



Modeling seasonal and diurnal $p\text{CO}_2$ variations in the northern South China Sea

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ABSTRACT

This paper describes the simulated temporal variation of surface seawater CO_2 partial pressure ($p\text{CO}_2$) in the northern South China Sea. We produced the simulations with a one-dimensional (1-D) coupled physical–biogeochemical model that had high-frequency, time-dependent atmospheric forcing and that were validated with field observations. We also examined the associated processes that modulate seawater $p\text{CO}_2$ at different time scales, from diurnal to seasonal, using a series of process-oriented experiments. At seasonal time scales, we revealed that the sea–air CO_2 exchange was a primary process that modulated surface $p\text{CO}_2$ and exceeded the role of sea surface temperature (SST) even though the phase of the $p\text{CO}_2$ variation generally followed the strong seasonal cycle of SST. This was because sea–air CO_2 exchange is a slow process and has an accumulative effect on surface water $p\text{CO}_2$ due to the buffering effect of the carbonate system once CO_2 has dissolved in the seawater, which leads to a long equilibration time of CO_2 between the atmosphere and seawater. The mixing effect on $p\text{CO}_2$ induced by total alkalinity and dissolved inorganic carbon variations was, generally, positively correlated with the seasonal evolution of wind speed. Biological processes were the smallest contributors to $p\text{CO}_2$ variations at the seasonal scale because of the oligotrophic characteristic of the region. At diurnal time scales, the dominant $p\text{CO}_2$ controlling factor was mainly associated with the local physical and biological conditions. Temperature and wind-induced vertical mixing played major roles in $p\text{CO}_2$ when the winter heat flux and upward transport of low temperature and high $p\text{CO}_2$ in deep water were intensified. Phytoplankton blooms generally occur after a period of strong wind, as a result, biological metabolism becomes the most important $p\text{CO}_2$ regulator when the surface chlorophyll-*a* reached its highest level. Unlike that in the seasonal scale, the effect of sea–air CO_2 exchange was minor at diurnal time scales due to the long equilibration time of CO_2 between the atmosphere and seawater. We also found that the frequency of the model driving force was important in reproducing the sea surface $p\text{CO}_2$. The high frequency forcing was important in controlling the $p\text{CO}_2$ variation through the feedback effect to the corresponding physical and biogeochemical responses.

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1. Introduction

It is known that the ocean has been a major sink for anthropogenic CO_2 (Falkowski et al., 2000), and its capacity to uptake atmospheric CO_2 can be manifested by the difference in the partial pressure of CO_2 ($p\text{CO}_2$) between the air and ocean surface. While $p\text{CO}_2$ in the atmosphere is largely homogeneous due to relatively rapid atmospheric circulation, the surface seawater $p\text{CO}_2$ field varies greatly in time and space. This variability drives the CO_2 source or sink traits of a particular oceanic region and has received great attention during the past 10 years (Takahashi et al., 2009).

$p\text{CO}_2$ in seawater is generally modulated by both physical and biogeochemical processes such as mixing with different water masses, temperature changes, chemical buffering, sea–air exchange, and

biological metabolic activities (Murnane et al., 1999; Zhai and Dai, 2009). There have been many attempts (Cai et al., 2006; Takahashi et al., 2009), primarily based on ship-board observations, to obtain a mechanistic understanding of the CO_2 variability in order to improve our knowledge of CO_2 behavior within a specific system and to generalize to global scales ultimately to acquire a predictive capacity. The current challenge is to differentiate the fractional influences of the different sources that modulate the CO_2 variations based on the analysis on an integrated understanding of the coupled physical–biogeochemical processes in time and space (McKinley et al., 2006; Previdi et al., 2009). Such attempts are compounded by the fact that CO_2 variability may be dominated by different controls at different time scales which have not been well-understood thus far (Bates et al., 1998; Dai et al., 2009). For this purpose, numerical simulations of coupled physical–biogeochemical processes, combined with *in situ* observations, necessarily provide a dynamic interpolation or extrapolation of incomplete measurements and compensate for the temporal and spatial limitations of field CO_2 measurements (Fujii et al., 2009).

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More importantly, the examinations are performed through process-oriented numerical experiments that can identify intrinsic controlling mechanisms of $p\text{CO}_2$.

The South China Sea (SCS) is the second largest marginal sea in the world. Driven by the strong Asian monsoon, it is characterized by diverse spatio-temporal physical and biological dynamics, and it plays an important role in regional climate variability (Liu et al., 2002). Using their observed $p\text{CO}_2$ data from three cruises that were conducted in the spring, summer, and late fall, Zhai et al. (2005, 2007) reported a $p\text{CO}_2$ variation range of 360 to 450 μatm , and suggested that the northern SCS (NSCS) was a weak/moderate CO_2 source ($-0.86 \text{ mol m}^{-2} \text{ year}^{-1}$) for the atmosphere on an annual basis.

To investigate the carbon cycle controlling mechanisms and to study the effect of interactions between the upper ocean and the sea surface atmosphere on the biogeochemical processes in the NSCS, the South East Asia Time Series Study established a station (the SEATS station) that is located at the edge of the continental margin close to the deep basin in the NSCS (116°E, 18°N) in 1999, and observed onsite every 2–4 months (Wong et al., 2007). Chou et al. (2005) found that the $f\text{CO}_2$ (fugacity of CO_2) reached a minimum of 347 μatm in winter and a maximum of 382 μatm in summer by using bimonthly $p\text{CO}_2$ data collected from March 2002 to April 2003 at SEATS. Unlike Zhai et al. (2005), they identified that the annual sea–air CO_2 flux was a weak sink to the atmosphere (-0.11 to $-0.23 \text{ mol C m}^{-2} \text{ yr}^{-1}$). Subsequently, Tseng et al. (2007) reported an intra-annual fluctuation of $p\text{CO}_2$ between 340 and 400 μatm and a nearly zero sea–air flux of $0.02 \text{ mol C m}^{-2} \text{ yr}^{-1}$. These previous observation-based studies pointed out that the temperature effect overwhelms biological forcing and is the major controlling factor of surface water $p\text{CO}_2$.

Based on a three-dimensional coupled physical–biogeochemical model, Chai et al. (2009) simulated the physical variation, ecosystem response, and carbon cycle in the SCS basin. They pointed out that SST has a greater influence than biological forcing, and is the dominant controlling factor on surface seawater $p\text{CO}_2$ through an empirical estimation given by Takahashi et al. (2002). They also found that total alkalinity (TA) and dissolved inorganic carbon (DIC) have less influence on $p\text{CO}_2$ than SST based on their sensitivity experiments.

We contend, however, that to resolve the CO_2 dynamics in a complex system like the SCS, studies performed solely with qualitative evaluations derived from spatially and temporally limited field measurements are not enough. We also contend that temporal variations and the intrinsic controls are subject to spatial variations, and should be examined on an individual spatial domain basis. A continuously stratified vertical 1-D coupled physical–biogeochemical model with high-frequency, time-dependent atmospheric forcing would effectively identify the fundamental controlling processes of $p\text{CO}_2$ at different time scales. We selected the SEATS stations to start our modeling efforts because time series observational data have been available at this station since 1999. Furthermore, we only used a 1-D model to emphasize the determination of CO_2 dynamics on different time scales.

The organization of this paper is as follows. The study methods, including a brief description of the 1-D model framework, model setup, and observational data are introduced in Section 2. Section 3 mainly focuses on comparison between model results and observational data. In Section 4, we analysis different processes that modulate seawater $p\text{CO}_2$ at seasonal and diurnal time scales, and the role of driving force frequency in the model is also discussed. A summarization of the results obtained in this study is presented in Section 5.

2. Methods

2.1. Model description

The 1-D model is an implementation of the Regional Ocean Modeling System (ROMS, <http://www.myroms.org>) (Haidvogel et al., 2008;

Shchepetkin and McWilliams, 2005) coupled with the Fasham-type ecosystem model (Fasham et al., 1990). We applied the model to the SEATS station data (Fig. 1). Hydrodynamics of the model are governed by the primitive equations and a local closure scheme that is based on level-2.5 turbulent kinetic energy equations (Mellor and Yamada, 1982) and that is adopted in the vertical mixing parameterization. In our application, the domain was centered at 18°N, 116°E with a water depth of 3770 m. The model has 60 vertical levels with vertically variable grid-spacing. To better resolve the surface boundary layer, we adopted a grid-spacing of about 5 m in the upper layer, and spacing was about 60 m and 130 m in the bottom and middle layers, respectively. The model time step is 800 s.

The ecosystem module was embedded in the ROMS (Fennel et al., 2006). It is a nitrogen-based ecosystem model that includes 7 prognostic variables: nitrate (NO_3 , N), ammonium (NH_4 , A), Chlorophyll-*a* (Chl_a), phytoplankton (P), zooplankton (Z), large detritus (LD), and small detritus (SD). The details of the model were described in Gan et al. (2010) and Lu et al. (2010), both of who successfully simulated the dynamics of the biological response to coastal upwelling and a river plume over the shelf of the NSCS.

The carbonate system module was also embedded in the ROMS. The surface seawater $p\text{CO}_2$ depends on salinity, SST, TA, and DIC. TA and DIC are altered by biological processes as well as by physical mixing. The calculation of the surface seawater $p\text{CO}_2$ follows Zeebe and Wolf-Gladrow (2005). The equations governing TA and DIC in seawater are:

$$\frac{\partial[\text{TA}]}{\partial t} = \left(\frac{\partial[\text{TA}]}{\partial t}\right)_M + \left(\frac{\partial[\text{TA}]}{\partial t}\right)_B \quad (1)$$

$$\frac{\partial[\text{DIC}]}{\partial t} = \left(\frac{\partial[\text{DIC}]}{\partial t}\right)_M + \left(\frac{\partial[\text{DIC}]}{\partial t}\right)_F + \left(\frac{\partial[\text{DIC}]}{\partial t}\right)_B \quad (2)$$

$$\left(\frac{\partial[\text{TA}]}{\partial t}\right)_B = \left(\frac{\partial[\text{TA}]}{\partial t}\right)_{NP} - \left(\frac{\partial[\text{TA}]}{\partial t}\right)_{\text{Nitri}} \quad (3)$$

$$\left(\frac{\partial[\text{TA}]}{\partial t}\right)_{NP} = t_{pp\text{max}} \cdot \frac{K_N \cdot [\text{N}] \cdot [\text{P}]}{(1 + K_A \cdot [\text{A}]) \cdot (1 + K_N \cdot [\text{N}])} \quad (4)$$

$$\left(\frac{\partial[\text{TA}]}{\partial t}\right)_{\text{Nitri}} = [\text{A}] \cdot n_{\text{max}} \cdot \left(1 - \max\left(0, \frac{\text{PAR} - I_0}{K_I + \text{PAR} - 2 \cdot I_0}\right)\right) \quad (5)$$

$$\text{PAR}_k = \text{PAR}_{k+1} \cdot e^{-0.5 \cdot (k_{\text{water}} + k_{\text{Chla}} \cdot [\text{Chla}]_k) \cdot \Delta z_k} \quad (6)$$

$$\left(\frac{\partial[\text{DIC}]}{\partial t}\right)_B = \left(\frac{\partial[\text{DIC}]}{\partial t}\right)_P + \left(\frac{\partial[\text{DIC}]}{\partial t}\right)_Z + \left(\frac{\partial[\text{DIC}]}{\partial t}\right)_R \quad (7)$$

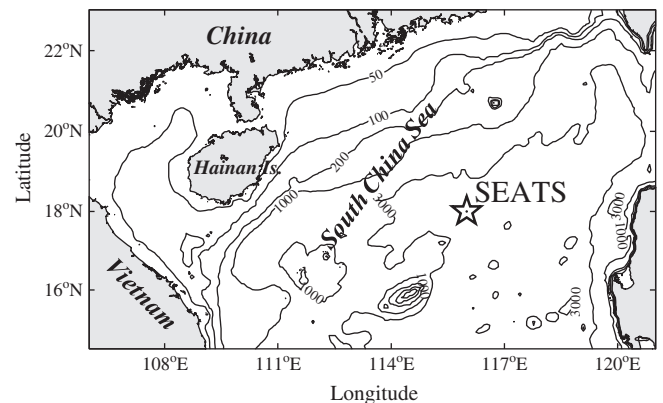


Fig. 1. Map with isobaths of the northern South China Sea showing the major study site (SEATS) as a pentagram.

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