_{arag} was <2.0 in the central SYS. During autumn, surface water Ω_{arag} was 2.0–2.9, lower than that in summer due to ventilation between surface and low Ω_{arag} (1.0–1.4) subsurface waters in the central SYS. Community respiration and/or aerobic remineralization dominated low Ω_{arag} in subsurface waters, while water stratification influenced the level and scale of acidity accumulation. By the end of this century, waters with $\Omega_{arag} > 2.0$ could disappear from the SYS with increasing atmospheric CO_2, while bottom waters Ω_{arag} may become undersaturated due to the impact of eutrophication.

1. Introduction

As a sink of atmospheric CO_2, oceans absorb about 25% of anthropogenic atmospheric CO_2 emissions annually, progressively lowering levels of seawater pH and aragonite saturation state (Ω_{arag}), a process referred to as ocean acidification (OA) (Doney et al., 2009; Feely et al., 2004; IPCC, 2014; Orr et al., 2005). However, OA in coastal regions is more complex as these areas are impacted by multiple natural and anthropogenic processes other than CO_2 uptake (Cai et al., 2011; Chou et al., 2013; Duarte et al., 2013; Gruber et al., 2012; Hagens et al., 2014; Zhai et al., 2012), such as upwelling of CO_2-enriched waters (Feely et al., 2008), metabolism processes (Zhai et al., 2014b), and river input (Salisbury et al., 2008). Recent studies have revealed that hypoxia and acidification of subsurface waters are usually associated with eutrophication in coastal regions (Borges and Gypens, 2010; Cai et al., 2011; Waldbusser et al., 2011). Eutrophication can lead to algal blooms and red tides, which will sink and be remineralized through oxygen-consumption processes in subsurface waters. Remineralization can be roughly estimated by the traditional Redfield equation (Redfield et al., 1963):

$$(CH_2O)_{106}(NH_3)_{16}H_3PO_4 + 138O_2 \rightarrow 106CO_2 + 16HNO_3 + H_3PO_4 + 122H_2O \quad (1)$$

If local hydrological dynamics cannot enable a water mass to ventilate to the atmosphere, metabolic CO_2 will accumulate, resulting in a decrease in pH and Ω_{arag} as well as a depletion in dissolved oxygen (DO). Although coastal water acidification is a regional and seasonal phenomenon, it is usually characterized by a significant pH decrease of 0.2–0.3 on seasonal or shorter timescales (e.g. Taguchi and Fujiwara, 2010; Cai et al., 2011; Zhai et al., 2012). This differs from that observed in the upper open ocean, which has experienced a pH decline of 0.06 in the past 15 years (Byrne et al., 2010).

As a measure of the thermodynamic stability of the mineral form of calcium carbonate used by carbonate-secreting organisms, Ω_{arag} may better represent the effect of OA on biologically mediated $CaCO_3$ precipitation (Riebesell, 2004; Waldbusser and Salisbury, 2014). Seawater is considered supersaturated when $\Omega_{arag} > 1$ and undersaturated when $\Omega_{arag} < 1$. Currently, the mean global ocean saturation state of aragonite is 3.0 (Feely et al., 2009). Increased acidity can cause a series of changes in ocean water chemistry (Caldeira and Wickett, 2005; Feely et al., 2009), especially lowering Ω_{arag} and affecting carbonate-secreting organisms (Fabry et al., 2008; Ries et al., 2009), such that it becomes more difficult and energetically costly to build shells, with subsequent impact on marine systems and human communities due to changing marine resource availability (Doney et al., 2009; Fabry et al., 2008; IPCC, 2014). For example, seawater Ω_{arag} in the nearshore areas of California is projected to become undersaturated in the top 60 m of water during summer within the next 30 years, and more than half of the water will be undersaturated year-round by 2050, leading to sea floor habitats experiencing perennial exposure to undersaturation within the next 20 to 30 years (Gruber et al., 2012). With increasing atmospheric CO_2, OA has garnered increasing

* Correspondence to: J. Y. Wang, National Marine Environmental Monitoring Center, Linghe Street 42, Shahekou District, Dalian 116023, Liaoning Province, China.
** Correspondence to: B. Sun, College of Environment Science and Engineering, Dalian Maritime University, Linghai Street 1, Shahekou District, Dalian 116026, Liaoning Province, China.
E-mail addresses: jywang@nmemc.org.cn (J. Wang), sunb88@dlmu.edu.cn (B. Sun).

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attention due to its potential impact on marine organisms and ecosystems, especially along coastal oceans with concentrated human populations and high anthropogenic activities. Thus, examining baseline OA parameters and identifying their controlling processes are important, particularly in productive marine ecosystems that sustain commercially valuable fisheries, but that are also under complicated environmental stressors such as eutrophication.

The southern Yellow Sea (SYS), a semi-enclosed shallow sea of the northwest Pacific, is surrounded by rapidly developing and highly populated regions, which are also major and expanding marine aquaculture zones in China. Although the northern Yellow Sea (NYS) is considered vulnerable to the potentially negative effects of OA, limited studies on the carbonate saturation state and its dynamic mechanisms have been conducted in the SYS. Thus, based on field surveys conducted in November 2012 and June 2013, the distribution and variability of Ω_{arag} were investigated in this marine aquaculture region. This research has important implications in furthering our understanding of OA in this area as well as in other coastal productive marine ecosystems.

2. Materials and methods

2.1. Study area

The SYS has an area of 3.09×10^5 km^2 and an average depth of 50 m. It is a semi-enclosed shallow sea of the northwest Pacific and is located between China's mainland and the Korean Peninsula (Fig. 1). It is characterized by a temperate climate, with wind dominated by the East Asian monsoon, while the rain-bearing southwest monsoon prevails in summer and the strong northeast monsoon dominates in winter (Su, 1998; Su and Yuan, 2005). The most distinguishing characteristic of the SYS is the seasonally changing thermocline formed by the Yellow Sea Cold Water Mass (YSCWM) in the deep layer, which develops in spring, forms completely in summer, subsides in autumn, and disappears in winter (Yu et al., 2006). In winter, the Yellow Sea Warm Current flows northwestward along the Yellow Sea trough and transports saline SYS water to the NYS (Bao et al., 2009; Su, 1998). The Changjiang Diluted Water (CDW) mass is formed in summer by the mixing of SYS shelf waters and Changjiang (Yangtze) River freshwater (with 12–27% of its discharge (9.6×10^{11} m^3 yr^{-1}) empting into the SYS from June to October) (Mao et al., 1963; Riedlinger and Preller, 1995). The whole study area is an important support system for economic development in the region. During the past few years, however, due to rapid industrialization and expanding human populations, intensifying eutrophication has led to an increased frequency in harmful algal blooms (State Oceanic Administration of China, 2014), resulting in water quality decline. Thus, the spatial and seasonal variability of the hydrological and biogeophysical properties of the SYS are regulated by both oceanic dynamics and terrigenous material importation.

2.2. Sampling and analytical methods

Two field surveys were conducted aboard the R/V *Dong Fang Hong II*, with the 23–29 June 2013, cruise undertaken during the summer and flood season and the 2–13 November 2012, cruise conducted during autumn. The scope of the study area (31–37°N to 120–126°E) and the sampling stations varied slightly between the two cruises (Fig. 1b), having 41 and 51 sampling stations during the summer and autumn cruises, respectively.

During each survey, temperature and salinity in the water column were recorded with a calibrated conductivity, temperature, depth (pressure) (CTD) recorder (SBE 911, Sea-Bird Electronics Inc., USA). Water samples were collected to determine DO, dissolved inorganic carbon (DIC), and total alkalinity (TAlk) concentrations in the water column at three to four different depths (depending on water depth and thermocline) using a rosette sampler fitted with 8 L Niskin bottles and mounted with CTD units.

The DO samples were collected, fixed, and titrated aboard following the Winkler procedure. The uncertainty of DO data was estimated to be <0.5% (Zhai et al., 2012; Zhai et al., 2014b). DO saturation (DO%) was computed from the measured O_2 concentrations, and the O_2 concentration at saturation was determined as per the equation of Benson and Krause (1984).

The DIC and TAlk samples were unfiltered (Zhai et al., 2014b; Xu et al., 2016) and stored in bottles (Huang et al., 2012), then preserved at room temperature after the addition of saturated $HgCl_2$. The samples were allowed to settle before measurement. DIC was measured using a total inorganic carbon analyzer based on infrared detection (AS-C3, Apollo SciTech, Inc., USA). TAlk was determined by Gran titration based on an alkalinity titrator (AS-ALK2, Apollo SciTech, Inc., USA). The DIC and TAlk measurements were both calibrated against certified reference materials from A.G. Dickson's laboratory for quality assurance at a precision level of ± 2 μmol kg^{-1} (Cai et al., 2004; Dickson et al., 2007).

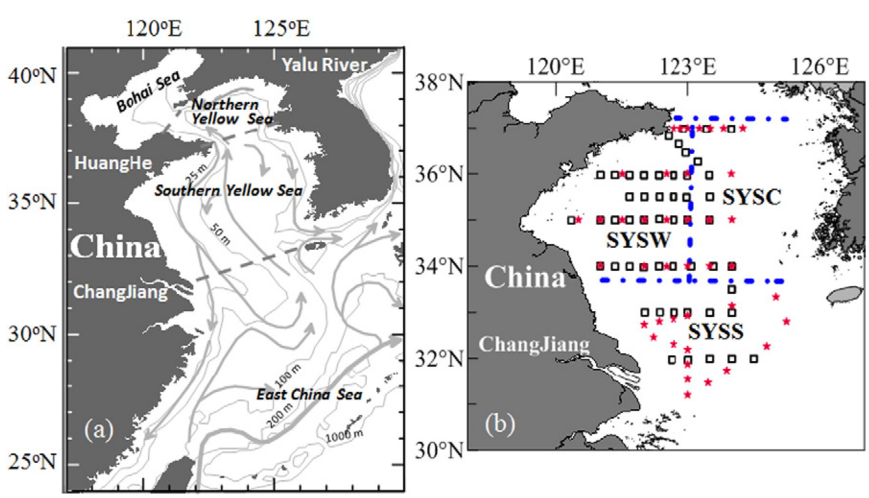

Fig. 1. Study area and sampling stations. (a) Relative location of study area in the China coastal seas; dashed lines indicate the traditional boundary between the NYS and SYS, and the SYS and East China Sea. Arrows denote major currents in the coastal seas during the northeast monsoon season (Chen, 2009; Zang et al., 2003). (b) Stars denote stations investigated in summer, hollow squares denote stations investigated in autumn. Dashed blue lines are the boundary between three distinct subregions: western SYS (SYSW), southern SYS (SYSS) and central SYS (SYSC).