

Impact of external nitrogen and phosphorus input between 2006 and 2010 on carbon cycle in China seas

Yang Gao · Nianpeng He · Guirui Yu ·
Jing Tian · Chiyuan Miao · Tiantian Yang

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Abstract It is widely accepted that excess nutrients change the dissolved inorganic carbon (DIC) system, which drives air–sea carbon dioxide (CO₂) exchanges, so the changes in the DIC system will then affect the oceans' carbon (C) biogeochemistry cycle. This study explores the impact of external nutrient input from 2006 to 2011 on the DIC system and air–sea CO₂ exchanges in four largest coastal seas in China. The result demonstrates that external nutrient input significantly facilitates the biological uptake of DIC and promotes air–sea CO₂ fluxes in coastal waters. The C sink caused by nitrogen (N) and phosphorus (P) input for the Bohai Sea, the Yellow Sea, the East China Sea, and the South China Sea account for 46, 45, 11, and 59 % of the total C sink, respectively. The excess nutrient input significantly changes the DIC system and C biogeochemistry cycle process in China Ocean. Up to a certain point, these effects are positive in increasing DIC levels and enhancing air–sea CO₂ exchanges. However, the DIC levels may decrease if the nutrient increase is greater than

the capacity of the oceanic C system. In addition, the other impact factors, including sea level, winds, water, and air temperatures, and various human activities, such as agriculture, industry, and domestic discharge, also affect N and P transport, air–sea CO₂ fluxes, and C biogeochemistry cycles.

Keywords Eutrophication · Air–sea CO₂ exchange · Coastal · Nitrogen · Phosphorus · Dissolved inorganic carbon · Biogeochemistry

Introduction

Being the largest of the world's carbon (C) pools, oceanic ecosystems store an approximate 39,120 Pg of inorganic C between surface water (670–1,020 PgC) and the deep sea (36,730–38,100 PgC), including 1,000 Pg total organic C and 3 Pg marine organism C (Siegenthaler and Sarmiento 1993; Falkowski et al. 2000). The oceans largely contribute to the C flux that takes place between oceanic ecosystems and the atmosphere. Of all carbon dioxide (CO₂) emitted into the atmosphere, one-quarter is absorbed by oceans, an approximate total of 2.3 ± 0.4 PgC of annual net C absorption, which is equivalent to the global net annual C uptake of terrestrial plant life (IPCC 2005; Global Carbon Project 2010). This is largely due to the structure of oceans, consisting of relatively simple producers, mostly in the form of short-lived, single-celled organisms. Photosynthetic organic products cannot fully be fixed after life cycle completion. Instead, the decomposition stage is rapidly entered, and the decomposition product is released back into the oceans and the atmosphere in the form of CO₂ (Houghton 2007; Bouillon et al. 2008).

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Y. Gao (✉) · N. He · G. Yu · J. Tian
Key Laboratory of Ecosystem Network Observation and Modeling, Institute of Geographic Sciences and Natural Resources Research, CAS, Beijing 100101, People's Republic of China
e-mail: gaoyang@igsnr.ac.cn

C. Miao · T. Yang
Department of Civil and Environmental Engineering,
University of California, Irvine, CA 92697, USA

C. Miao
State Key Laboratory of Earth Surface Processes and Resource Ecology, College of Global Change and Earth System Science, Beijing Normal University, Beijing 10085, People's Republic of China

One of the largest anthropogenic impact factors on oceanic C cycle is the discharge of nutrients (fertilizer, wastewater, etc.) into ocean waters, resulting in the eutrophication of coastal marine waters and the change of productivity and water acidity. As is well known, there are several biogeochemical processes leading to C sequestration in the ocean through photosynthesis. Eutrophication causes high water nutrient concentrations and lowers water transparency (Gao et al. 2012, 2014a), which favors some species and hurts others, distorting or disrupting coastal ecological ecosystem (Invers et al. 2004). Phytoplankton photosynthesis is the result of interplay between physical factors (irradiance and temperature) and phytoplankton nutrient and C storage and remobilization (Invers et al. 2002, 2004), so this process will fix approximately 45 PgC a^{-1} (Falkowski et al. 2000). In addition, some of the particulate organic material formed by phytoplankton is deposited at the ocean floor and is thus sequestered (Raven and Falkowski 1999). As the increase of water acidity, the performance of algal growth potential is weakened, mainly because of acidification reducing phosphorus (P) bioavailability, resulting in aquatic ecosystem being oligotrophic and the formation of sulfate deposition in the ocean (Larssen et al. 2011).

Owing to this, the interaction of the dissolved inorganic carbon (DIC) system with nutrient uptake of algae in sea water has aroused international concern (Gao et al. 2014b). Most aquatic plants photosynthesize by means of CO_2 , and only a few species use HCO_3^- (Raven and Falkowski 1999; Zhi et al. 2008). It is clear that phytoplankton growth is affected by the DIC levels as well as by the available nutrients. The availability of HCO_3^- and CO_2 fluctuates since the composition of the DIC depends on the biological activity (Zhang et al. 2012). Huertas et al. (2000) have reported that the uptake of NO_3^- and PO_4^{3-} by phytoplankton depended on the level of DIC. Excess anthropogenic nitrogen (N) and P input change sea water chemistry, leading to sea water acidification and a reduction in total alkalinity, which in turn cause changes in DIC concentration (Doney et al. 2007). Hence, it is very important to estimate the impact of anthropogenic N and P input by measuring the changes in DIC. In addition, an increase in temperature or salinity would also decrease the solubility of CO_2 (Bakker et al. 1999). DIC and total alkalinity are conservative parameters when the water in the top layers mixes with that in the lower layers; this mixing process helps determine sea water pH and the partial pressure of CO_2 (pCO_2) as well as temperature and salinity (Bakker et al. 1999; Zeebe and Wolf-Gladrow 2005). Higher values of pCO_2 drive increased air–sea CO_2 exchange (Frankignoulle et al. 1998).

The area of the China seas is vast and has a total area of $4.71 \times 10^6 \text{ km}^2$ (including $1.71 \times 10^6 \text{ km}^2$ of inland and

offshore maritime expanse and a seazone comprising of a $3 \times 10^6 \text{ km}^2$ continental shelf), which accounts for 1.3 % of the total area of the world's oceans, ranking fifth in nations. Several large Chinese river systems discharge freshwater, burdened with nutrients, into this larger marine area. This nutrient input is responsible for the increasing of water eutrophication and changing water quality and productivity. Moreover, the phytoplankton consumes large amounts of DIC, resulting in lower pCO_2 , and strengthens air–sea CO_2 flux. This study investigates the impact of N and P input on the DIC system in China coastal ecosystem for the period of 2006–2011 and then estimates the contribution of external N and P input to C cycle in China seas.

Methods

Study area

The study area is bordered by the P. R. China coastline and includes four named seas (Fig. 1): the Bohai Sea, the Yellow Sea, the East China Sea, and the South China Sea. The Bohai Sea ($37^\circ 07'–41^\circ 0' \text{N}$, $117^\circ 35'–121^\circ 10' \text{E}$) is the only inland sea. It spans an area of $7.7 \times 10^4 \text{ km}^2$ and is bordered by 2,688 km of P. R. China coastline. The annual average temperature is 10°C ; salinity is 30; and pH values range from 7.86 to 8.30. The Yellow Sea ($35^\circ–45^\circ \text{N}$, $120^\circ–123^\circ \text{E}$) covers an area of $3.8 \times 10^5 \text{ km}^2$. The annual average temperature is 12°C ; salinity is 32 or more; and pH values range from 7.9 to 8.10. The East China Sea ($23^\circ 00'–33^\circ 10' \text{N}$, $117^\circ 11'–131^\circ 00' \text{E}$) spans an area of $7.52 \times 10^5 \text{ km}^2$. The annual average temperature is 20°C ; salinity is 33; and pH values range from 7.8 to 8.20. The South China Sea ($3^\circ 40'–11^\circ 50' \text{N}$, $109^\circ 33'–117^\circ 50' \text{E}$) is an open sea covering an area of $3.5 \times 10^6 \text{ km}^2$. The annual average temperature is 25°C ; salinity is 32; and pH values range from 8.0 to 8.2.

Relationship between nutrient input and DIC system

DIC in sea water consists of roughly 90 % bicarbonate (HCO_3^-), 9 % carbonate (CO_3^{2-}), 0.5–1 % CO_2 , and 0.002 % carbonic acid (H_2CO_3)

$$\text{DIC} = [\text{HCO}_3^-] + [\text{CO}_3^{2-}] + [\text{CO}_2] + [\text{H}_2\text{CO}_3]. \quad (1)$$

Zhang et al. (2007) reported effect of external N and P addition on the sea water DIC system and the results of N and P inputs at a temperature of 15°C over a range of pH values. The relationship between N and P input and DIC values was shown in Table 1. Therefore, there would be a synergistic effect if different nutrients were added to the DIC system in combination. This synergistic effect was best expressed as a multiple regression:

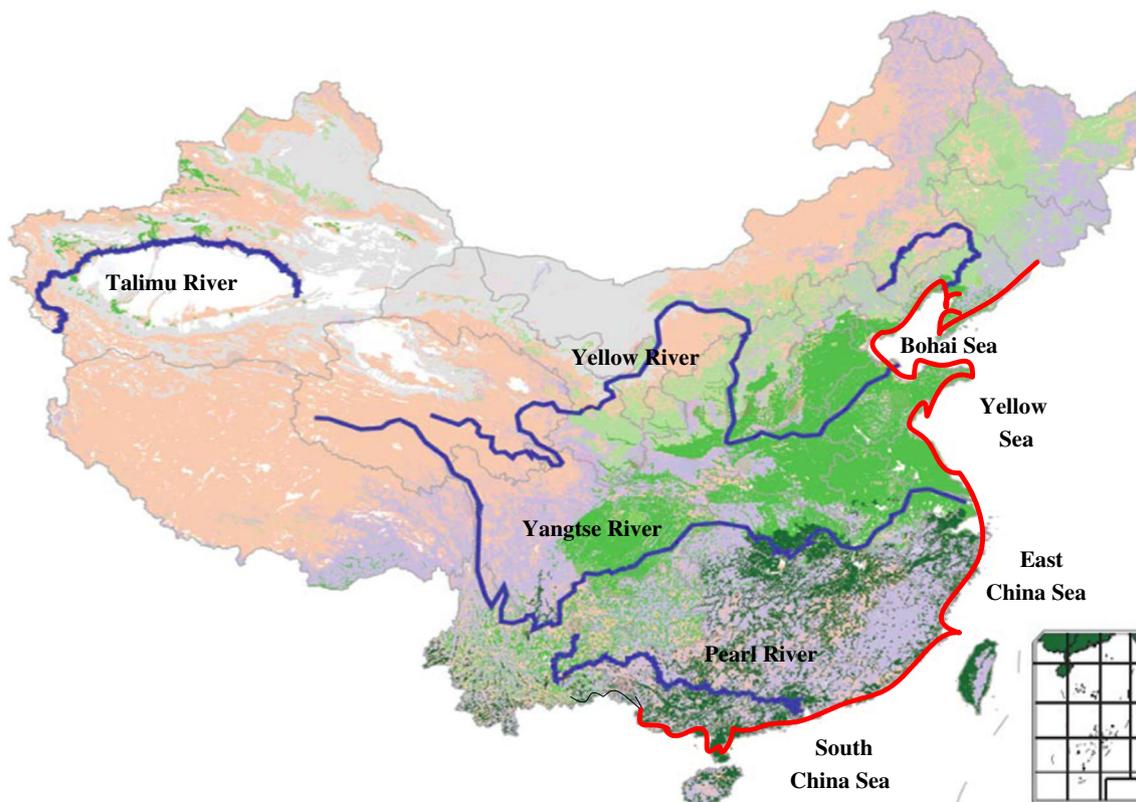


Fig. 1 The geographic location for the Bohai Sea, the Yellow Sea, the East China Sea, and the South China Sea, wherein *red line* is coastline and *blue line* is main river system in China (colour figure online)

Table 1 Correlation between nutrients and constituents of DIC system

Nutrient	DIC	HCO ₃ ⁻	CO ₃ ²⁻	pCO ₂
NO ₃ ⁻	-0.502**	-0.579**	0.628**	-0.713**
NH ₄ ⁺	-0.514**	-0.644*	0.647**	-0.675**
NO ₂ ⁻	-0.316*	ns	0.323*	-0.394*
PO ₄ ³⁻	-0.542**	-0.592***	0.672**	-0.766**

ns: $p > 0.05$; * $p < 0.05$; ** $p < 0.01$; *** $p < 0.001$

$$Y = a + b_1X_1 + b_2X_2 + \dots + b_kX_k \quad (2)$$

where Y is a dependent variable; a is a constant term; b is a partial regression coefficient; and X_k is an environmental factors variable, such as ΔNO_3^- , ΔNH_4^+ , ΔNO_2^- , and ΔPO_4^{3-} .

The relationship between different forms of N and P input and DIC can be expressed by the partial regression:

$$\begin{aligned} \Delta\text{DIC} = & -0.937(\Delta\text{PO}_4^{3-}) - 0.34(\Delta\text{NO}_3^-) \\ & - 0.46(\Delta\text{NH}_4^+) + 0.11(\Delta\text{NO}_2^-) \end{aligned} \quad (3)$$

($R^2 = 0.69$, $n = 30$, $p < 0.05$)

$$\begin{aligned} \Delta\text{pCO}_2 = & -1.321(\Delta\text{PO}_4^{3-}) - 0.12(\Delta\text{NO}_3^-) \\ & - 0.31(\Delta\text{NH}_4^+) - 0.032(\Delta\text{NO}_2^-) \end{aligned} \quad (4)$$

($R^2 = 0.85$, $n = 35$, $p < 0.01$)

where the units of ΔDIC , ΔNO_3^- , ΔNH_4^+ , ΔNO_2^- , and ΔPO_4^{3-} in Eqs. 3 and 4 are expressed in $\mu\text{mol L}^{-1}$; the unit of ΔpCO_2 is μatm . Equations 3 and 4 imply that variations of DIC components show significantly correlation with nutrient input/concentration. The most pronounced relationship is the one between ΔpCO_2 and nutrient input. This may be due to the phytoplankton photosynthesis, and decomposition consumes the free state of CO_2 in sea water.

Air–sea CO_2 flux and sink calculations

The air–sea fluxes (F) of CO_2 are calculated according to the equation:

$$F = ks(f\text{CO}_2^{\text{water}} - f\text{CO}_2^{\text{air}}) \quad (5)$$

where k is the gas transfer velocity in cm h^{-1} (depending on wind speed and temperature), which is determined by the two methods (Eqs. 6, 7); s is the solubility of CO_2 in

sea water in $\mu\text{mol m}^{-3} \mu\text{atm}^{-1}$; $f\text{CO}_2^{\text{water}}$ is the CO_2 fugacity in the ocean in μatm ; $f\text{CO}_2^{\text{air}}$ is the CO_2 fugacity in the atmosphere in μatm ; $f\text{CO}_2^{\text{water}} - f\text{CO}_2^{\text{air}}$ represent $\Delta p\text{CO}_2$; F is expressed in $\mu\text{mol CO}_2 \text{ m}^{-2} \text{ d}^{-1}$

$$\begin{aligned} k &= 0.17U_{10} \quad (U_{10} < 3.6 \text{ m s}^{-1}) \\ k &= 2.85U_{10} - 9.65 \quad (3.6 \text{ m s}^{-1} < U_{10} < 13 \text{ m s}^{-1}) \quad (6) \\ k &= 5.9U_{10} - 49.3 \quad (U_{10} > 13 \text{ m s}^{-1}) \\ k &= 0.39U_{10}^2(\text{Sc}/660) - 1/2 \quad (\text{long term average wind}) \\ k &= 0.31U_{10}^2(\text{Sc}/660) - 1/2 \quad (\text{steady/short term wind}) \end{aligned} \quad (7)$$

where U_{10} is the mean wind speed at 10-m distance to sea level; Sc is Schmidt constant; 660 is Schmidt constant (Liss and Merlivat 1986; Wanninkhof 1992).

Data analysis

Our analysis is based on the data from 204 water quality monitoring stations on the major river deltas in China and along the China coastline. Data are tracked and recorded by the China National Environmental Monitoring Center. Data on N and P discharge, concentration, and coastal water quality are taken from Chinese River and sediment Bulletin, Chinese Environment Bulletin, Chinese Oceanic quality Bulletin, and China Marine Environment Quality Bulletin, 2006–2011.

For the study years (2006–2011), the value of parameter k was 10.3 cm h^{-1} , which is the mean value for continental shelf off the China coast according to Tsunogai et al. (1999). The solubility of CO_2 is computed monthly as a function of temperature and salinity according to Weiss (1974), by the following formula:

$$\ln s = A_1 + A_2(100/T) + A_3 \ln(T/100) + S \times [B_1 + B_2(T/100) + B_3(T/100)^2] \quad (8)$$

where T is temperature in K; S is salinity; $A_1 = -58.0931$; $A_2 = 90.5096$; $A_3 = 22.2940$; $B_1 = 0.027766$; $B_2 = -0.025888$; $B_3 = 0.0050578$.

Results

Nutrient discharge from 2006 to 2011

As Fig. 2 shows, the main nutrient input was nitrate, which constitutes of 80 % of the nutrient discharged into Chinese coastal waters. From 2006 to 2011, the amount of nutrient discharged into Chinese waters increased, with the exception that there was a slight decrease in nitrate and ammonium salt discharge into the South China and East China seas. The East China Sea was subject to the most serious

eutrophication of all the waters monitored with exceptionally high-nutrient inputs. As Fig. 1 shows, the Yangtze River flows into the East China Sea, and the Yangtze River delta is the most developed industrial area in China and generates a large volume of industrial wastewater. Although wastewater discharge is gradually decreasing due to that Environmental Protection Bureau strengthens the control on wastewater discharge from industry, the level of nutrient discharge is still very high.

However, as Fig. 3 shows, the changes in individual nutrient concentrations were independent of nutrient discharge amounts to some extent. For example, nitrate concentration in the South China Sea grew more quickly than that in other seas. The rate of nitrate concentration growth was also pronounced for the East China Sea, but ranked behind the rate for the South China Sea. The Yellow Sea showed the highest rate of growth in ammonium salt concentration. For all seas, the rates of nitrate concentration changes showed more fluctuations than that for any other nutrient changes, and the changes in phosphate concentration from 2006 to 2011 were the least pronounced. This was easily explained by the fact that nitrate was the main component of non-point source pollution and accounted for the largest proportion of the nutrient export caused by agricultural and industrial discharge.

Changes in the DIC system

According to Eq. (3), the relationship between DIC and nutrient discharge showed significant partial correlation and the external nutrient input would consume DIC and lead to changes in the sea water DIC system. As Fig. 4 shows, annual DIC consumption in the East China Sea (approximately 4 Tg annually) was the highest and it was the lowest in the Bohai Sea. In addition, the changes in the DIC system, which were driven by nutrient input into the four seas, correlated with the changes in rates of nitrate discharge to a great extent.

Air–sea CO_2 fluxes

As Table 2 shows, the changes in DIC concentration did not correlate with the measurements of air–sea CO_2 flux. From 2006 to 2011, the greatest change in DIC concentration was shown in the Yellow Sea: minus $4.69 \mu\text{mol L}^{-1}$. External nutrient input into the body of water resulted in some $1.41 \text{ mmol m}^{-2} \text{ d}^{-1}$ of CO_2 input. The rate of change in DIC was the smallest in the East China Sea compared to that in any other Chinese coastal waters. The mean air–sea CO_2 flux in East China Sea was $4.89 \text{ gC m}^{-2} \text{ a}^{-1}$, while the CO_2 input into the East China Sea was estimated at $1.03 \text{ mmol m}^{-2} \text{ d}^{-1}$. The South

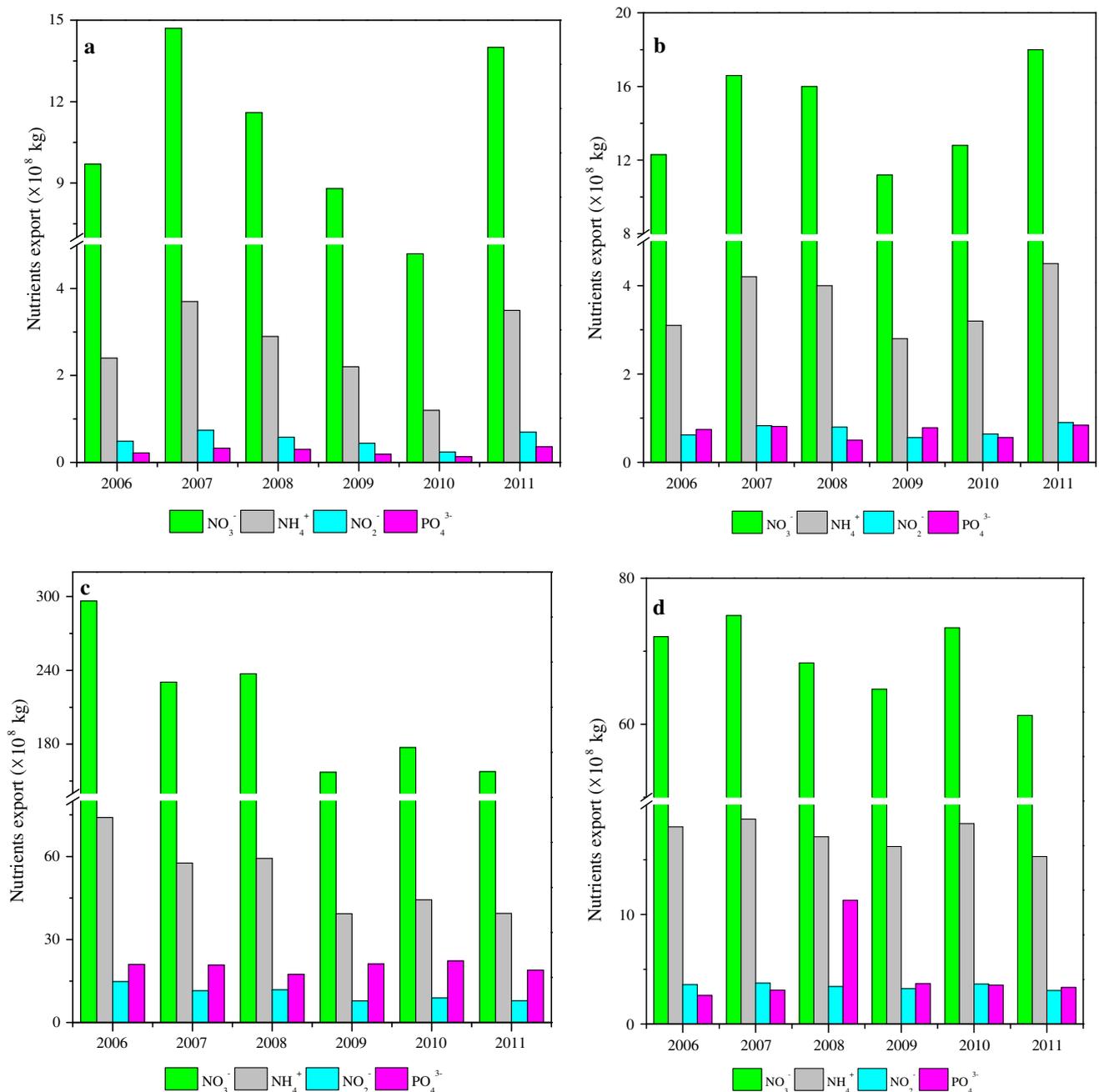


Fig. 2 Nutrients discharged into the Bohai Sea (a), the Yellow Sea (b), the East China Sea (c), and the South China Sea (d) from 2006 to 2011 (unit: × 10⁸ kg)

China Sea, as the largest seas in the PR China, had the lowest air–sea CO₂ flux: minus 4.32 gC m⁻² a⁻¹. The CO₂ sink fluctuated over the whole years with the highest value of 15.1 Tg. This accounted for 69.68 % of the total CO₂ sink (Fig. 5). The East China Sea was the second largest CO₂ sink in China Seas, amounting to 3.67 Tg at its highest annual value. It constituted 16.94 % of the total CO₂ sink. The Bohai Sea contained the smallest percentage of the total CO₂ sink.

Discussion

Impact of nutrients input on oceanic C sink for China

As Fig. 6 shows, the C flux of China seas exhibited great variations and large C sinks based on long-term monitoring. Oceans absorb atmospheric CO₂ in an attempt to reach equilibrium through direct air–sea exchanges, but this process takes place at an extremely slow rate (Chen et al.

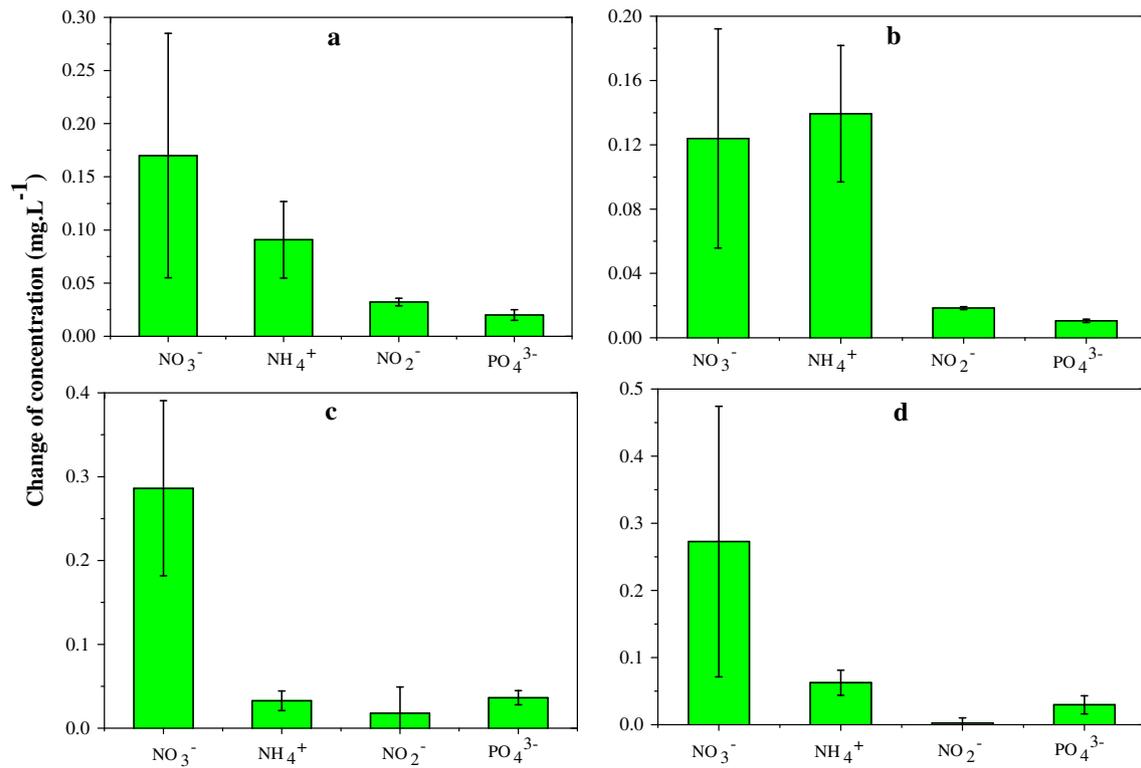


Fig. 3 Changes in nutrient concentrations in the Bohai Sea (a), the Yellow Sea (b), the East China Sea (c), and the South China Sea (d), 2006–2011

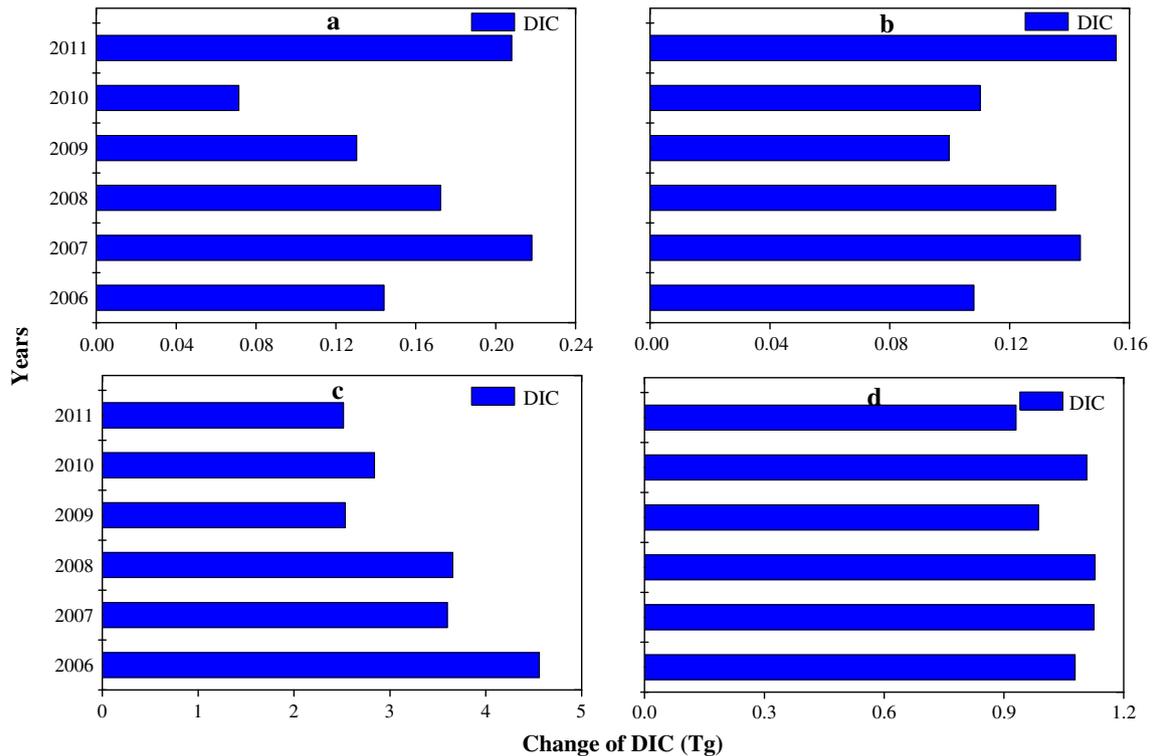
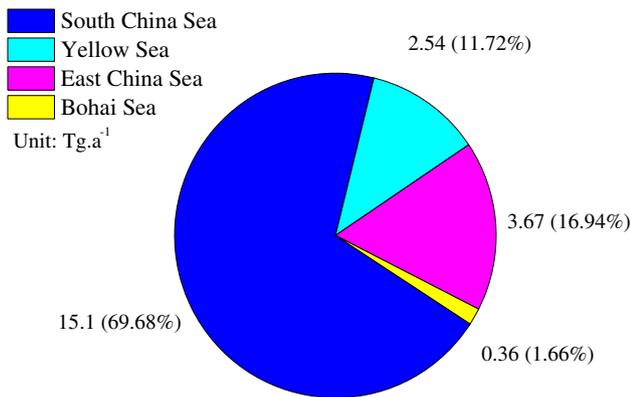
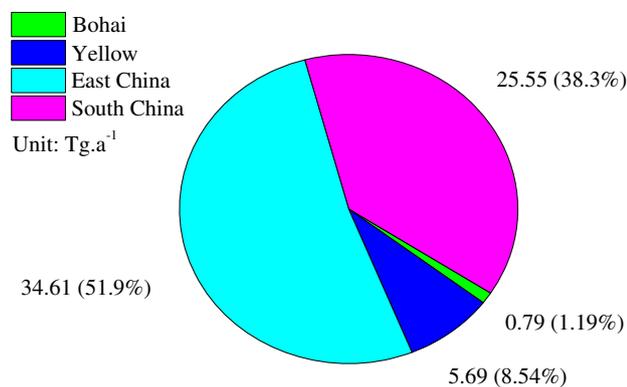


Fig. 4 Changes in DIC levels in the Bohai Sea (a), the Yellow Sea (b), the East China Sea (c), and the South China Sea (d), 2006–2011

Table 2 Changes in DIC levels and CO₂ flux in China coastal seas, 2006–2011

Sea	Area (km ²)	ΔDIC (μmol L ⁻¹)	ΔpCO ₂ (μatm)	ΔF (mmol m ⁻² d ⁻¹)	Mean flux (gC m ⁻² a ⁻¹)
Bohai Sea	7.7 × 10 ⁴	-3.48	-2.27	-0.98	-4.65
Yellow Sea	3.8 × 10 ⁵	-4.69	-3.24	-1.41	-6.69
East China Sea	7.5 × 10 ⁵	-3.31	-2.38	-1.03	-4.89
South China Sea	3.5 × 10 ⁶	-3.47	-2.08	-0.91	-4.32

**Fig. 5** Contribution of nutrient discharge to CO₂ sinks in the China seas**Fig. 6** The annual net CO₂ uptake or release by the China seas

2003). China's marine ecosystems can absorb 65.06 TgC from the atmosphere every year. Except the Bohai Sea showing annual net CO₂ release, annual net CO₂ uptakes from the Yellow Sea, the East China Sea, and the South China Sea were 5.69, 34.61, and 25.55 TgC, respectively, which were estimated according to Chinese Oceanic Quality Bulletin, 2006–2011 (Fig. 6), confirming their status as atmospheric CO₂ sinks. Given that the annual global C sink of oceans is 2.0–2.2 PgC (González et al. 2008), the China seas account for 3.0–3.3 % of the ocean net C sink globally. Compared to previous estimation (Table 3), the largest difference existed at East China Sea and South China Sea, which showed considerable annual changes. The difference could be largely attributed to the

Table 3 Estimation of C source/pool in the China seas

Name	C sink/(TgC a ⁻¹)	References
Bohai Sea	2.84	Song (2004)
	27.38	Fang et al. (1996)
Yellow Sea	8.96	Song (2004)
	6–12	Song (2004)
	1.2	Fang et al. (1996)
East China Sea	4.3	Hu and Yang (2001)
	1.88	Song (2004)
	30	Tsunogai et al. (1999)
	13–30	
South China Sea	34.1	Fang et al. (1996)
	16.65	Han et al. (1997)
	7.69	Fang et al. (1996)

extensive phytoplankton photosynthesis that takes place in surface sea water during spring and early summer, transforming CO₂ into organic C and thereby greatly reducing CO₂ partial pressure in sea water for increasing the absorption of atmospheric CO₂.

In present study, our result showed that the external N and P input significantly impacted on the C sink in China Seas. The ratio of C change caused by N and P input to total C sink for the Bohai Sea, the Yellow Sea, the East China Sea, and the South China Sea were 0.46, 0.45, 0.11, and 0.59, respectively, which indicated the effect of N and P input on C cycle in China seas was enormous. Eutrophication has such deleterious effects on near-shore industries, residents, and ecologies that research on nutrient input, and the offshore DIC system is of the utmost importance for economic and environmental reasons. Humans are discharging more and more N and P into coastal waters, resulting in the fluxes of N and P that far exceed their natural production rate (Galloway and Cowling 2002; Foley et al. 2005). Excess nutrient loading is fast becoming a crucial environmental problem for coastal areas because it has such detrimental effects on environments. The excess nutrients promote eutrophication: bloom (the proliferation of fast-growing surface species, including phytoplankton, epiphytes, and opportunistic macro-algae Duarte 1995), hypoxia, and disturbance of the whole coastal and marine ecosystem. As Fig. 2 shows, although the Chinese government and its environmental protection

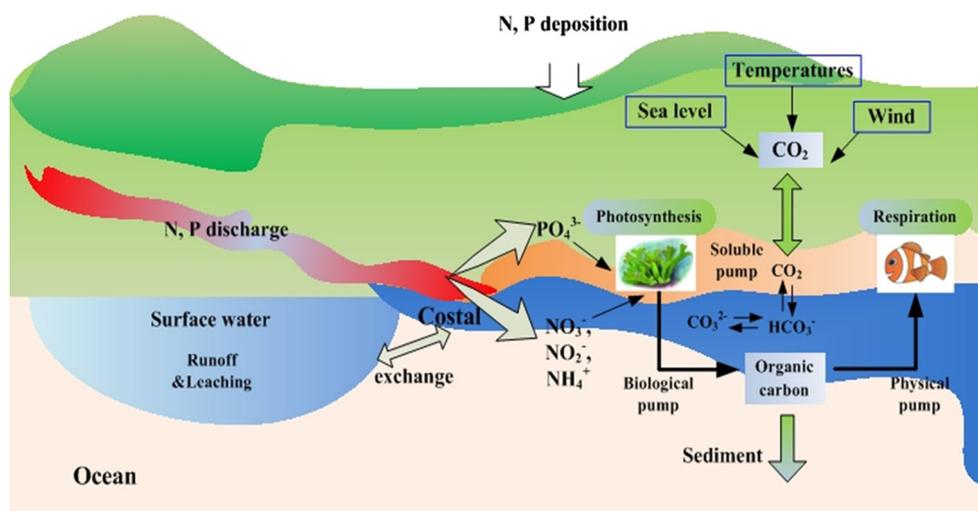


Fig. 7 Effect of N and P input on oceanic C cycle. Atmospheric CO_2 dissolved into in sea water in the forms of CO_3^{2-} and HCO_3^- is called as soluble pump effect. The CO_2 that enters into oceanic ecosystem is constantly transformed into organic C and biological carbonate through photosynthesis, and then further transferred from the ocean surface to the deep ocean, which of the process is called as biological pump effect. Soluble and biological pump can enhance the CO_2 absorption by ocean surface, impact on CO_2 dissolved, and C

transferred to the deep ocean. Ocean organisms' respiration mainly happens beneath the ocean mixed layer. The CO_2 gas produced by ocean organisms' respiration and its effect on decomposition of organic C would increase sea water CO_2 pressure increase and then result in the release of CO_2 into the atmosphere, which of the process is called as physical pump (Frankignoulle et al. 1998; Bakker et al. 1999; Díaz and Rosenberg 2008; Jiao et al. 2010)

agencies try to control N and P discharges from industry and residences, the N and P loading is still at an unacceptably high level. As long as China continues extensive economic development mode, it will be difficult to reach a satisfactory level of discharge.

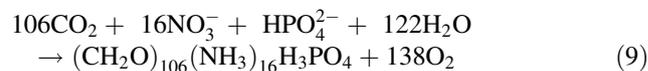
Impact of nutrient input on the ocean C cycle

Oceanic C fluxes were believed to be dominated by microbial activity largely because bacteria and microalgae were the dominant source of primary production and respiration in the world's ocean (Duarte and Cebrian 1996; del Giorgio and Duarte 2002). Under current conditions, the oceans can absorb approximately 20–33 % of the anthropogenic CO_2 emitted from fossil fuels and industrial processes (Baliño et al. 2001). However, the exchange of CO_2 that takes place in the air–sea interface, being regulated by the interplay between physical and biological processes, is not evenly distributed in space and time (Fig. 7).

As Fig. 7 shows, in the course of the primary production process, phytoplankton needs to absorb nutrients, such as nitrate and phosphate, from sea water. This leads to an increase in the alkalinity of surface waters, which reduces their pCO_2 . These two processes promote the increase of pCO_2 on both of sea and air interface. This increase then strengthens the diffusion of atmospheric CO_2 into the sea water and enhances CO_2 sequestration by the sea. Bakker et al. (1999) also have reported that photosynthetic uptake of CO_2 can lower DIC and pCO_2 . However, it must be

noted that the growth in the C content of sea water cannot increase unboundedly. If the increase in nutrients is greater than the capacity of the system to absorb the increased phytoplankton production, negative consequences follow. Algal blooms may result in increased sedimentation of organic matter on the seabed and subsequent oxygen depletion when they decompose (Glibert et al. 2005). Marine organisms begin to die as dissolved oxygen decreases to a critical level (Díaz and Rosenberg 2008).

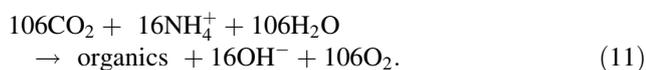
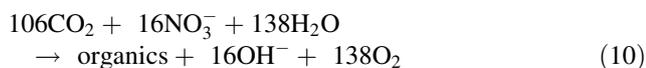
In the present study, increased N and P input had markedly changed air–sea CO_2 fluxes and C cycle in the coastal zone. This can be explained in part by purely chemical processes: nutrient input leads to the changes in the oceanic C circulation, which change sea water pH and air–sea CO_2 fluxes, and then impacts on the C system. The biogeochemical changes due to eutrophication of sea water also stimulate ocean primary production and organic matter export (Invers et al. 2004). Phytoplankton in the euphotic zone takes up CO_2 through photosynthesis, converting it to organic C. The conversion of inorganic nutrient ions into primary productivity is expressed by the following reaction Eq. (9):



Biological growth and decay both involve CO_2 . Biological uptake of CO_2 and organic growth is accompanied by the consumption of nutrients; oxidation of organic detritus is normally accompanied by the release of nutrients

and the production of CO₂. This biological cycle is one of the main reasons to explain why increased nutrient input drives changes in the DIC system. Phytoplankton take up CO₂ from sea water in the course of photosynthesis, so inorganic C thus becomes organic C and biologically available. When the phytoplankton is consumed by other marine flora and fauna, their organic C enters the food chain as particulate organic C. If the phytoplankton die and sink to the sea floor, or the species that have fed upon them do so, the particulate organic C thus deposited may be decomposed and transformed into dissolved organic C by fungi or bacteria, or simply buried in sediment. This process affects other elements as well. Ocean thermohaline circulation and sedimentation of particulate matter would transport C from the ocean surface to the deep ocean, and finally, C is buried in the sediments, all of which form the main pathway for the ocean C cycle (IPCC 2005).

The elevated and well-balanced nutrient input can stimulate primary production and increase the CO₂ uptake capacity of the sea; low or unbalanced nutrient inputs can limit coastal primary production, so the sea would act as the source for atmospheric CO₂. Kevin (2005) has reported that deficiency or excess of N would both inhibit photosynthesis and prevent absorption of C in the DIC system. Ferial et al. (2001) have suggested that the biological drawdown of DIC and nutrients showed fixed ratios. Doney et al. (2007) have also reported that increased primary production stimulated by nitrogen lowers surface DIC, with a C/N ratio of 6.6 (Eqs. 10, 11)



The importance of nutrient and phytoplankton growth limitation on air–sea CO₂ flux in coastal area was also pointed by Cunha et al. (2007). Mackenzie et al. (2004) pointed out that both increased anthropogenic CO₂ emissions and increasing nutrient inputs were the key players in the reversal of the air–sea CO₂ flux in the global coastal zone. Our research also showed that nutrient inputs were the main drivers of the long-term air–sea CO₂ sink. This study demonstrated that the calculated inter-annual variability of air–sea CO₂ fluxes, and sink was related to the changes in C cycling driven by variations in nutrient loads. The increase in organic C input would stimulate heterotrophic activities and the emission of CO₂, but this effect was counteracted by primary production stimulated by the concomitant increase of nutrient input (Gypens et al. 2009). Hence, it is clear that continued increase in nutrient inputs does not translate to a limitless increase in marine CO₂ sinks.

Implications for future research

Like most of the world's oceans, the strength of the biological pump in the China seas is controlled by the availability of essential plant macronutrients, such as nitrate, phosphate, and silicate. The availability of nitrate or silicate can be altered if climate changes affect patterns of oceanic circulation, i.e. changes in upwelling of such macronutrients that are essential for the growth of phytoplankton, the engine that drives the biological pump (Smith et al. 1999; Xu et al. 2001; Carstensen et al. 2011). Moreover, climate change and episodic events can change the structure of ocean ecosystems and thus influence the efficiency and magnitude of the biological pump (Baliño et al. 2001; Larssen et al. 2011).

Our study suggests that changes in coastal waters could have global effects. The effect of nutrient inputs on oceanic C sink is enormous; the excess nutrients would impact on the C biogeochemistry cycle and the oceanic DIC system. Air–sea CO₂ fluxes are driven both by climate change and human activity. Climate change will strengthen the average global temperature rises, which significantly impact on sea levels, sea water temperatures, enhanced hydrological cycles, and shifts in wind patterns, resulting in changes of air–sea CO₂ fluxes. According to Pipko et al. (2002) and Orgeta et al. (2004), the DIC system in sea water is mainly determined by pH values, salinity, and pCO₂. Increasing temperatures due to climate change have the potential effect on temperature and salinity in sea water. For example, a 1 °C increase in temperature would lead to a 1-psu decline in salinity, which changes sea water density (Fonfonoff and Millard 1983). Increased temperatures may also change regional wind patterns, which may either aggravate or alleviate low oxygen conditions in coastal waters. The largest human activities lead to excess N and P (both point and non-point sources) discharge and atmospheric deposition into ocean, which can also alter pH values and reduce total alkalinity (Fig. 7).

From Fig. 7, we see that any effect that climate change has on the nature and intensity of ocean circulation could have a strong impact on atmospheric CO₂. Moreover, ocean warming may reduce the strength of the thermohaline circulation overturning cell, having an indirect effect on the efficiency of both physical and biological pumps. This in turn would feed back into the climate, potentially accelerating the rate of change. Changes in ocean chemistry due to increasing CO₂ in surface waters are also likely to alter the long-term capacity for C uptake and influence the functioning of marine ecosystems dominated by calcifying organisms. At present, many uncertainties remain when estimating C cycles in the China seas. This is largely related to a lack of oceanic knowledge and partially due to current limitations on monitoring methods and associative

instrumentation. Moving into the future, research should be intensified in China in order to cope with climate change, especially research that focuses on the following: (1) CO₂ sources, sinks, and distribution patterns in the air–sea interface; (2) regulation of marine biogeochemical processes on atmospheric CO₂; (3) driving factors of atmospheric and hydrological mechanisms on critical processes of ocean C cycles; (4) atmospheric N deposition estimations and terrestrial input impacts on C cycle processes; and (5) sustainable development of coastal biological C fixation.

Conclusion

This study demonstrates that external nutrient input significantly facilitates biological uptake of DIC and promotes air–sea CO₂ fluxes and sink in Chinese coastal ecosystem. Coastal water quality is currently declining, due to eutrophication, but it can serve as a sink for atmospheric CO₂. The excess nutrient inputs may account for 11–59 % of the C in the China seas, so the water eutrophication would significantly affects oceanic C sequestration and water quality. The effects of N and P on the changes in DIC and pCO₂ also demonstrate that physiological and biochemical processes of C, N, and P are interconnected. The N and P import process is likely to cause cascade responses affecting C biochemical mechanisms. However, that excess nutrient input into coastal waters would result in negative effects on DIC and air–sea CO₂ fluxes if the increase in nutrients is above the capacity of the C system. We can only conclude that the link between nutrient input and oceanic C sequestration is complex in which we know little about the effects of human activities and global climate change on eutrophication and oceanic C cycles.

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