Deep-Sea Research II 117 (2015) 119–130

Contents lists available at ScienceDirect

Deep-Sea Research II

journal homepage: www.elsevier.com/locate/dsr2

Carbonate chemistry in the Northern South China Sea Shelf-sea in June 2010

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ARTICLE INFO

Available online 5 March 2015

Keywords:
Northern South China Sea Shelf-sea (NoSoCS)
Carbonate chemistry
Aragonite saturation state
Net community production (NCP)
Marginal sea

ABSTRACT

The distributions of dissolved inorganic carbon (C_T), total alkalinity (A_T) and pH at 25 °C (pH_{25}) were determined in the Northern South China Sea Shelf-sea (NoSoCS) in early June, 2010 during a low flow period. The distributions of the partial pressure of CO_2 (pCO_2), *in situ* pH, and temperature normalized pCO_2 ($NpCO_2$) were derived from the measured values. The distribution of A_T is linearly related to salinity indicating that its distribution is controlled primarily by mixing between the surface water and the subsurface North Pacific Tropical Water. Aside from physical mixing, the distribution of C_T is also influenced by its loss through biological uptake and CO_2 evasion to the atmosphere. The net community production (NCP) rate in the NoSoCS is estimated to be 10 ± 20 (with a range of 4–13) mmol C m^{-2} d^{-1}. Within the NoSoCS, the NCP is elevated in the coastal upwelling area, where it is estimated to reach 30 ± 17 mmol C m^{-2} d^{-1}. In addition to temperature, upwelling and biological uptake also affect the distribution of the surface pCO_2 and *in situ* pH.

The waters in the NoSoCS are super-saturated with respect to aragonite at all depths as the saturation horizon is at 600–800 m in the open northern South China Sea. Nevertheless, the aragonite saturation state, Ω_{Ar}, in the surface water, which is mostly between 3.3 and 3.5, is already within the range that has been suggested as barely adequate to marginal for the growth of the tropical shallow-water corals. The Ω_{Ar} is linearly related to *in situ* pH. At the reported rate of pH decrease in the oceans as a result of ocean acidification, Ω_{Ar} might reach a value that is considered "extremely marginal" within several decades and the existence of this type of coral reef ecosystem in the NoSoCS may then be threatened.

1. Introduction

Coastal and marginal seas play an important role in the global carbon cycle since they link the terrestrial, oceanic and atmospheric carbon reservoirs. Although they constitute only ~7% of the ocean by surface area, they contribute 14–30% of the oceanic primary production and 80% of the organic matter burial (Gattuso et al., 1998b). Marginal seas beyond the estuaries are also important sinks of the atmospheric CO_2, contributing 27–30% of the oceanic CO_2 sequestration (Chen and Borges, 2009).

In view of the importance of the marginal seas in oceanic CO_2 sequestration, their carbonate system has been actively studied (Chen and Borges, 2009; Laruelle et al., 2010). However, while the marginal seas at the middle and high latitudes, such as the Middle Atlantic Bight, South Atlantic Bight, the East China Sea, the North Sea, and the Bering Sea have been studied rather extensively (Bates et al., 2011; Cai et al., 2010; Chen and Wang, 1999; Thomas et al., 2004; Wang et al., 2013; Wong, 1979, 1988; Zhai and Dai, 2009), their counterparts in the lower latitudes are still relatively under-studied (Cai et al., 2006; Chen and Borges, 2009; Laruelle et al., 2010). Nevertheless, it is well known that the major processes controlling the carbonate system in the oceans vary with latitude and there is no reason to believe that the marginal seas should be the exception (Cai et al., 2006; Gruber et al., 2009; Takahashi et al., 2009). For example, Cai et al. (2008) report that the global input of bicarbonate to the coastal seas varies with latitude. Wang et al. (2013) find that total alkalinity, A_T, in shelf waters decreases northward along the eastern seaboard of the United States. The recent recognition of ocean acidification (OA) as an imminent global environmental issue (Orr et al., 2005) has provided further impetus for understanding the behavior of the carbonate system in the tropical marginal seas as they may be more susceptible to OA than the open ocean when accompanied by other biogeochemical processes (Cai et al., 2011). Tropical shallow water coral reef ecosystems, which are frequently found in tropical marginal seas, have been predicted as early victims of OA (Gattuso et al., 1998a; Kleypas et al., 1999a; Langdon et al., 2003; Leclercq et al., 2000; Tribollet et al., 2006). Nevertheless, how

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http://dx.doi.org/10.1016/j.dsr2.2015.02.024
0967-0645/

the carbonate system in the low latitude marginal seas may respond to terrestrial input, biological processes, local forcing (such as river runoff, coastal upwelling, and atmospheric pumping by tropical cyclones) and exchange with the open ocean are still inadequately documented and understood.

The Northern South China Sea Shelf-sea (NoSoCS) of the northern South China Sea (SCS) is a major sub-tropical coastal sea of the world where coral reef ecosystems are widely found. Previous studies on its carbonate chemistry tend to cover only selected sub-regions and significant sub-regional variations have been found (Zhai et al., 2005, 2009; Dai et al., 2008b; Cao et al., 2011). A characterization of the carbonate system in the NoSoCS as a whole has yet to be attempted. In this study, we report the distributions of dissolved inorganic carbon (C_T), total alkalinity (A_T), pH, pCO_2 and the aragonite saturation state (Ω_{Ar}) in the entire NoSoCS during the early summer of 2010 as an example of the characteristics of the carbonate system in a major sub-tropical marginal sea. Furthermore, the processes controlling these distributions and the response of the NoSoCS to OA are assessed.

2. Material and methods

2.1. Study area

The SCS is located in the northwestern Pacific and extends from 23°N in the sub-tropics at southern Taiwan to 3°S in the tropics at the coasts of Borneo and Sumatra. The NoSoCS is situated at the northwestern corner of the SCS in its subtropical section (Fig. 1). It extends in a northeast to southwest direction from the southern Chinese coast to the shelf edge between 19 and 23°N and between Hainan Island and the southern end of the Taiwan Strait from 110 to 118°E (Fig. 1). The western half of the shelf is narrower and broadens eastward off Shanwei towards Shantou. In response to the southwest monsoon and topographic forcing, a well-documented summer upwelling occurs along the coast in this broadened section of the shelf (Gan et al., 2009a). Vertical mixing within the NoSoCS is also enhanced by internal waves whose occurrence has been observed along the entire outer shelf (Li et al., 2008). The NoSoCS is also the receiving water of a nutrient-rich river draining a heavily urbanized part of the world (Dai et al., 2008a), the Pearl River, whose annual freshwater discharge is about 3.26×10^{11} m^3 (Zhao, 1990). The highest discharge from the Pearl River occurs during the summer and its lowest discharge is in late winter and early spring (Fig. 2). Recently, Liu et al. (2012) report that significant quantities of submarine groundwater may also enter the NoSoCS. While the adjoining open northern SCS is generally oligotrophic (Chen et al., 2001; Chen, 2005; Chen and Chen, 2006; Wong et al., 2007), the biological productivity in the NoSoCS is significantly higher as a result of enhanced vertical mixing and exogenous sources of nutrients (Tan and Shi, 2009).

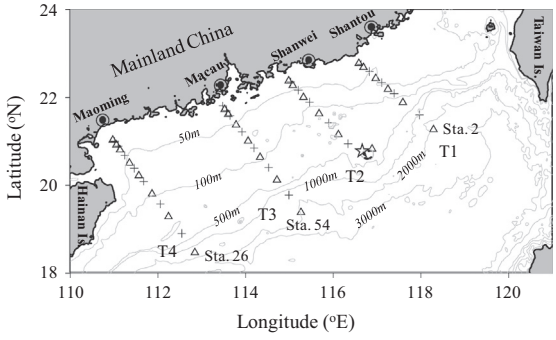

Fig. 1. The study area in the northern South China Sea. Δ – stations along the four transects T1–T4 at which discrete water samples were collected; + – CTD only stations; and open star – Dongsha Atoll.

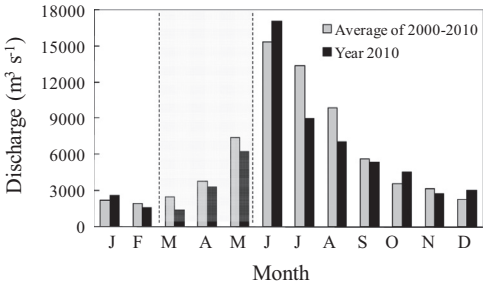

Fig. 2. Monthly averaged freshwater discharge of the largest tributary of the Pearl River system, the West River, at the Wuzhou gauging station (at 111.3290°E, 23.4688°N, Guangxi Zhuang Autonomous Region) (the *Hydrological Information Annual Report* (2000–2010), Ministry of Water Resources, PR China). Shaded area – spring months.

The hydrography and general pattern of circulation in the northern SCS and the NoSoCS are reasonably well known (Chao et al., 1996; Gan et al., 2009a, 2009b; Shaw and Chao, 1994; Wong et al., 2007; Xue et al., 2004). The monsoonal wind is a major forcing of the circulation in the NoSoCS and leads to a generally southwestward flow in the winter and a northeastward flow in the summer (Gan et al., 2006; Xue et al., 2004). However, the details, such as the rate of mass exchange between the NoSoCS and the northern SCS, remain poorly quantified. More extensive reviews on the general oceanography of the NoSoCS appear elsewhere in this special issue (Wong et al., 2015-a, 2015-b).

Previous sub-regional studies on the carbonate chemistry of the NoSoCS were conducted primarily in the summer. Zhai et al. (2005, 2009) report that some sub-regions are sources of CO_2 to the atmosphere, probably as a result of low productivity and high temperature in warm seasons. On the other hand, others (Cao et al., 2011; Dai et al., 2008b) find consistently high uptake rates of dissolved inorganic carbon in the Pearl River plume and in the upwelling waters off the coast between Shantou and Shanwei, where biological productivity is high. A characterization of the carbonate system in the NoSoCS as a whole has yet to be attempted and this information is especially helpful if the impact of OA on the extensive tropical water coral reef ecosystems in the NoSoCS (Guo et al., 1994) is to be assessed.

2.2. Sampling and analysis

Stations were occupied in four cross-shelf transects extending from the inner shelf to the open northern SCS off Shantou, Shanwei, Macou and Maoming from the southern end of the Taiwan Strait (transect T1) to Hainan Island (transect T4), on board R/V Ocean Researcher I (ORI) during cruise ORI 929 on 3–12 June, 2010. At each station, depth profiles of salinity and temperature were recorded with a Seabird® SBE 911 Conductivity–Temperature–Depth/pressure (CTD) sensor package. Discrete water samples were collected at selected stations with 20-L Go-Flo bottles mounted on a Rosette sampler. Following the protocols of the best practices for measuring the ocean carbonate system parameters (Dickson et al., 2007), subsamples for C_T, A_T and pH measurements were taken with Tygon® tubing free of air bubbles, with ample sample overflow in order to minimize any contamination from atmospheric CO_2. Samples for C_T, and A_T measurements were taken into 500 mL borosilicate bottles and poisoned with a saturated $HgCl_2$ solution. The samples were stored in the dark and returned to a land-based laboratory for analyses within one and two months of sample collection for C_T and A_T, respectively. pH samples were taken into 10 cm optical cells. pH measurements were made onboard the ship within two hours of sample collection.