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RECEIVED 14 September 2024

ACCEPTED 22 January 2025

PUBLISHED 19 February 2025

## CITATION

Cao L, Li S, Zhang S, Wu N, Zhang K, Li W,  
Ma R, Chu D, Wang N and Liu Y (2025) Buoy-  
based monitoring of sea surface carbon  
dioxide partial pressure at Qingdao  
coastal area.

*Front. Mar. Sci.* 12:1496359.

doi: 10.3389/fmars.2025.1496359

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# Buoy-based monitoring of sea surface carbon dioxide partial pressure at Qingdao coastal area

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Continuous time series observations of seawater carbon dioxide partial pressure ( $p\text{CO}_2$ ) are crucial for documenting temporal variations in air-sea  $\text{CO}_2$  fluxes. To examine the seawater  $p\text{CO}_2$  variation and its influence factors at Qingdao coastal waters, a high-resolution observation of seawater  $p\text{CO}_2$  near the Xiaomaidao Island was conducted from May 29 to July 25 in 2024. Sea surface  $p\text{CO}_2$  varied from 519  $\mu\text{atm}$  to 717  $\mu\text{atm}$  during this monitoring period, with an obvious decline and rise from July 12 to 21. The variation of seawater  $p\text{CO}_2$  was mainly affected by the increasing sea surface temperature, except for the period of  $p\text{CO}_2$  decrease which was caused by *Ulva prolifera* bloom. Accompanied by the increase of *U. prolifera*, sea surface  $p\text{CO}_2$  decreased to 563  $\mu\text{atm}$ , then the coverage of *U. prolifera* decreased and sea surface  $p\text{CO}_2$  rose to 669  $\mu\text{atm}$  during period of July 12 to 21. The observation site acted as a source for atmospheric  $\text{CO}_2$  throughout the monitoring period, with air-sea  $\text{CO}_2$  flux ranging from less than 1  $\text{mmol m}^{-2} \text{d}^{-1}$  to over 100  $\text{mmol m}^{-2} \text{d}^{-1}$ , resulting in a total  $\text{CO}_2$  release of 334  $\text{mmol m}^{-2}$ . Thus, it is essential for high-resolution measurement of  $p\text{CO}_2$  in coastal areas.

## KEYWORDS

carbon dioxide partial pressure, Qingdao Coast, *Ulva prolifera* influence, early bloom,  $\text{CO}_2$  flux

## 1 Introduction

The ocean is the largest reservoir of carbon, absorbing approximately 30% of the anthropogenic  $\text{CO}_2$  emitted into the atmosphere (Sabine et al., 2004). This process has induced ocean acidification and variations of carbonate system (Doney et al., 2009; Mostofa et al., 2016). Ongoing global warming and associated climate changes are expected to alter  $\text{CO}_2$  fluxes at the air-sea interface and the regulatory mechanism. Therefore, regular assessment of the temporal and spatial variabilities of marine  $p\text{CO}_2$  is urgently needed for research on carbon cycle and carbon budgets (Murata et al., 2022; Regnier et al., 2022; Wu et al., 2024).

The coastal region significantly influences the carbon cycle (Cai, 2011; Dai et al., 2022). Due to the strong terrestrial input and anthropogenic disruptions in coastal regions, the carbonate system and CO<sub>2</sub> flux exhibit complex fluctuations (Lin and Lin, 2022; Xue et al., 2016), leading to alteration of coastal waters function as source or sink to atmospheric CO<sub>2</sub>. The temporal variations of seawater pCO<sub>2</sub> influenced by factors such as temperature effects, mixing processes, biological processes and air-sea exchange and other contributing processes (Borges et al., 2006; Xue et al., 2016). As a transition zone connecting the southern Yellow Sea with Jiaozhou Bay, the Qingdao coastal region is strongly affected by anthropogenic activities and green tides. The green tides caused by *U. prolifera* have occurred annually in the southern Yellow Sea since 2007, usually appearing along the Qingdao coast in June and dissipating in August or early September (Yuan et al., 2022; Shao et al., 2024; Zhang et al., 2019). The *U. prolifera* bloom has resulted in extensive harm to the ecology and economy of coastal cities and led to significant alterations in the carbon system (Zhang et al., 2019; Xiong et al., 2023). Thus, the time series observation is essential for further understanding the temporal variation in seawater pCO<sub>2</sub> and its associated influencing factor. In particular, the impact of *U. prolifera* on the carbonate system in Qingdao coast was mainly studied previously based on cruises sample collection (Hu et al., 2024; Li et al., 2021; Xiong et al., 2023; Deng et al., 2018; Hu et al., 2015), and lack of continuous high-resolution observations.

In this work, a time serious observation based on buoy near the Xiaomaidao Island at Qingdao coastal area was conducted during May 29 – July 25, 2024. Based on the collected data, we reported the variation in seawater pCO<sub>2</sub> and the air–sea CO<sub>2</sub> flux, identified the factors affecting the temporal changes in seawater pCO<sub>2</sub>, and explored the continuous influence of *U. prolifera* bloom on seawater pCO<sub>2</sub>.

## 2 Materials and methods

### 2.1 Study site

The observation site (120.44°E, 36.05°N) is located at Qingdao coastal area (Figure 1), near Xiaomaidao Island, and is in a

transition zone connecting the southern Yellow Sea with Jiaozhou Bay. This site is dominated by semi-diurnal currents, with a water depth of about 23 m. The rainfall is highest in summer and lowest in winter, with an average annual precipitation of approximately 660 mm (<http://www.qingdao.gov.cn>). The investigation area is affected by the southeast monsoon and coastal waters in summer. The sea surface salinity (SSS) is the highest in winter, and the peak sea surface temperature (SST) generally occurs in August. Since 2007, *U. prolifera* has occurred annually in the southern Yellow Sea, and Qingdao is one of the cities receiving the macroalga.

### 2.2 Field observations based on buoy

The 15 m intelligent buoy was deployed at the observation site from May 29 to July 25 in 2024. There was an air-water equilibrator (MAPCO<sub>2</sub>) (Friederich et al., 1995; Sutton et al., 2014) placed in the buoy shaft floating on the sea surface based on float, and a customized gas control module and standard gas (Figure 2) fixed in the buoy chamber without contact with seawater for pCO<sub>2</sub> measurement. During monitoring, the seawater pCO<sub>2</sub> was measured with a frequency of 1 h or 2 h and the calibration frequency was 24 h. The atmosphere pCO<sub>2</sub> data which was measured at sit on May 29, 2024, was used for air-sea CO<sub>2</sub> flux calculation. The sea surface temperature (SST) and sea surface salinity (SSS) were determined by SBE37 (Sea-bird Scientific). The dissolved oxygen saturation (DO%) which refers to the ratio of seawater DO content to its solubility, was measured using the probe developed by the institute of Oceanographic Instrumentation. The wind speed was measured using an ultrasonic anemometer (windmaster pro, Gill Instruments) installed at a height of 10 m.

### 2.3 Determination of pCO<sub>2</sub>

The *in-situ* non-dispersive infrared (NDIR) seawater pCO<sub>2</sub> instruments (Fietzek et al., 2014; Sutton et al., 2014; Hunt et al.,

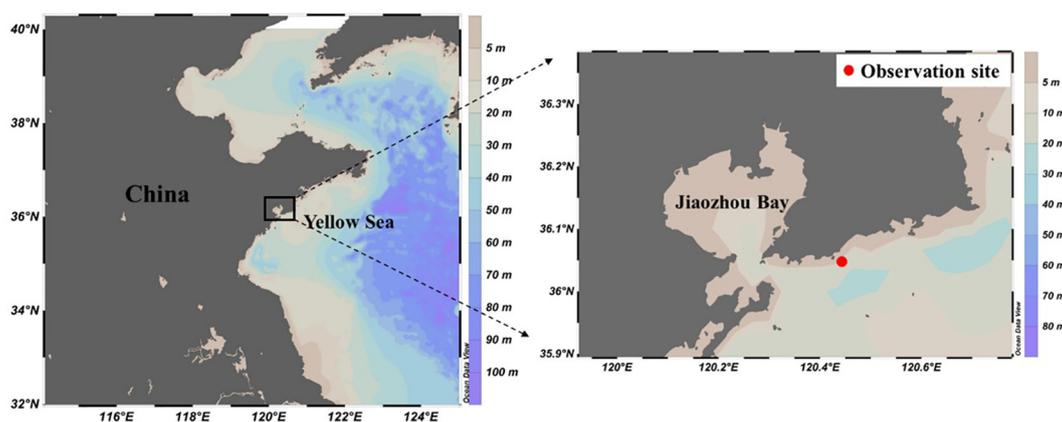
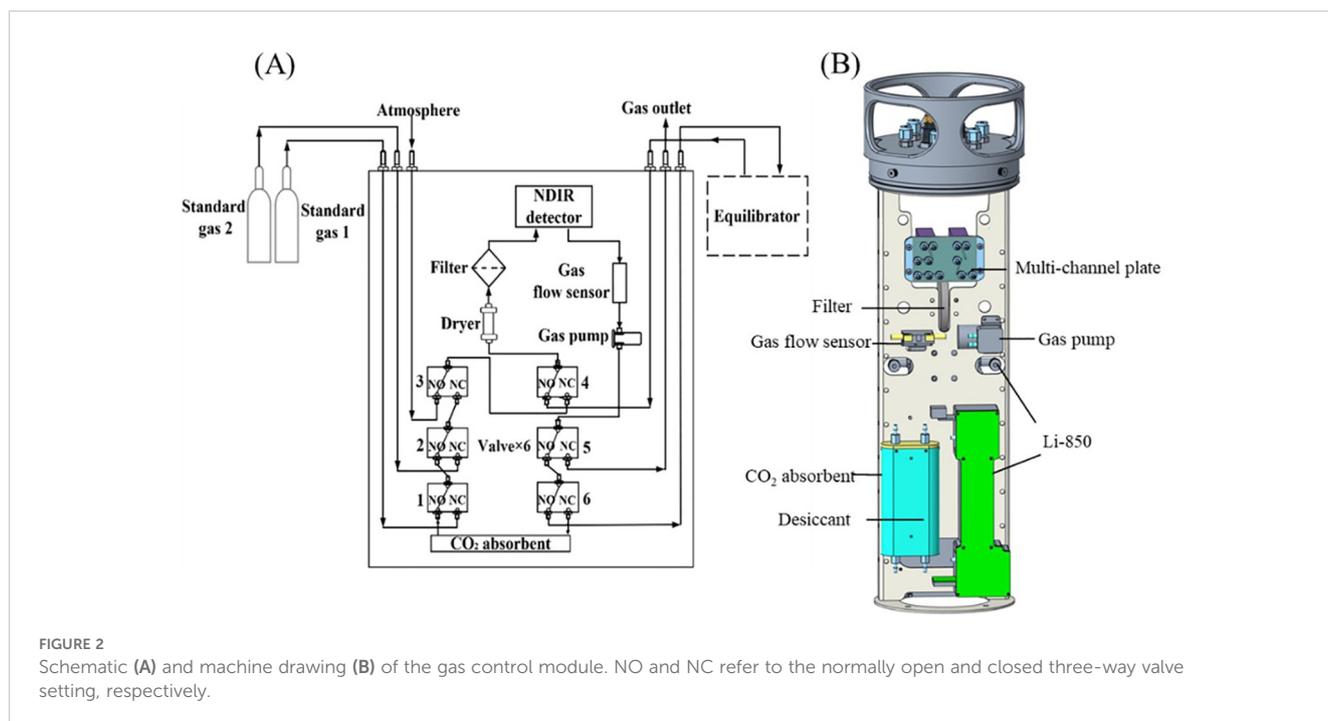


FIGURE 1  
Location of observation site near the Xiaomaidao Island.



2017; Ribas-Ribas et al., 2018) are often employed on the buoy to describe the temporal variations of  $p\text{CO}_2$  and  $\text{CO}_2$  fluxes at the air-sea interface (Atamanchuk et al., 2015; Xue et al., 2016; Liu Q. et al., 2019). They used the gas-permeable membrane (Fietzek et al., 2014) or continuous bubbling air-water equilibrator (Sutton et al., 2014) to equilibrate the headspace air with seawater. After equilibration, the  $\text{CO}_2$  composition of headspace air reflects that of seawater. The evaluation and comparison of commercial *in-situ*  $p\text{CO}_2$  instruments demonstrated that the system employing bubble equilibration technique (Sutton et al., 2014) had high accuracy and stability (Alliance for Coastal Technologies, 2010a, b, c). Though the commercial *in-situ* instrument using bubble equilibration ( $\text{MAPCO}_2$ ) is widely used, it is sometimes inflexible for installation, inconvenient self-maintenance and expensive. The water quality monitoring buoys have been well developed by integrating biochemical sensors, optical devices for absorption, fluorescence and scattering, and communication devices (Błażejowski et al., 2024, 2023; Agade et al., 2022; Ng et al., 2012) for field applications. Therefore, easily integrated seawater  $p\text{CO}_2$  instruments are needed for future collaborative observations.

To flexibly investigate the seawater  $p\text{CO}_2$  variations in Qingdao coastal waters, a customized and concise gas control module combined with standard gas (National Standard Material Research Center) and the bubble equilibrator of  $\text{MAPCO}_2$  (Friederich et al., 1995; Sutton et al., 2014) which connects gas control module with two gas pipelines were deployed on a 15m intelligent buoy in this article. The module operates in three modes: seawater measurement, atmosphere measurement and calibration modes (Figure 2A). During seawater  $p\text{CO}_2$  measurement, the gas driven by pump circularly goes out from the gas pipe (1.6 mm i.d., 3.2 mm o.d.) beneath seawater surface and continuously bubbles in the equilibrator which floated on the sea surface, then the gas returns to the gas control module through the other pipe (3.2 mm

i.d., 6.4 mm o.d.). The equilibrator was made of copper-nickel alloy to prevent biofouling. More details for bubble equilibrator can be found in the paper by Sutton et al. (2014). During monitoring, the control module timed measured standard gas by switching different modes. The 12V voltage for gas control module was provided by buoy's solar power, and data is transmitted over 3G/4G networks.

The gas control module is housed in a sealed cylindrical cabin, including NDIR detector (Licor850, LI-COR Biotechnology), gas flow sensor (AWM3300, Honeywell Automation & Control, Inc.), desiccant (silica gel),  $\text{CO}_2$  absorbent (soda lime), filter (1.0  $\mu\text{m}$ ), gas pump (KLVP-SB12, Kamoer Fluid Tech Shanghai Co., Ltd., China), electromagnetic three-way valves (LVM105R-6B, SMC), customized multi-channel plate, gas pipe and the control circuit (Figure 2). The NDIR detector measures mole fraction of  $\text{CO}_2$  ( $x\text{CO}_2$ ) and  $\text{H}_2\text{O}$  ( $x\text{H}_2\text{O}$ ) in gas path at about 51.5  $^\circ\text{C}$ , and has a thermal insulation cavity outside to ensure the stability and accuracy measurements. The desiccant is used to absorb vapor in the gas path. The soda lime is used to absorb  $\text{CO}_2$  during zero gas calibration. The gas flow sensor is used to monitor the condition of system during measurement. The three-way valves were connected to the gas pipe through channels (diameter 1.5 mm) inside the multi-channel plate (Figure 2B). The gas control module could be operated in different modes based on the positions of three-way valves, similar to other instruments. The gas control module has the characteristics of simple structure and good integration.

Given the lack of drying methods for long-term autonomous measurements, the determined  $x\text{CO}_2$  should be converted to dry  $x\text{CO}_2$ . Finally, the  $p\text{CO}_2$  of seawater at 100% humidity was calculated.

The dry  $x\text{CO}_2$  was calculated using the following equation:

$$x\text{CO}_2^{\text{dry}} = \frac{x\text{CO}_2}{1 - x\text{H}_2\text{O}} \quad (1)$$

where the  $x\text{CO}_2^{\text{dry}}$  ( $\mu\text{mol mol}^{-1}$ ) is  $x\text{CO}_2$  in dry air, and  $x\text{CO}_2$  ( $\mu\text{mol mol}^{-1}$ ) and  $x\text{H}_2\text{O}$  ( $\text{mol mol}^{-1}$ ) denote the measured concentrations.

The partial pressure of the surface seawater  $\text{CO}_2$  ( $p\text{CO}_2$ ,  $\mu\text{atm}$ ) is calculated as follows:

$$p\text{CO}_2 = x\text{CO}_2^{\text{dry}} \times (p - VP^{\text{H}_2\text{O}}) \quad (2)$$

$$VP^{\text{H}_2\text{O}} = \exp(24.4543 - 67.4509 \times \left(\frac{100}{t + 273.15}\right) - 4.8489\text{LN}\left(\frac{t + 273.15}{100}\right) - 0.000544 \times S) \quad (3)$$

where  $x\text{CO}_2^{\text{dry}}$  is the corrected  $x\text{CO}_2$ ,  $p$  denotes the pressure (atm) of atmosphere, and  $VP^{\text{H}_2\text{O}}$  refers to the water vapor pressure at 100% humidity obtained using the *in-situ* temperature ( $t$ , °C) and salinity ( $S$ ) (Weiss and Price, 1980).

The precision of the  $p\text{CO}_2$  measurement system was evaluated through repeated measurements of seawater samples, and the results were expressed as standard deviation (SD) of  $x\text{CO}_2$ . The seawater samples were adjusted to various  $p\text{CO}_2$  values using NaOH and HCl solutions. Table 1 shows the precision of the seawater  $p\text{CO}_2$  measurement system during repeated measurements of three seawater samples in the laboratory. With  $x\text{CO}_2$  values in the range of 390–800  $\mu\text{mol mol}^{-1}$ , the measurement system exhibited a precision better than 1  $\mu\text{mol mol}^{-1}$ , with the SD ranging from 0.67  $\mu\text{mol mol}^{-1}$  to 0.84  $\mu\text{mol mol}^{-1}$ . Good precision here provides a prerequisite for obtaining good accuracy.

The accuracy was evaluated by comparing with an underway seawater  $p\text{CO}_2$  instrument (GO8050, General Oceanics, INC.). The accuracy was expressed as the relative error of  $x\text{CO}_2$  (Table 2). Prior to comparison, the underway instrument was calibrated using standard gases. For comparison, equilibrator and water pump of the underway instrument were placed in a thermostatic bath containing the seawater samples. The accuracy was estimated in a  $x\text{CO}_2$  range of 200 – 1000  $\mu\text{mol mol}^{-1}$  through adjustment of seawater with HCl and NaOH solutions. The average of 10 continuous measurements obtained by the GO8050 analyzer after equilibrium was considered the true value. In the  $x\text{CO}_2$  range of 200 – 1000  $\mu\text{mol/mol}$ , the error was -5.1 – 2.3  $\mu\text{mol mol}^{-1}$ , and the relative error was within 1%.

## 2.4 Data processing

To eliminate the thermodynamic influence of temperature, we normalized  $p\text{CO}_2$  to the average temperature of the investigation

TABLE 1 Precision test in the laboratory.

$x\text{CO}_2$ ( $\mu\text{mol mol}^{-1}$ )	Standard Deviation ( $\mu\text{mol mol}^{-1}$ )	Measurements
390.0	0.79	10
633.8	0.67	6
799.5	0.84	8

TABLE 2 Accuracy test in the laboratory.

Measured $x\text{CO}_2$ of developed instrument ( $\mu\text{mol mol}^{-1}$ )	Measured $x\text{CO}_2$ of GO ( $\mu\text{mol mol}^{-1}$ )	Error ( $\mu\text{mol mol}^{-1}$ )	Relative error
226.7	229.0	-2.3	1.0%
467.0	467.6	-0.6	0.1%
605.1	602.8	2.3	0.4%
1065.7	1070.8	-5.1	0.5%

( $np\text{CO}_2$ ) by Takahashi et al. (1993):

$$np\text{CO}_2 = p\text{CO}_2 \times \exp(0.0423 \times (t_m - \text{SST})) \quad (4)$$

where  $np\text{CO}_2$  is the normalized  $p\text{CO}_2$ , and  $t_m$  denotes the average temperature during the time series monitoring. Meanwhile, simulated  $p\text{CO}_2$  changes solely caused by temperature could be calculated when SST is the initial temperature and  $t_m$  is the observed temperature.

Air–sea  $\text{CO}_2$  flux ( $F\text{CO}_2$ ,  $\text{mmol m}^{-2}\text{d}^{-1}$ ) was estimated according to the following equation:

$$F\text{CO}_2 = k \times K_0 \times (p\text{CO}_2^{\text{water}} - p\text{CO}_2^{\text{air}}) \quad (5)$$

where  $k$  indicates the gas transfer velocity,  $K_0$  represents the solubility coefficient of  $\text{CO}_2$  (Weiss, 1974), and  $p\text{CO}_2^{\text{water}}$  and  $p\text{CO}_2^{\text{air}}$  are the  $p\text{CO}_2$  in the surface water and atmosphere, respectively.  $k$  was estimated using the formula proposed by Sweeney et al. (2007).

$$k = 0.27 \times U_{10}^2 \times (Sc/660)^{-0.5} \quad (6)$$

where  $U_{10}$  ( $\text{m s}^{-1}$ ) refers to the wind speed at 10 m height.  $Sc$  denotes the Schmidt number of  $\text{CO}_2$  in seawater (Wanninkhof, 1992). In this paper, a positive value of  $F\text{CO}_2$  denoted  $\text{CO}_2$  release from water to the atmosphere.

## 3 Results and discussion

### 3.1 Variations of monitoring data at coastal site

During the buoy-based time series observation period of May 29 – July 25, 2024, *U. prolifera* bloom was observed at Qingdao coastal region based on satellite remote images. Its coverage increased in mid-July and then decreased in late July (Figure 3). The SST increased from approximately 16°C to 22°C (Figure 4A) due to the increase in solar radiation. By contrast, SSS showed a decreased trend and ranged from ~31.0 PSU to ~29.2 PSU (Figure 4A). The sudden decrease in SSS during the observation period was possibly due to rainfall. On the days when the salinity dropped to about 29.2 PSU (July 8, July 16 and July 22), the daily rainfall at the observatory near Xiaomaidao Island was 58 mm, 39 mm and 48 mm, respectively (<http://swglj.qingdao.gov.cn>). During the observation period, the tidal height varied between 56 cm and 437 cm (Figure 4B). DO% also showed a general downward trend,

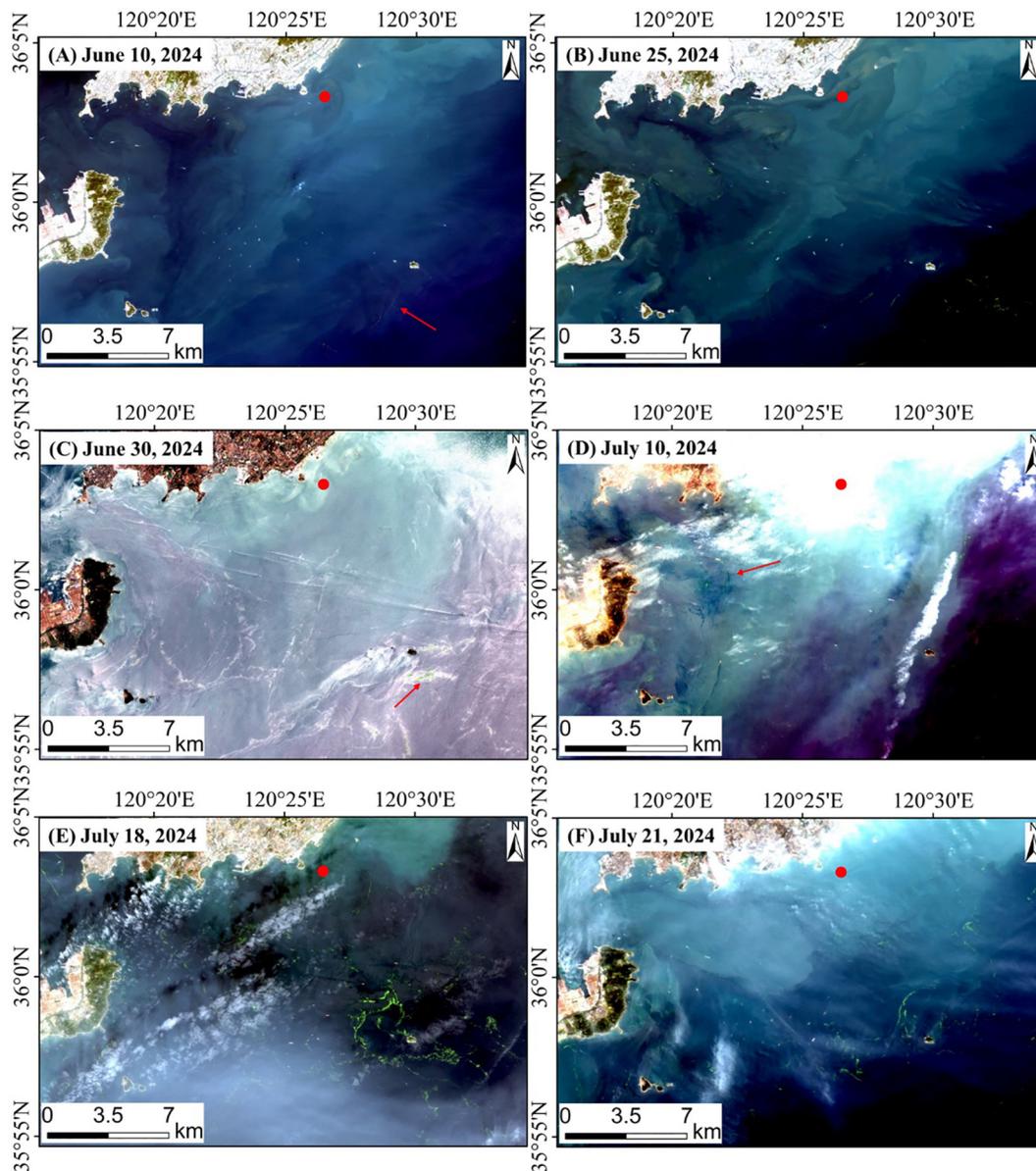


FIGURE 3

Satellite images of *U. prolifera* distribution. Panels (A-F) showed the distributions of *U. prolifera* on June 10, June 25, June 30, July 10, July 18 and July 21, 2024, respectively. These images were obtained using the monitoring data of GF-6 WFV and HJ-2A/2B CCD satellites (<https://www.cresda.com/zgzywxyyzx/index.html>) with 16m spatial resolution. The *U. prolifera* on June 10, June 30 and July 10 were indicated by red arrows.

varying within a range of 112% to 89% during the investigation period, and temporarily high values were observed in July (Figure 4D). Sea surface  $p\text{CO}_2$  ranged from 519  $\mu\text{atm}$  to 717  $\mu\text{atm}$ , with an average of  $615 \pm 45 \mu\text{atm}$ , and the daily average sea surface  $p\text{CO}_2$  increased by  $\sim 110 \mu\text{atm}$  at the end of observation compared with that in the beginning (Figure 4C). While the  $np\text{CO}_2$  of seawater showed a slightly decreasing trend, and a  $\sim 30 \mu\text{atm}$  lower daily average  $np\text{CO}_2$  was observed at the end of observation compared with that in the beginning (Figure 4D). In addition, both surface  $p\text{CO}_2$  and  $np\text{CO}_2$  showed a rapid decline and rise from July 12 to 21, and then the values remained stable.

The atmospheric  $p\text{CO}_2$  was 417  $\mu\text{atm}$ , which is lower than that of seawater. Thus, this observation site served as a  $\text{CO}_2$  source for the

atmosphere throughout the observation period in 2024. The wind speed ranged from  $0.1 \text{ m s}^{-1}$  to  $18.5 \text{ m s}^{-1}$ , and the average was  $3.0 \text{ m s}^{-1}$  (Figure 4E). The large variations in wind speed and seawater  $p\text{CO}_2$  induced considerable changes in  $\text{CO}_2$  flux. The influence of wind speed is particularly important. According to Equation 6, the influence of wind speed on  $\text{CO}_2$  flux is quadratic. The  $\text{CO}_2$  flux ranged from less than  $1 \text{ mmol m}^{-2} \text{ d}^{-1}$  to over  $100 \text{ mmol m}^{-2} \text{ d}^{-1}$ , roughly consistent with wind speed, with an average value of  $5.9 \text{ mmol m}^{-2} \text{ d}^{-1}$  (Figure 4F). Furthermore, the variations in  $\text{CO}_2$  flux during the observation period demonstrated the importance of high-resolution monitoring in carbon flux estimation. Based on collected data, the seawater at investigation site near Xiaomaidao Island released  $334 \text{ mmol CO}_2 \text{ m}^{-2}$  to the atmosphere during May 29 – July 25, 2024.

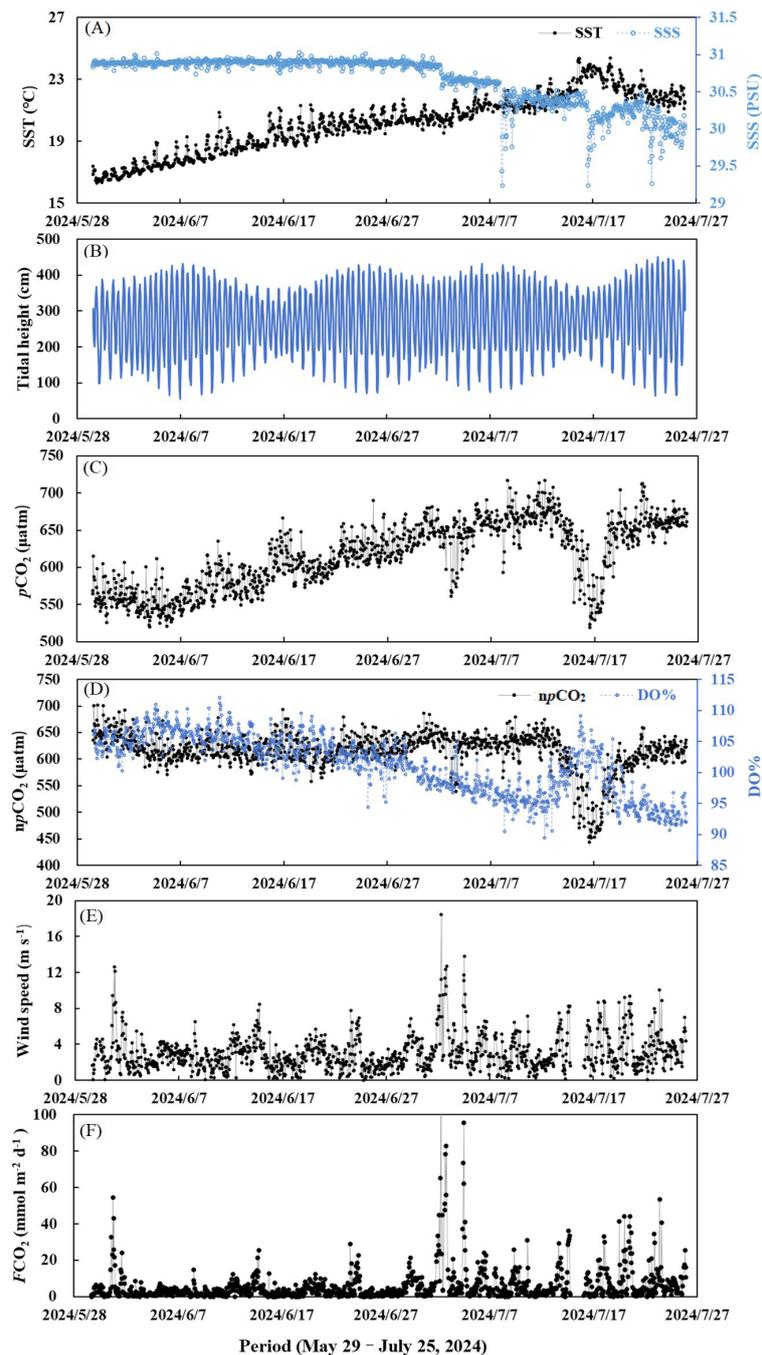


FIGURE 4 Variations in SST and SSS (A), tidal height (B), surface  $p\text{CO}_2$  (C),  $\text{npCO}_2$  and DO% (D), wind speed (E), and  $\text{FCO}_2$  (F) from May 29 to July 19, 2024.

The data collected in the western part of the southern Yellow Sea which lies approximately between  $33^\circ\text{N}$  and  $37^\circ\text{N}$  and west of the 50m isobath (Wang and Zhai, 2021) and Jiaozhou Bay (Li et al., 2023) during summer were compared with the investigation results of this study (Table 3). It was shown that the western part of the southern Yellow Sea had relatively lower SST, seawater  $p\text{CO}_2$ ,  $\text{CO}_2$  flux, and higher SSS, while lower SSS accompanied with higher SST, seawater  $p\text{CO}_2$  and  $\text{CO}_2$  flux were observed in Jiaozhou Bay compared with this study. During summer the Jiaozhou Bay

became a strong source of atmospheric  $\text{CO}_2$ . In addition to the higher SST, terrestrial inputs were also the reason for the high sea surface  $p\text{CO}_2$  and  $\text{CO}_2$  flux in Jiaozhou Bay. It was reported that except for the Dagu River, most rivers in Jiaozhou Bay had no pristine runoff and almost became channels of wastewater which was abundant in  $p\text{CO}_2$ , resulting in the high seawater  $p\text{CO}_2$  values observed in Jiaozhou Bay (Gao et al., 2008; Li et al., 2023). Though there was no freshwater input from rivers near Xiaomaidao Island, the Qingdao coast area was significantly disturbed by human

TABLE 3 Means and ranges (in brackets) of SST, SSS, seawater  $p\text{CO}_2$ , and  $\text{FCO}_2$  at the time series site during 2024 and comparisons of these data with those obtained on the western part of southern Yellow Sea and the Jiaozhou Bay from literature.

Time	SST (°C)	SSS	$p\text{CO}_2$ ( $\mu\text{atm}$ )	$\text{FCO}_2$ ( $\text{mmol m}^{-2} \text{d}^{-1}$ )
<b>Coastal time series site near Xiaomaidao Island (This study)</b>				
2024 – 06 (1 – 30 Jun, 2019)	19.1 ± 1.2 (16.5 – 21.7)	30.9 ± 0.04 (30.7 – 31.0)	593 ± 35 (520 – 690)	3.4 ± 3.9
2024 – 07 (1 – 25 Jul, 2019)	21.8 ± 0.9 (19.5 – 24.4)	30.4 ± 0.3 (29.2 – 31.0)	648 ± 35 (519 – 717)	9.1 ± 14.4
<b>Western part of southern Yellow Sea (Wang and Zhai, 2021)</b>				
2011 – 06	17.8 ± 1.6 (15.0 – 20.4)	31.6 ± 0.3 (31.0 – 32.0)	430 ± 69 (323 – 538)	2.6 ± 4.3
2016 – 07	21.7 ± 1.7 (18.4 – 24.0)	30.9 ± 1.1 (28.4 – 31.9)	440 ± 130 (221 – 574)	3.6 ± 9.2
<b>Jiaozhou Bay (Li et al., 2023)</b>				
13 Jun. 2014	21.39 ± 1.54	30.52 ± 0.34	675 ± 138	17.4 ± 6.9
01 Jul. 2014	23.14 ± 1.22	30.63 ± 0.15	723 ± 118	17.6 ± 5.1

activities (Yang et al., 2018; Liu X. et al., 2019), making its sea surface  $p\text{CO}_2$  higher than that of the western part of the southern Yellow Sea.

### 3.2 Factors affecting sea surface $p\text{CO}_2$ during time serious observation

The temporal variation of seawater  $p\text{CO}_2$  in coastal regions resulted from the interaction of multiple processes, at least including temperature effect, air-sea  $\text{CO}_2$  exchange, mixing processes and phytoplankton activity (Borges et al., 2006; Xue et al., 2016). Consistent with other studies of seawater  $p\text{CO}_2$  (Xue et al., 2016; Hu et al., 2024; Li et al., 2023), we used Pearson correlation analysis to explore the factors affecting sea surface  $p\text{CO}_2$  variations, where the square of the correlation coefficient  $r^2$  represents relevance and the p-value of less than 0.01 in the analysis results represented 99% confidence level (Figure 5). Consistent with the  $\sim 6^\circ\text{C}$  increase in SST, sea surface  $p\text{CO}_2$  except for the low values from July 12 – 21 showed an increasing trend during the time series monitoring, and it was strongly positive correlated with SST ( $r^2 = 0.76$ ,  $p < 0.01$ ) (Figure 5A), indicating the important influence of increasing temperature on the variations in  $p\text{CO}_2$  during this period. In addition, the temperature driven  $p\text{CO}_2$  values simulated according to the model proposed by Takahashi et al. (1993) were in good agreement with the observed values except for the low values during July 12 – 21 (Figure 5A), also suggesting the major control of SST on seawater  $p\text{CO}_2$  during this period. However, the daily average temperature simulated  $p\text{CO}_2$  value on July 25 was 34  $\mu\text{atm}$  higher than that of the observed value, indicating influence of other factors.

By normalizing the  $p\text{CO}_2$  values to the average SST,  $np\text{CO}_2$  values were obtained to evaluate influence of other factors on sea surface  $p\text{CO}_2$ . SSS showed a decreased trend in this study, while  $np\text{CO}_2$  did not evidently increase, and no correlation between  $np\text{CO}_2$

and tide (Figure 5B), suggesting that the influence of terrestrial inputs with abundant  $p\text{CO}_2$  was offset by other processes, such as biological activity and air-sea  $\text{CO}_2$  exchange. During the whole observation period, the decreased trend of DO% and a  $\sim 30 \mu\text{atm}$  decrease in  $np\text{CO}_2$  implied that biological activity was not an important factor controlling the seawater  $p\text{CO}_2$  change. Considering the slight decrease in the level of  $np\text{CO}_2$  during the overall period, the release of  $\text{CO}_2$  from seawater to atmosphere in the air-sea exchange process may also influence the  $p\text{CO}_2$  variations.

### 3.3 *U. Prolifera* blooms affecting sea surface $p\text{CO}_2$

Since July 12, both the surface  $p\text{CO}_2$  and  $np\text{CO}_2$  showed an obvious decrease and the daily average of seawater  $p\text{CO}_2$  and  $np\text{CO}_2$  reached the lowest on July 16 – 17, with values of 563  $\mu\text{atm}$  and  $\sim 488 \mu\text{atm}$ , respectively, which were 116  $\mu\text{atm}$  of  $p\text{CO}_2$  and 147  $\mu\text{atm}$  of  $np\text{CO}_2$  lower than those in July 12, and then the daily average  $p\text{CO}_2$  and  $np\text{CO}_2$  value increased to 669  $\mu\text{atm}$  and 615  $\mu\text{atm}$  on July 21, respectively. On the contrary, the daily average DO% reached  $\sim 102\%$  on July 16 – 17 and then decreased. The  $np\text{CO}_2$  exhibited a negative correlation with DO% during July 12 – 21 ( $r^2 = 0.51$ ,  $p < 0.01$ ) (Figure 5C), indicating the important influence of biological activity on the variation in  $p\text{CO}_2$  during this special period.

Based on satellite remote images, *U. prolifera* was observed to increase obviously on July 18 (Figure 3E), which was roughly consistent with the date of the seawater  $p\text{CO}_2$  reduction, indicating the influence of *U. prolifera* bloom on carbonate system. The rapidly decreasing  $p\text{CO}_2$  and increasing DO% in seawater was caused by the biological production of *U. prolifera*. It was reported that at the early bloom stage, photosynthesis of macroalga can quickly absorb dissolved inorganic carbon in seawater, leading to a decrease of  $p\text{CO}_2$  in seawater (Li et al.,

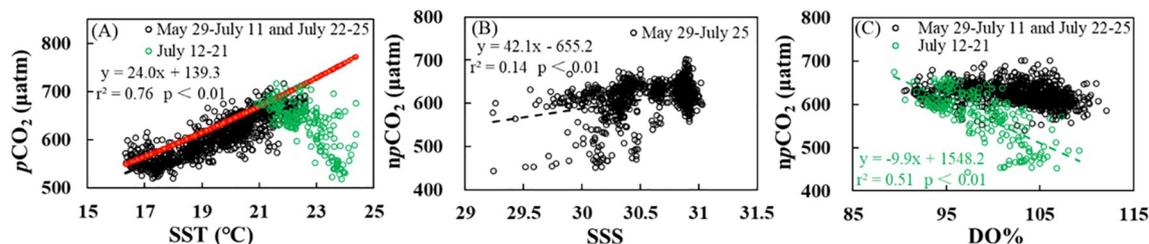


FIGURE 5

Sea surface  $p\text{CO}_2$  versus SST (A),  $np\text{CO}_2$  versus SSS (B), and  $np\text{CO}_2$  versus DO% (C) from May 29 to July 25, 2024. Positive correlation between  $p\text{CO}_2$  and SST on May 29 – July 11 and July 22 – 25, and negative correlation between  $np\text{CO}_2$  and DO% on July 12 – 21 were observed. In panel (A), red lines indicate simulated  $p\text{CO}_2$  driven by temperature variations based on Equation 4.

2014; Zhang et al., 2019). The cruise investigation at offshore area of Qingdao (Hu et al., 2024) also showed the decreased dissolved inorganic carbon and increased pH in seawater during bloom phase. Subsequently, as shown in satellite image on July 21 (Figure 3F), the amount of *U. prolifera* decreased, which may be caused by manual cleaning and sink of the decaying macroalga. Thus, the rising  $p\text{CO}_2$  and decreased DO% in seawater after July 17 was related to the decomposition and respiration of decaying algae by microorganisms. Previous studies on the *U. prolifera* affecting the carbonate system in the Qingdao coastal area usually focused on the late bloom or after bloom period. These reports also found the release of  $\text{CO}_2$  and reduced DO during the late bloom period (Deng et al., 2018; Xiong et al., 2023). However, previous studies were based on limited sample collection, and the effect of *U. prolifera* on carbonate system mostly examined vis incubation experiment, lacking *in-situ* continuous observations (Deng et al., 2018; Xiong et al., 2023). The time series observation in this work captured the significant effect of the continuous changing *U. prolifera* on seawater  $p\text{CO}_2$ , especially the influence on obvious decrease of seawater  $p\text{CO}_2$  at early bloom stage, which confirms that the high-resolution measurements are essential for the study of carbonate system during algal blooms and provides a reference for the future study of the *U. prolifera* blooms influence on carbonate system.

## 4 Conclusion

The buoy-based time series monitoring seawater  $p\text{CO}_2$  near Xiaomaidao Island during summer showed the necessity for high-resolution measurement of  $p\text{CO}_2$  in coastal seawater. During the observation period, the surface seawater  $p\text{CO}_2$  showed a generally increased trend, with an average value of  $615 \pm 45$  μatm, and it was mainly affected by the increased temperature except for the decreased  $p\text{CO}_2$  during July 12–21. We captured the rapid decline and rise of seawater  $p\text{CO}_2$  and  $np\text{CO}_2$  during this special period which was caused by the *U. prolifera* bloom, and the daily mean seawater  $p\text{CO}_2$  and  $np\text{CO}_2$  decreased by 116 μatm and 147 μatm, respectively, compared with the values before decrease. Jiaozhou Bay was a strong source of atmospheric  $\text{CO}_2$  during summer, and the observation site was also acted as a  $\text{CO}_2$  source. The  $\text{CO}_2$  flux of observation site was greatly affected by wind speed and seawater  $p\text{CO}_2$ , releasing 334 mmol  $\text{CO}_2$   $\text{m}^{-2}$  throughout the investigation period.

## Data availability statement

The raw data supporting the conclusions of this article will be made available by the authors, without undue reservation.

## Author contributions

LC: Conceptualization, Data curation, Funding acquisition, Writing – original draft. SL: Formal analysis, Writing – review & editing. SZ: Investigation, Methodology, Writing – review & editing. NWu: Investigation, Writing – review & editing. KZ: Data curation, Writing – review & editing. WL: Investigation, Writing – review & editing. RM: Investigation, Writing – review & editing. DC: Methodology, Writing – review & editing. NWA: Supervision, Writing – review & editing. YL: Supervision, Methodology, Writing – review & editing.

## Funding

The author(s) declare financial support was received for the research, authorship, and/or publication of this article. This work was supported by the Natural Science Foundation of China (42106185).

## Conflict of interest

The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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## References

- Agade, P., Bean, E. Z., Dean, R. N., Blerch, D., Vasconcelos, J., Knappenberger, T., et al. (2022). GatorByte: A Water-Quality Mapping Buoy for Locating Watershed Pollution Sources. *Proceedings of IEEE Sensors*, 2022-October. doi: 10.1109/SENSOR52175.2022.9967172
- Alliance for Coastal Technologies (ACT) (2010a). Performance demonstration statement for Contros HydroC<sup>TM</sup>/CO<sub>2</sub>, ACT DS10-01 UMCES/CBL 10-091.
- Alliance for Coastal Technologies (ACT) (2010b). Performance demonstration statement for Pro-Oceanus Systems Inc. PSI CO<sub>2</sub>-Pro<sup>TM</sup>, ACT DS10-03 UMCES/CBL 10-093.
- Alliance for Coastal Technologies (ACT) (2010c). Performance demonstration statement for PMEL MAPCO<sub>2</sub>/Battelle seaology pCO<sub>2</sub> monitoring system, ACT DS10-02 UMCES/CBL 10-092.
- Atamanchuk, D., Tengberg, A., Aleynik, D., Fietzek, P., Shitashima, K., Lichtschlag, A., et al. (2015). Detection of CO<sub>2</sub> leakage from a simulated sub-seabed storage site using three different types of pCO<sub>2</sub> sensors. *Int. J. Greenh. Gas Con.* 38, 121–134. doi: 10.1016/j.ijggc.2014.10.021
- Błażejowski, A., Pecolt, S., Grunt, M., Wiczorek, G., and Królowski, T. (2024). Multi-domain, Autonomous measurement buoy as an element of the water quality monitoring and early warning system in rivers and water reservoirs. *Rocznik Ochrona Środowiska* 26, 18–29. doi: 10.54740/ros.2024.002
- Błażejowski, A., Pecolt, S., Królowski, T., Grunt, M., and Bielicki, F. (2023). Project of innovative open multi-domain early warning platform enviwise for adverse events in water bodies and streams. *Proc. Comput. Sci.* 225, 27433–2753. doi: 10.1016/j.procs.2023.10.266
- Borges, A. V., Schiettecatte, L. S., Abril, G., Delille, B., and Gazeau, F. (2006). Carbon dioxide in European coastal waters. *Estuar. Coast. Shelf Sci.* 70, 375–387. doi: 10.1016/j.ecss.2006.05.046
- Cai, W. J. (2011). Estuarine and coastal ocean carbon paradox: CO<sub>2</sub> sinks or sites of terrestrial carbon incineration? *Annu. Rev. Mar. Sci.* 3, 123–145. doi: 10.1146/annurev-marine-120709-142723
- Dai, M., Su, J., Zhao, Y., Hofmann, E. E., Cao, Z., Cai, W.-J., et al. (2022). Carbon fluxes in the coastal ocean: synthesis, boundary processes and future trends. *Annu. Rev. Earth Pl. SC.* 50, 593–626. doi: 10.1146/annurev-earth-032320-090746
- Deng, X., Liu, T., Liu, C. Y., Liang, S. K., Hu, Y. B., Jin, Y. M., et al. (2018). Effects of *Ulva prolifera* blooms on the carbonate system in the coastal waters of Qingdao. *Mar. Ecol. Prog. Ser.* 605, 73–86. doi: 10.3354/meps12739
- Doney, S. C., Fabry, V. J., Feely, R. A., and Kleypas, J. A. (2009). Ocean acidification: the other CO<sub>2</sub> problem. *Annu. Rev. Mar. Sci.* 1, 169–192. doi: 10.1146/annurev.marine.010908.163834
- Fietzek, P., Fiedler, B., Steinhoff, T., and Körtzinger, A. (2014). *In situ* quality assessment of a novel underwater pCO<sub>2</sub> sensor based on membrane equilibration and NDIR spectrometry. *J. Atmos. Ocean. Tech.* 31, 181–196. doi: 10.1175/JTECH-D-13-00083.1
- Friederich, G. E., Brewer, P. G., Herlien, R., and Chavez, F. P. (1995). Measurement of sea surface partial pressure of CO<sub>2</sub> from a moored buoy. *Deep-Sea Res. Pt. I* 42, 1175–1186. doi: 10.1016/0967-0637(95)00044-7
- Gao, Z., Yang, D., Qin, J., Xiang, L., and Zhang, K. (2008). The land-sourced pollution in the Jiaozhou Bay. *Chin. J. Oceanol. Limn.* 26, 229–232. doi: 10.1007/s00343-008-0229-7
- Hu, Z. X., Li, T., Ge, T. T., Hu, J. W., Wang, P., Liu, C. Y., et al. (2024). Inter-annual and spatial variations of air-sea CO<sub>2</sub> fluxes and acidification mechanism in the coastal waters of Qingdao, China during 2011–2019. *Mar. pollut. Bull.* 209, 117195. doi: 10.1016/j.marpolbul.2024.117195
- Hu, Y. B., Liu, C. Y., Yang, G. P., and Zhang, H. H. (2015). The response of the carbonate system to a green algal bloom during the post-bloom period in the southern Yellow Sea. *Cont. Shelf Res.* 94, 1–7. doi: 10.1016/j.csr.2014.12.006
- Hunt, C. W., Snyder, L., Salisbury, J. E., Vandemark, D., and McDowell, W. H. (2017). SIPCO2: A simple, inexpensive surface water pCO<sub>2</sub> sensor. *Limnol. Oceanogr.: Methods* 15, 291–301. doi: 10.1002/lom3.10157
- Li, B. H., Liu, C. Y., Deng, X., Wang, K. K., Han, L., Huang, Y. H., et al. (2021). Responses of the marine carbonate system to a green tide: a case study of an *Ulva prolifera* bloom in Qingdao coastal waters. *Harmful Algae* 110, 102133. doi: 10.1016/j.hal.2021.102133
- Li, Y. X., Xue, L., Yang, X. F., Wei, Q. S., Xin, M., Xue, M., et al. (2023). Wastewater inputs reduce the CO<sub>2</sub> uptake by coastal oceans. *Sci. Total Environ.* 901, 165700. doi: 10.1016/j.scitotenv.2023.165700
- Li, S. X., Yu, K. F., Huo, Y. Z., Zhang, J. H., Wu, H. L., Wu, Q., et al. (2014). The photosynthetic physiological characteristics and evaluation of carbon fixation capacity of *Ulva prolifera* in Binhai sea area, Jiangsu Province. *Mar. Fish* 36, 306–313. doi: 10.13233/j.cnki.mar.fish.2014.04.005
- Lin, G., and Lin, X. (2022). Bait input altered microbial community structure and increased greenhouse gases production in coastal wetland sedimen. *Water Res.* 218, 118520. doi: 10.1016/j.watres.2022.118520
- Liu, Q., Dong, X., Chen, J. S., Guo, X. H., Zhang, Z. R., Xu, Y., et al. (2019). Diurnal to interannual variability of sea surface pCO<sub>2</sub> and its controls in a turbid tidal-driven nearshore system in the vicinity of the East China Sea based on buoy observations. *Mar. Chem.* 216, 103690. doi: 10.1016/j.marchem.2019.103690
- Liu, X. Y., Yang, X. F., Li, Y. X., Zang, H., and Zhang, L. J. (2019). Variations in dissolved inorganic carbon species in effluents from large-scale municipal wastewater treatment plants (Qingdao, China) and their potential impacts on coastal acidification. *Environ. Sci. Pollut. Res.* 26, 15019–15027. doi: 10.1007/s11356-019-04871-2
- Mostofa, K. M. G., Liu, C. Q., Zhai, W., Minella, M., Vione, D., Gao, K., et al. (2016). Reviews and syntheses: ocean acidification and its potential impacts on marine ecosystems. *Biogeosciences* 13, 1767–1786. doi: 10.1196/annals.1439.013
- Murata, A., Inoue, J., Nishino, S., and Yasunaka, S. (2022). Early Wintertime CO<sub>2</sub> uptake in the western Arctic Ocean. *J. Geophys. Res.-Oceans.* 127, e2021JC018037. doi: 10.1029/2021JC018037
- Ng, C. L., Senft-Grupp, S., and Hemond, H. F. (2012). A multi-platform optical sensor for *in situ* sensing of water chemistry. *Limnol. Oceanogr: Methods* 10, 978–990. doi: 10.4319/lom.2012.10.978
- Regnier, P., Resplandy, L., Najjar, R. G., and Ciais, P. (2022). The land-to-ocean loops of the global carbon cycle. *Nature* 603, 401–410. doi: 10.1038/s41586-021-04339-9
- Ribas-Ribas, M., Kilcher, L. F., and Wurl, O. (2018). Sniffle: A step forward to measure *in situ* CO<sub>2</sub> fluxes with the floating chamber technique. *Elem. Sci. Anth.* 6. doi: 10.1525/elementa.275
- Sabine, C. L., Feely, R. A., Gruber, N., Key, R. M., Lee, K., and Bullister, J. L. (2004). The oceanic sink for anthropogenic CO<sub>2</sub>. *Science* 305, 367–371. doi: 10.1126/science.1097403
- Shao, K. S., Gong, N., Shen, L. Y., Han, X., Wang, Z. X., Zhou, K., et al. (2024). Why did the world's largest green tides occur exclusively in the southern Yellow Sea? *Mar. Environ. Res.* 200, 106671. doi: 10.1016/j.marenvres.2024.106671
- Sutton, A. J., Sabine, C. L., Maenner-Jones, S., Lawrence-Slavas, N., Meinig, C., Feely, R. A., et al. (2014). A high-frequency atmospheric and seawater pCO<sub>2</sub> data set from 14 open-ocean sites using a moored autonomous system. *Earth. Syst. Sci. Data.* 6, 353–366. doi: 10.5194/essd-6-353-2014
- Sweeney, C., Gloor, E., Jacobson, A. R., Key, R. M., Mckinley, G., Sarmiento, J. L., et al. (2007). Constraining global air-sea gas exchange for CO<sub>2</sub> with recent bomb <sup>14</sup>C measurements. *Global Biogeochem. Cy* 21, GB2015. doi: 10.1029/2006GB002784
- Takahashi, T., Olafsson, J., Goddard, J. G., Chipman, D. W., and Sutherland, S. C. (1993). Seasonal variation of CO<sub>2</sub> and nutrients in the high-latitude surface oceans: a comparative study. *Global Biogeochem. Cy* 7, 843–878. doi: 10.1029/93GB02263
- Wang, S. Y., and Zhai, W. D. (2021). Regional differences in seasonal variation of air-sea CO<sub>2</sub> exchange in the Yellow Sea. *Cont. Shelf Res.* 218, 104393. doi: 10.1016/j.csr.2021.104393
- Wanninkhof, R. (1992). Relationship between wind speed and gas exchange over the Ocean. *J. Geophys. Res.* 97, 7373–7382. doi: 10.1029/92JC00188
- Weiss, R. F. (1974). Carbon dioxide in water and seawater: the solubility of a non-ideal gas. *Mar. Chem.* 2, 203–215. doi: 10.1016/0304-4203(74)90015-2
- Weiss, R. F., and Price, B. A. (1980). Nitrous oxide solubility in water and seawater. *Mar. Chem.* 8, 347–359. doi: 10.1016/0304-4203(80)90024-9
- Wu, Z. L., Wang, H. J., Liao, E. H., Hu, C. M., Edwing, K., Yan, X.-H., et al. (2024). Air-sea CO<sub>2</sub> flux in the Gulf of Mexico from observations and multiple machine-learning data products. *Prog. Oceanogr.* 223, 103244. doi: 10.1016/j.pocean.2024.103244
- Xiong, T. Q., Li, H. M., Yue, Y. F., Hu, Y. B., Zhai, W. D., Xue, L., et al. (2023). Legacy effects of late macroalgal blooms on dissolved inorganic carbon pool through alkalinity enhancement in coastal ocean. *Environ. Sci. Technol.* 57, 2186–2196. doi: 10.1021/acs.est.2c09261
- Xue, L., Cai, W.-J., Hu, X., Sabine, C., Jones, S., Sutton, A. J., et al. (2016). Sea surface carbon dioxide at the Georgia time series site, (2006–2007): Air-sea flux and controlling processes. *Prog. Oceanogr.* 140, 14–26. doi: 10.1016/j.pocean.2015.09.008
- Yang, X., Xue, L., Li, Y., Han, P., Liu, X., Zhang, L., et al. (2018). Treated wastewater changes the export of dissolved inorganic carbon and its isotopic composition and leads to acidification in coastal oceans. *Environ. Sci. Technol.* 52, 5590–5599. doi: 10.1021/acs.est.8b00273
- Yuan, C., Xiao, J., Zhang, X. L., Zhou, J., and Wang, Z. L. (2022). A new assessment of the algal biomass of green tide in the Yellow Sea. *Mar. pollut. Bull.* 174, 113253. doi: 10.1016/j.marpolbul.2021.113253
- Zhang, Y., He, P. M., Li, H. M., Li, G., Liu, J. H., Jiao, F. L., et al. (2019). *Ulva prolifera* green-tide outbreaks and their environmental impact in the Yellow Sea, China. *Natl. Sci. Rev.* 6, 825–838. doi: 10.1093/nsr/nwz026