Seasonal changes and controlling factors of sea surface pCO$_2$ in the Yellow Sea

B Y Qin, Z Tao, Z W Li, X F Yang

State Key Laboratory of Remote Sensing Science, Jointly Sponsored by the Institute of Remote Sensing Applications of Chinese Academy of Sciences and Beijing Normal University, Beijing, China.

E-mail: bangyong_whu@163.com

Abstract. Sea surface partial pressure of carbon dioxide (pCO$_2$) is an important parameter in the ocean carbon cycle system. By using accurate global sea surface pCO$_2$ data, we can directly estimate the ratio of net CO$_2$ uptake of global ocean, which can provide a support for further research of global carbon cycle. This article mainly discussed the seasonal changes of sea surface pCO$_2$ and the relationships of pCO$_2$ with sea surface temperature (SST) and chlorophyll-a concentration (Chla) in the Yellow Sea during winter, spring and summer, based on the data obtained by the shipboard measurements in February, May and August 2010. The results showed that the correlations of pCO$_2$ with SST and Chla were different in different seasons. SST and pCO$_2$ had a strong positive correlation in the range of higher SST for both spring and summer, and a relative weak correlation in winter, which can be fitted by a quadratic curve in each season. There was a linear correlation between pCO$_2$ and Chla in each season. The data of pCO$_2$ and Chla showed a negative correlation during winter and summer, and a positive one during spring. Based on the correlation analyses, we proposed a regression equation of pCO$_2$ with SST and Chla as two parameters in the Yellow Sea for summer, which showed a root mean squared error (RMSE) of 16.68μatm when the shipboard-observed data were used. By using the satellite-observed SST and Chla instead of the field data, the RMSE of the result is 21.46μatm.

1. Introduction

In recent years, the research on global carbon cycle has drawn more and more attentions. As one of the most important repository of the Earth's carbon, ocean plays a vital role in regulating global atmospheric concentration of carbon dioxide (CO$_2$)[1]. Sea surface partial pressure of CO$_2$ (pCO$_2$) is a principal parameter in the ocean carbon cycle system [2]. Accurate global sea surface pCO$_2$ data can be used to evaluate the ratio of net CO$_2$ uptake of global ocean [2], which can support the further study of global carbon cycle.

The Yellow Sea is an important shelf sea of China [3]. Because of the influence of the input of terrigenous rivers and biological activities, the distribution of pCO$_2$ in the Yellow sea is complicated. Currently, some researchers have done some investigations on the distribution and controlling factors of pCO$_2$ in the Yellow Sea and Bohai Sea. Zhang L. and Zhang Y. have analyzed the distribution characteristics of surface seawater pCO$_2$ in the Bohai Sea in summer [4]; Zhang et al. have discussed the distribution and controlling factors of pCO$_2$ in Northern Yellow Sea in winter, spring and autumn respectively [5-7]; Jiang et al. have studied the air-sea exchange flux of CO$_2$ in the Southern Yellow
Sea in spring and its difference with that in summer [8]. Overall, many studies about sea surface pCO$_2$ focused on a single sea or a single season, few of them addressed the seasonal variability of sea surface pCO$_2$.

First of all, the seasonal variability of sea surface pCO$_2$ is recapitulated in this article. Moreover, the relationships of pCO$_2$ with sea surface temperature (SST), and chlorophyll-a concentration (Chla) in the Yellow Sea were discussed. Finally, a multiple regression equation of pCO$_2$ with SST, Chla in the Yellow Sea was proposed, and confirmed by shipboard measurement and satellite observation.

2. Data

In-situ data used in this study were derived from CO$_2$ air-sea exchange flux data obtained by shipboard measurement in the Yellow Sea in February, May and August 2010. The shipboard routes are shown in figure 1, the blue lines stand for the route in February, while the red lines are for May and August. There were a total of 6375 sets of data records collected in the three months. A small portion of the data was removed because their pCO$_2$ value has significant deviation. Some were discarded due to the lack of synchronous Chla concentration data. Finally, in total 5503 sets of data were valid in our study.

![Figure 1. Distribution map of shipboard lines.](image)

3. Data analysis

The Yellow Sea is a Chinese shelf sea [3], here the distribution of pCO$_2$ is affected by many factors, such as temperature, strong plankton activity, river input, upwelling and so on [3]. Because the routes of this experiment were not located in the near-shore area, we do not consider the impacts on pCO$_2$ from carbonate system caused by river input and coastal aquaculture activities. SST and Chla play an important role in affecting the distribution and seasonal variability of the pCO$_2$ in shelf seas. We will discuss the relationship of pCO$_2$ with SST and Chla in different seasons.

SST has a double impact on pCO$_2$. On one hand, in the absence of external exchange, the equilibrium of carbonate system in seawater would alter due to the influence of temperature. The pCO$_2$ will be enhanced as temperature rises [9]. On the other hand, the solubility of carbon dioxide in seawater decreases as temperature increases, which leads to a decrease of pCO$_2$ [10].

The impact of Chla on pCO$_2$ is primarily concerned with the respiration of plankton and the photosynthesis of phytoplankton [11]. Respiration absorbs oxygen and releases carbon dioxide, which makes pCO$_2$ rise, while photosynthesis absorbs carbon dioxide and releases oxygen, which makes pCO$_2$ reduce. Respiration and photosynthesis are also influenced by temperature, salinity, pH, light conditions and so on.
Due to different seawater temperature and changing of marine plankton in number and activity, pCO$_2$ has different distribution characters in different seasons. In order to study the seasonal variation of pCO$_2$, it is necessary to analyze pCO$_2$ variation in each season, respectively.

3.1. The pCO$_2$ data in winter

![Figure 2](image1.png)

**Figure 2.** Scatter plot of pCO$_2$ against SST in winter.

As shown in figure 2, the SST was low in winter, ranged from -2℃ to 12℃; the Chla varied from 0.6 mg/m$^3$ to 1.8 mg/m$^3$; pCO$_2$ values had some ups and downs but were low in general, ranged from 342μatm to 384μatm. The relationship between pCO$_2$ and SST can be approximated with a quadratic curve shown in figure 2. Chla had a more pronounced effect on pCO$_2$ than SST in winter. The pCO$_2$ decreased gradually as Chla increased; there was a negative correlation between the two variables, as shown in figure 3.

3.2. The pCO$_2$ data in spring

As shown in figure 4, the SST in May was higher than that in February; the Chla varied from 0.6 mg/m$^3$ to 1.8 mg/m$^3$; pCO$_2$ values had some ups and downs but were low in general, ranged from 342μatm to 384μatm. The relationship between pCO$_2$ and SST can be approximated with a quadratic curve shown in figure 2. Chla had a more pronounced effect on pCO$_2$ than SST in winter. The pCO$_2$ decreased gradually as Chla increased; there was a negative correlation between the two variables, as shown in figure 3.

![Figure 3](image2.png)

**Figure 3.** Scatter plot of pCO$_2$ against Chla in winter.

Except some abnormal data, which has been marked with a green circle, the distribution of pCO$_2$
versus SST can be fitted by a quadratic curve in figure 4. The relationship between pCO$_2$ and Chla was a positive correlation in spring, which was different from in winter. There was a linear relationship between pCO$_2$ and Chla, with an exception of some abnormal data, which has been marked with a green circle in figure 5.

![Figure 4. Scatter plot of pCO$_2$ against SST in spring.](image1)

![Figure 5. Scatter plot of pCO$_2$ against Chla in spring.](image2)

### 3.3. The pCO$_2$ data in summer

SST in summer was relative high, ranged from 21°C to 29°C. The maximum value of pCO$_2$ has reached up to 450μatm, and even the minimum value was higher than 348μatm. As shown in figure 6, pCO$_2$ rose rapidly as SST increased, the correlation between them was positive in the range higher than 23°C and negative in the range less than 23°C, which could be fitted with a quadratic curve. Because of high temperatures and adequate lighting in summer, the photosynthesis efficiency of phytoplankton improved a lot. Chla had a significant negative effect on pCO$_2$. With Chla increased from 0.4 mg/m$^3$ to 1.4 mg/m$^3$, pCO$_2$ decreased from 450μatm to 348μatm. As shown in figure 7, the two variables present with a significant linear relationship.
3.4. Seasonal variability of pCO$_2$

According to the analysis above, the distribution of pCO$_2$ could be affected by both SST and Chla. The correlations between them are different in each season.

SST and pCO$_2$ had a strong positive correlation in the range of higher SST for both spring and summer, and a relative weak correlation in winter. The relationship between Chla and pCO$_2$ was a little complicated, which presented a negative correlation in winter and summer, and a positive one in spring. The reason why Chla has a different correlation with pCO$_2$ in spring may be that the effect of SST on pCO$_2$ is larger than that of Chla. In addition, there may be other factors related to the distribution of pCO$_2$ such as salinity and wind speed.

3.5. Multiple regression analysis

According to the analysis above, temperature change and plankton activity are two important influencing factors of pCO$_2$. The relationship between pCO$_2$ and SST could be fitted by a quadratic curve, whereas Chla and pCO$_2$ had a significant linear relationship.

Ono T, Saino T and Kurita N proposed a second-order multi-regression equation to fit pCO$_2$ with SST and Chla [2], as shown as

\[ pCO_2 = AT + BT^2 + CChla + DChla^2 + E \]  (1)
Equation (1) has good agreement with observations in some regions of the North Pacific (20° N-50° N, 140° E-200° E). However, ONO’s equation was not quite suitable for the Yellow Sea which presents different hydrological properties. This study simplified the regression equation by removing the second-order variable of Chla, because the relationship between pCO$_2$ and Chla was always linear correlation as analyzed above. The modified regression equation is shown as

$$pCO_2 = AT + BT^2 + CChla + D$$

(2)

Through carrying out a multiple regression analysis of pCO$_2$ obtained in the Yellow Sea in August 2010 with SST and Chla data obtained by the shipboard measurement, we can obtain equation (3), i.e.

$$pCO_2 = -85.8SST + 1.8SST^2 - 21.1Chla + 1395.7, \text{RMSE} = 16.68$$

(3)

Figure 8. Results of the multiple regression of pCO$_2$ in summer.

As shown in figure 8, the horizontal ordinate represents the pCO$_2$ obtained by the shipboard observations, while the vertical ordinate stands for the pCO$_2$ evaluated by SST and Chla.

By using the satellite monthly averaged SST and Chla data, downloaded from the NASA Goddard Space Flight Center (http://oceans.gsfc.nasa.gov), to replace the field data in equation (3), we can achieve the evaluate data of pCO$_2$ in the Yellow Sea in August 2010, the root mean square error between the evaluate pCO$_2$ and the field pCO$_2$ is 21.46μatm.

4. Conclusions

Through analyzing the data including pCO$_2$ and other parameters obtained by shipboard in February, May and August 2010, we found that the relationships of pCO$_2$ with SST and Chla were different in different seasons. The pCO$_2$ and SST had a strong positive correlation in the range of higher SST for both spring and summer, and a relative weak correlation in winter. The distribution of pCO$_2$ could be fitted with SST by a quadratic curve in each season. The pCO$_2$ and Chla were negatively correlated in winter and summer, and positively in spring. They were linearly correlated in each season.

We further fit the pCO$_2$ data in summer using multiple regression equation with SST and Chla data obtained by shipboard measurement and satellite observation in August 2010, and obtained that the RMSE of regression equation is 16.68μatm and 21.46μatm, respectively.

As a perspective for future improvement, we will do further exploration about the influence factors of pCO$_2$ to achieve a better result. To accurately evaluate the pCO$_2$ using satellite-observed SST and Chla instead of shipboard data, if not impossible, will be of great significance for monitoring the CO$_2$ air-sea exchange flux in the Yellow Sea.
Acknowledgments
Authors wishing to acknowledge the North China Sea Environmental Monitoring Center, State Oceanic Administration for providing field data and Yuguang Liu for valuable suggestions.

References
[1] Zhang Z B 2004 Marine Chemistry (Qingdao: China Ocean University Press)
[2] Ono T, Saino T and Kurita N 2004 Basin-scale extrapolation of shipboard pCO2 data by using satellite SST and Chla International Journal of Remote Sensing 25(19) 3803-15
[3] Zhang Y 2008 The carbon flux and maintaining mechanism of pCO2 in the Bohai Sea in summer (Qingdao: Ocean University of China)
[4] Zhang L J, Zhang Y 2008 The distribution of partial pressure of CO2 in the Bohai Sea in summer Periodical of Ocean University of China 38(4) 635-9
[5] Zhang L J, Wang J J, Zhang Y 2008 Distribution and controlling factors of surface seawater partial pressure of CO2 in the northern Yellow Sea during winter Periodical of Ocean University of China 38(6) 955-60
[6] Sun T M, Zhang L J, Xue L 2009 Distribution and controlling factors of surface seawater partial pressure of CO2 in the northern Yellow Sea during spring Periodical of Ocean University of China 39(Sup.) 171-6
[7] Zhang L J, Guo C, Xue L 2009 Distribution and controlling factors of surface seawater partial pressure of CO2 in the northern Yellow Sea during autumn Periodical of Ocean University of China 39(4) 587-91
[8] Jiang C B 2006 The CO2 flux at sea-atmosphere interface in the south Yellow Sea in spring and comparing with it in summer (Qingdao: Ocean University of China)
[9] Copin-moutegut C 1988 A formula of the effect of temperature on the partial pressure of carbon dioxide in seawater Marine Chemistry 25 29-37
[10] Wang J J 2008 Distribution and controlling factors of surface seawater partial pressure of CO2 in the northern Yellow Sea during winter (Qingdao: Ocean University of China)
[11] Sun T M 2009 The controlling factors of surface seawater partial pressure of CO2 and the air-sea flux in the northern Yellow Sea in spring (Qingdao: Ocean University of China)