

The spatiotemporal variation and control mechanism of surface pCO₂ in winter in Jiaozhou Bay, China

Article

Accepted Version

Creative Commons: Attribution-Noncommercial-No Derivative Works 4.0

Li, Y., Yang, H. ORCID: <https://orcid.org/0000-0001-9940-8273>, Zhang, L., Yang, X., Zang, H., Fan, W. and Wang, G. (2020) The spatiotemporal variation and control mechanism of surface pCO₂ in winter in Jiaozhou Bay, China. *Continental Shelf Research*, 206. 104208. ISSN 0278-4343 doi: <https://doi.org/10.1016/j.csr.2020.104208> Available at <https://centaur.reading.ac.uk/95935/>

It is advisable to refer to the publisher's version if you intend to cite from the work. See [Guidance on citing](#).

Published version at: <https://www.sciencedirect.com/science/article/pii/S0278434320301631>

To link to this article DOI: <http://dx.doi.org/10.1016/j.csr.2020.104208>

Publisher: Elsevier

All outputs in CentAUR are protected by Intellectual Property Rights law, including copyright law. Copyright and IPR is retained by the creators or other copyright holders. Terms and conditions for use of this material are defined in the [End User Agreement](#).

www.reading.ac.uk/centaur

CentAUR

Central Archive at the University of Reading

Reading's research outputs online

1 **The spatiotemporal variation and control mechanism of surface $p\text{CO}_2$ in winter in Jiaozhou**
2 **Bay, China**

3 Yunxiao Li^a, Hong Yang^b, Longjun Zhang^{c*}, Xufeng Yang^d, Han Zang^e, Wenhua Fan^a, Gailing
4 Wang^a

5 ^a Environment Science Laboratory, College of Resource and Environment, Shanxi Agricultural
6 University, Taigu 030801, China

7 ^b Department of Geography and Environmental Science, University of Reading, Whiteknights,
8 Reading RG6 6AB, UK

9 ^c Key Laboratory of Marine Environmental Science and Ecology, Ministry of Education, College of
10 Environmental Science and Engineering, Ocean University of China, Qingdao 266100, China

11 ^d Second Institute of Oceanography, Ministry of Natural Resources, Hangzhou 310012, China

12 ^e College of Environmental Science and Engineering, Shanghai Jiao Tong University, Shanghai
13 200240, China

14 * Corresponding author at: College of Environmental Science and Engineering, Ocean University of
15 China, Qingdao 266100, China.

16 E-mail address: longjunz@ouc.edu.cn (L Zhang).

17 **Abstract**

18 In many mid-latitude coastal waters during winter months, in addition to temperature, the large
19 change in biogeochemical processes often influence and complicate the surface partial pressure of
20 CO₂ (*p*CO₂). Based on the hydrological and carbonate parameters in seven cruises, this study
21 analysed the evolution process and explored the control mechanism of the surface *p*CO₂ in Jiaozhou
22 Bay, China, from December to March. The results showed that the *p*CO₂ ranged from 157 μatm to
23 647 μatm, and the bay represented a sink for atmospheric CO₂ (-3.8 mmol m⁻² d⁻¹) in the whole
24 winter. The non-temperature processes were the dominant factors affecting intra-winter *p*CO₂
25 variation. In December, the bay was dominated by aerobic respiration and acted as a CO₂ source
26 (3.0 mmol m⁻² d⁻¹). From early January to late February, however, the vigorous growth of cold algae
27 caused strong primary production, and the bay presented as a CO₂ sink (from -6.4 mmol m⁻² d⁻¹ in
28 early January to -15.5 mmol m⁻² d⁻¹ in late February). In March, primary production weakened and
29 the effects of the CaCO₃ precipitation appeared, and the strength of the CO₂ sink was obviously
30 weakened (-1.1 mmol m⁻² d⁻¹). Meanwhile, the water temperature decreased gradually from
31 December to late January and then increased until March, and it further expanded the variation range
32 of *p*CO₂. Our results highlight the obvious source/sink change in mid-latitude seawater CO₂ in
33 winter, while more field observations are still needed to further understand the complicated
34 biogeochemical processes and its influence on seawater *p*CO₂.

35 **Keywords:** *p*CO₂; Aerobic respiration; Primary production; CaCO₃ precipitation; Controlling
36 mechanism; Jiaozhou Bay

37 **1. Introduction**

38 The absorption intensity of CO₂ in coastal waters has received increasing attention (Borges,
39 2011; Cai et al., 2011; Gruber, 2015). The current estimate accounts for 10~20% of the CO₂
40 absorbed by the world's oceans (Chen et al., 2013; Laruelle et al., 2014; Wanninkhof et al., 2013).
41 However, the rapid change in biogeochemical processes produces large uncertainties in the
42 estimates. Therefore, a more comprehensive and in-depth understanding of the spatiotemporal
43 pattern and mechanisms controlling coastal CO₂ system is extremely necessary.

44 In winter, a decrease in seawater temperature increases the solubility of CO₂, resulting in a
45 decrease in the surface partial pressure of CO₂ (*p*CO₂). In most of the mid-latitude sea areas in the
46 world, the temperature variation from summer to winter accounts for more than 50% of the change
47 in *p*CO₂ (Takahashi et al., 2002). Many studied areas, such as the western area of the North Atlantic
48 Ocean (Heike et al., 2004), the North Sea (Thomas et al., 2005), the US South Atlantic Bight (Jiang
49 et al., 2013) and the North Yellow Sea (Xue et al., 2012), have shown that low temperature in winter
50 often results in low *p*CO₂ levels, and some ocean areas even appear as sinks of atmospheric CO₂.
51 However, affected by the coupled influence of low temperature, vertical mixing, runoff variation,
52 nutrient supply and light intensity in winter, vigorous growth of phytoplankton often occurs in many
53 mid-latitude coastal waters, such as the waters near Blanca (Argentina) in South America (Popovich
54 et al., 2008), the Narragansett Bay and the Sargasso Sea in North America (Oviatt et al., 2002; Tin
55 et al., 2016), the waters near the Loire estuary and the Adriatic Sea in Europe (Guillaud et al., 2008;
56 Ljubimir et al., 2017), and the nearshore areas of the Bohai Sea and the Hokkaido in North-east Asia
57 (Sakamoto et al., 2008; Zhao et al., 2004). In addition, a certain degree of aerobic respiration occurs
58 in some areas, for example, the central area of the Baltic Sea and the North Yellow Sea (Wesslander
59 et al., 2010; Xu et al., 2016). Therefore, in addition to the effects of temperature variation, the
60 influence of non-temperature biogeochemical processes on the CO₂ source/sink change should not
61 be neglected in mid-latitude coastal waters in winter.

62 The CO₂ sinks caused by primary production in winter have been reported in some mid-latitude
63 coastal waters. In the Patagonia Sea in South America, Bianchi et al. (2009) conducted a cruise
64 survey in winter. Their results showed that *p*CO₂ values had a significant negative correlation with
65 Chlorophyll *a* (Chl *a*), and the region of 60~61.1°W with the highest Chl *a* value of >3.5 µg/L acted
66 as a sink of atmospheric CO₂. In the nearshore areas of the Loire estuary, based on one cruise data
67 in February, Bozec et al. (2012) found that the increase in river discharge promoted the vertical
68 stratification of seawater and brought large amounts of nutrients. Consequently, the phytoplankton
69 bloom consisting mainly of diatoms caused the seawater surface *p*CO₂ to be lower than the
70 atmosphere by 42 µatm. Regarding the phenomenon of an increase in *p*CO₂ caused by aerobic
71 respiration, Xu et al. (2016) found that vertical mixing carried the subsurface organic matter to the

72 surface layer and aerobic respiration made the northern Yellow Sea act as a CO₂ source in December
73 (the average *p*CO₂ was 464 μatm). In spite of some field observation in different areas, more cruise
74 surveys and analyses are still needed to more comprehensively reveal the detailed spatiotemporal
75 pattern of *p*CO₂ and its control mechanisms throughout the winter months.

76 Jiaozhou Bay (JZB) (35°18'~36°18'N, 120°04'~120°23'E) is a typical mid-latitude semi-
77 closed shallow water in northern China. The water area is 302.9 km² and the average water depth is
78 7 m. The climate is dominated by the East Asia Monsoon, with northerly wind in winter and
79 southerly wind in summer (Li et al., 2006). The tidal current is a regular semi-diurnal tide that
80 induces strong vertical mixing and good vertical homogeneity of the seawater temperature and
81 salinity (Chen et al., 1999; Liu et al., 2004). The bay is an ideal area for characterizing the natural
82 variation in *p*CO₂ and understanding their controlling processes, particularly in winter. First, as a
83 typical mid-latitude water body, JZB has a strong seasonal change of physically properties. In
84 particular, the average seawater surface temperature increases by ~ 10 °C from winter to spring (Li
85 et al., 2007). Second, approximately 37% of the human population in the world lives within 100 km
86 of the coastline (Cohen et al., 1997) and especially in the mid-latitude area, making this area subject
87 to intense human impact (Bauer et al., 2013). JZB is a typical bay that is highly affected by
88 urbanization. The eastern area of the bay is adjacent to the downtown of Qingdao City, with a
89 population of 4.8 million, and the major estuaries (Licun River, Haibo River and Loushan River)
90 have already become conduits for wastewater (Gao et al., 2008). Large amounts of nutrient and
91 organic pollutant input have caused eutrophication and other problems in the JZB, with strong
92 influence on carbon cycle in the area (Wang and Wang, 2011). The measurement of phytoplankton
93 biomass, determined by using Chl *a*, in the past two decades indicated a clear bimodal pattern with
94 peaks in summer and winter in the bay (Sun et al., 2011a; Wang et al., 2015; Wu et al., 2004). Same
95 as many coasts in China, JZB is also an important shellfish-farming area with a breeding area of
96 107 km² (Yang et al., 2007; Zhang et al., 2005), suggesting the possible effect of calcification on
97 *p*CO₂.

98 In the previous studies on controlling mechanisms of *p*CO₂ in the JZB during winter, Zhang et
99 al. (2012) conducted one cruise in autumn and the other in winter. Their results indicated that the

100 bay experienced a process of intense organic degradation in autumn and strong primary production
101 in winter, causing the bay from a CO₂ source to a sink during the period. Recently, Zang et al. (2018)
102 found that the decrease in seawater temperature and enhancement of primary production together
103 resulted in the bay acting as a CO₂ sink. However, *p*CO₂ changes throughout the winter and the
104 mechanism for the variation are far from clearly understood. To fill the knowledge gap, this study
105 researched the variation in seawater surface *p*CO₂ from December to March in the JZB and explored
106 the factors determining the change of *p*CO₂. In particular, this study analysed the effect of the
107 biogeochemical process induced by phytoplankton bloom on CO₂ source/sink patterns, with the
108 consideration of water temperature variation (decrease first and increase later). The results can
109 improve the understanding of the *p*CO₂ control mechanism in mid-latitude coastal waters where
110 strong biological activities occur in winter.

111 **2. Material and methods**

112 **2.1 Survey stations and sample processing**

113 Seven cruises were conducted in the JZB during winter from 2008 to 2016. Survey time and
114 number of stations are listed in Table 1. In each cruise, samples were collected from 24~33 stations
115 (Figure 1). During the cruises, seawater samples were collected from the water surface at a depth of
116 approximately 1.5 m because of the homogeneous vertical profiles in the JZB water column (Chen
117 et al., 1999). Seawater surface temperature, salinity, oxygen saturation (DO%) and *p*CO₂ data were
118 collected continuously, and discrete water samples were collected using 5 L Niskin bottles for later
119 analysis of dissolved inorganic carbon (DIC), total alkalinity (TA), and Chl *a*.

120 Surface temperature and salinity were measured using a SBE 45 Micro TSG (Sea-Bird, Inc.,
121 Bellevue, WA, USA), with a nominal precision of 0.002 °C for temperature and 0.005 for salinity.
122 The DO% was measured with a YSI-5000 oxygen analyser (YSI Corporation, Yellow Spring, OH,
123 USA), which was calibrated using the Winkler titration method (nominal precision: 0.1%). The
124 surface *p*CO₂ was measured with a non-dispersive infrared (NDIR) spectrometer (Li-Cor Model Li-
125 7000, Lincoln, NE, USA) or a G2131-I Analyser (PICAROO, USA) using wavelength-scanned
126 cavity ring-down spectroscopy (WS-CRDS), coupled to an equilibrator. The *p*CO₂ data in cruises
127 before 2014 were measured using a Li-7000 NDIR spectrometer with a measurement uncertainty of

128 less than 1%, and those in 2014 and after were measured using a G2131-I Analyser with a nominal
129 precision of < 50 ppbv over 5-min intervals. Before and after each cruise, the $p\text{CO}_2$ measurement
130 instruments were calibrated against three CO_2 gas standards (202, 401 and 1010 ppm CO_2 in air)
131 and one N_2 reference (National Research Center for Certified Reference Materials, Beijing, China).

132 To measure DIC and TA of water samples, filtration treatment was needed to avoid the
133 influence of the particular matter. The DIC samples were directly collected from the Niskin bottles
134 using a syringe and filtered through a 0.45 μm disposable syringe filter to avoid exchange with the
135 air. TA samples were filtered through cellulose acetate membranes (0.45 μm) using a borosilicate
136 glass filter. The DIC and TA samples were all poisoned with saturated mercury chloride (final
137 concentration: *c.* 0.02% by volume) and preserved at 4 °C (Li et al., 2017). The DIC values were
138 determined by acid extraction using a total organic analyser (TOC-VCPN, Shimadzu Corporation,
139 Kyoto, Japan) (Liu et al., 2014) or a DIC analyser (AS-C2, Apollo SciTech, USA). The TA values
140 were determined by Gran titration using a Total Alkalinity Titrator (AS-ALK2, Apollo SciTech,
141 USA). Measurements of DIC and TA were both calibrated against Certified Reference Materials
142 (CRMs) from Scripps Institution of Oceanography at a precision and accuracy level of 0.2%.

143 Samples for Chl *a* measurement were filtered through GF/F glass fibre membranes (0.7 μm ;
144 Whatman, Maidstone, UK) at pressures below 0.04 MPa. Saturated magnesium carbonate was
145 added to the membranes after filtration, and the samples were preserved at -20 °C. Before analysis,
146 the samples were extracted with 90% acetone, and the supernatant fluid was analysed using a
147 fluorescence spectrophotometer (F4500, Hitachi Co, Tokyo, Japan).

148 **2.2. Methodology**

149 **2.2.1. Aragonite saturation state**

150 The aragonite saturation state (Ω_{arag}) at *in situ* temperatures ($\Omega_{\text{arag}@\text{situ}}$) was calculated from
151 the DIC, TA, *in situ* temperature, and *in situ* salinity values using the CO_2 program (Lewis and
152 Wallace, 1998) and the CO_2 system coefficients of Mehrbach et al. (1973) as refitted by Dickson
153 and Millero (1987). The K_{sp}^* values for aragonite were taken from Mucci (1983), and the Ca^{2+}
154 concentrations were assumed to be proportional to salinity, as presented in Millero (1979).

155 **2.2.2. $p\text{CO}_2$ normalization**

156 Considering that our $p\text{CO}_2$ data were collected over several years, this study normalized the
157 surface water $p\text{CO}_2$ values of the cruises in December to the year 2015 and those of other cruises to
158 the year 2016 by assuming that seawater surface $p\text{CO}_2$ increased at the same growth rate ($1.5 \mu\text{atm}$
159 yr^{-1}) of the $p\text{CO}_2$ in the air according to Nakaoka et al. (2006).

160 **2.2.3. The temperature effect on $p\text{CO}_2$**

161 To assess the temperature effect on the distribution of $p\text{CO}_2$ in each cruise, this study normalized
162 the observed *in situ* $p\text{CO}_2$ data to the average seawater temperature of the corresponding cruise
163 using the equations proposed by Takahashi et al. (1993), and then temperature-normalized $p\text{CO}_2$
164 ($np\text{CO}_2$) was calculated:

$$165 \quad np\text{CO}_2 = (p\text{CO}_2)_{\text{obs}} \times \text{EXP}[0.0423 \times (T_{\text{nor}} - T_{\text{obs}})] \quad (1)$$

166 where $(p\text{CO}_2)_{\text{obs}}$, T_{obs} and T_{nor} are the observed *in situ* surface $p\text{CO}_2$, *in situ* temperature and the
167 temperature to which the *in situ* $p\text{CO}_2$ needs to be normalized, respectively. Then, the difference
168 between $np\text{CO}_2$ and $(p\text{CO}_2)_{\text{obs}}$ was the temperature effect on $p\text{CO}_2$ distribution in the cruise.

169 Similarly, to assess the temperature effect on $p\text{CO}_2$ between the cruises, the average $p\text{CO}_2$ for
170 each cruise was normalized to the average seawater temperature of all cruises. Then, the $p\text{CO}_2$ in
171 each cruise under the average seawater temperature in winter ($Np\text{CO}_2$) was calculated:

$$172 \quad Np\text{CO}_2 = (p\text{CO}_2)_{\text{mean}} \times \text{EXP}[0.0423 \times (T_{\text{Mean}} - T_{\text{mean}})] \quad (2)$$

173 where $(p\text{CO}_2)_{\text{mean}}$ and T_{mean} are the average surface $p\text{CO}_2$ and temperature in each cruise. T_{Mean} is
174 the average seawater temperature of all cruises.

175 To assess the relative importance of temperature and non-temperature effect (including the
176 effect of biological activities) on $p\text{CO}_2$ between the cruises, this study used equations developed by
177 Takahashi et al. (2002):

$$178 \quad \text{T: } p\text{CO}_2 \text{ at } T_{\text{obs}} = (p\text{CO}_2)_{\text{Mean}} \times \text{EXP}[0.0423 \times (T_{\text{obs}} - T_{\text{Mean}})] \quad (3)$$

$$179 \quad \text{B: } p\text{CO}_2 \text{ at } T_{\text{Mean}} = (p\text{CO}_2)_{\text{obs}} \times \text{EXP}[0.0423 \times (T_{\text{Mean}} - T_{\text{obs}})] \quad (4)$$

$$180 \quad \Delta(p\text{CO}_2)_{\text{non-temp}} = (p\text{CO}_2 \text{ at } T_{\text{Mean}})_{\text{max}} - (p\text{CO}_2 \text{ at } T_{\text{Mean}})_{\text{min}} \quad (5)$$

$$181 \quad \Delta(p\text{CO}_2)_{\text{temp}} = (p\text{CO}_2 \text{ at } T_{\text{obs}})_{\text{max}} - (p\text{CO}_2 \text{ at } T_{\text{obs}})_{\text{min}} \quad (6)$$

182 where $(pCO_2)_{Mean}$ is the average pCO_2 of all cruises, and the subscripts “max” and “min” indicated
183 the maximum and minimum values, respectively.

184 The relative importance of each effect can be expressed in terms of the ratio between the
185 temperature effect (T) and non-temperature effect (B):

$$186 \quad T / B = \Delta(pCO_2)_{temp} / \Delta(pCO_2)_{non-temp} \quad (7)$$

187 **2.2.4. Statistical analyses**

188 The correlations between environmental variables were analysed using SPSS 21 (IBM SPSS
189 Statistics, IBM Corporation, Armonk, New York). All statistical analyses were at significance level
190 of 0.05.

191 **3. Results**

192 **3.1 Temperature and salinity**

193 The seawater temperature in the JZB in winter is shown in Figure 2. The temperatures in the
194 seven cruises surveyed were all below 10 °C, and the average temperature decreased from 7.1 °C in
195 December to 1.5 °C in late January and then gradually increased to 8.6 °C in March. The time span
196 of seven cruises (8 years) was relatively large. Compared with the multi-year diurnal average
197 seawater temperature data in the JZB during winter, the temperature in the five cruises from
198 December to late January was slightly lower and that in March. Even so, the overall variation trends
199 of temperature in these cruises were consistent with the changes of daily seawater temperature,
200 showing that these cruise data had a certain representativeness and can be used to analyse the pCO_2
201 variation between winter months in the JZB. The temperature increased from the upper end of the
202 bay to the mouth of the bay in the five cruises from December to late January (Figure 3). The
203 temperature gradient in each cruise in this period was relatively large, and the difference between
204 the lowest and the highest temperature values all exceeded 4.0 °C. The temperature values in the
205 two cruises during December were the highest (4.4~9.0 °C and 3.9~9.7 °C), while the temperature
206 values in the cruise in late January were the lowest (-1.3~4.6 °C). In late February, due to the impact
207 of land warming, no obvious temperature difference between the upper end of the bay and the mouth
208 area existed. The temperature in this period was evenly distributed with a range of 3.8~4.7 °C. In

209 March, the temperature decreased from the upper end of the bay to the mouth, with a range of
210 7.7~9.9 °C.

211 The seawater surface salinity values in December and early January were relatively close and
212 were basically between 29.0 and 30.9 (Figure 2). In the four cruises from mid-January to March,
213 the salinity levels were higher with values of >30.3. In late January, the salinity values were the
214 highest throughout the winter and ranged from 30.9 to 31.7. In late February and March, the salinity
215 decreased slightly, and the ranges were 30.3~31.2 and 30.5~31.2, respectively. In terms of
216 distribution in these seven cruises (Figure 3), the salinity increased from the northeastern area to the
217 mouth, and the difference between the highest and lowest values in each cruise was less than 2.0.
218 The salinity in the northeastern area was always the lowest, and the gradient variation was relatively
219 large, indicating the influence of terrestrial input. The rivers entering the JZB have no natural runoff
220 and the winter is the dry season. However, three wastewater treatment plants located near the
221 northeastern area and the daily total amount of treated sewage is up to ~510000 tons, indicating that
222 the direct treated sewage input was the main reason for the low salinity in this region.

223 **3.2 $p\text{CO}_2$**

224 The distribution of seawater surface $p\text{CO}_2$ in the JZB in winter is shown in Figure 4. According
225 to the average air CO_2 data (408 μatm) from December 2015 to March 2016 from the flask
226 measurements on the Tae-ahn Peninsula (126.131°E, 36.731°N) adjacent to the southern Yellow Sea,
227 the bay in two cruises during December acted as a source of atmospheric CO_2 as a whole, and the
228 $p\text{CO}_2$ ranges were 379~536 μatm and 382~647 μatm , respectively. The $p\text{CO}_2$ gradually decreased
229 from the northeastern area to the mouth area. Obviously, the $p\text{CO}_2$ in the northeastern area was the
230 largest (>450 μatm). In early January, the $p\text{CO}_2$ value was between 216 μatm and 520 μatm . The
231 northeastern area also acted as a CO_2 source, but the western area was unsaturated with respect to
232 atmospheric CO_2 . In mid-January (282~375 μatm), late January (202~324 μatm) and late February
233 (157~327 μatm), the CO_2 levels in the entire bay were all unsaturated and the $p\text{CO}_2$ decreased from
234 the mouth to the northeastern area. The $p\text{CO}_2$ value in the northeastern area was even below 190
235 μatm in late February. In March, the bay acted as a weak CO_2 sink as a whole with the $p\text{CO}_2$ values
236 of 357~415 μatm . The $p\text{CO}_2$ value was highest in the northern area and decreased gradually to the

237 mouth area, while the difference of $p\text{CO}_2$ between areas did not exceed $50 \mu\text{atm}$. Overall, the $p\text{CO}_2$
238 values throughout the winter showed a process of gradual decrease from December to the end of
239 February and then obvious increase in March (Figure 4h). The average $p\text{CO}_2$ value of all cruises
240 was $352 \mu\text{atm}$. Therefore, the bay acted as a sink of atmospheric CO_2 in winter as a whole.

241 **3.3 DO% and Chl *a***

242 The distribution of seawater surface DO% in the JZB in winter is shown in Figure 5. The
243 seawater surface DO in the JZB was unsaturated in both cruises in December (ranges: 79.8~98.1%
244 and 79.5~101.5%) and increased from the northeastern area to the mouth area. In the northeastern
245 area, which acted as the strongest CO_2 source, the unsaturated degree of DO was the highest and
246 the DO% values were approximately 85%, showing the presence of aerobic respiration. In early
247 January, DO remained unsaturated in the northeastern area which acted as a CO_2 source, but
248 oversaturated (~105%) in the western area which acted as a CO_2 sink. In mid-January, late January
249 and late February, when the entire JZB acted as a CO_2 sink, the DO% ranges were 101.0~117.5%,
250 109.4~120.2% and 102.0~147.0%, respectively. In these three cruises, DO was oversaturated and
251 decreased from the northeastern area to the mouth area. Moreover, in the northeastern area, DO%
252 values were highest and were above 110% (mid-January), 115% (late January) and 125% (late
253 February), respectively, showing a strong primary production process. In March, the DO was
254 slightly oversaturated with DO% values of 103.2~114.8%. The DO% distribution in the bay was
255 relatively uniform, and the values in most areas were approximately 109.0%. Overall, the variation
256 trend of DO% throughout the winter was opposite to $p\text{CO}_2$, a process of gradual increase from
257 December to late February and then decrease in March (Figure 5h).

258 The distribution of seawater surface Chl *a* in the JZB in winter is shown in Figure 5. The Chl
259 *a* concentration was low and below $0.60 \mu\text{g/L}$ in December when the DO was unsaturated. The
260 ranges of Chl *a* in these two cruises were $0.03\sim 0.61 \mu\text{g/L}$ and $0.12\sim 0.55 \mu\text{g/L}$, respectively. In early
261 January, the Chl *a* concentrations in the western and mouth areas were above $0.60 \mu\text{g/L}$. In mid-
262 January, late January and late February, when the DO in the entire bay was oversaturated, the ranges
263 of Chl *a* were $0.30\sim 2.30 \mu\text{g/L}$, $0.40\sim 9.12 \mu\text{g/L}$ and $1.78\sim 8.94 \mu\text{g/L}$, respectively. The Chl *a*
264 concentrations in the three cruises all decreased from the northeastern area to the mouth, and the

265 Chl *a* concentrations in the northeastern area were above 1.50 µg/L, 4.50 µg/L and 6.50 µg/L,
266 respectively. In March, when the DO was slightly oversaturated, the Chl *a* concentration was lower
267 with Chl *a* values of 0.04~0.40 µg/L. Overall, the variation of phytoplankton biomass represented
268 by Chl *a* concentration throughout the winter was in good agreement with that of DO%, showing a
269 process of gradual increase from December to the end of February and then obvious decrease in
270 March (Figure 5h).

271 **3.4 DIC and TA**

272 The seawater surface DIC in the JZB in winter is shown in Figure 6. In December and early
273 January, the DIC levels were relatively high and generally ranged between 2100 µmol/kg and 2300
274 µmol/kg. The DIC values were highest in the northeastern area and decreased gradually to the mouth,
275 with the difference of approximately 150 µmol/kg. In these two periods, the difference in DIC
276 distribution mainly occurred in the western area of the bay. In December, the DIC in the western
277 area was approximately 40 µmol/kg higher than that in the mouth, but they were close in early
278 January. In middle and late January, the DIC values (2142~2156 µmol/kg and 2130~2155 µmol/kg)
279 were lower than those in December. The DIC also decreased from the northeastern area to the mouth
280 area, but the difference between two areas was much smaller, just ~15 µmol/kg. In late February,
281 the DIC values were the lowest throughout the winter, with a range of 2000~2140 µmol/kg. The
282 DIC value increased gradually from the northeastern area to the mouth area and the difference was
283 up to ~90 µmol/kg. In March, the DIC values (2085~2126 µmol/kg) also maintained a lower level
284 but increased from the north area to the mouth area, with the difference of ~20 µmol/kg between
285 two areas.

286 Seawater surface TA in the JZB during winter is shown in Figure 6. In December and early
287 January, the TA values ranged generally between 2240 µmol/kg and 2400 µmol/kg. The spatial
288 distribution of TA was similar to that of DIC. The TA values were also highest in the northeastern
289 area and decreased gradually to the mouth. However, the decreasing gradient of TA was slightly
290 smaller than that of DIC, and the TA difference between the northeastern and the mouth area was
291 approximately 110 µmol/kg. In early January, TA values in the western area (where DIC values were
292 close to those in the mouth area) were ~30 µmol/kg higher than those in the mouth area. In middle

293 and late January, the TA ranges were 2297~2336 $\mu\text{mol/kg}$ and 2302 ~2360 $\mu\text{mol/kg}$, respectively.
294 Compared to December, the TA values of these two cruises were slightly higher in most areas except
295 for the northeastern area, and the TA difference between the northeastern area and the mouth area
296 was only ~45 $\mu\text{mol/kg}$. In late February, the TA was between 2302 $\mu\text{mol/kg}$ and 2364 $\mu\text{mol/kg}$, and
297 the spatial distribution was opposite to that of DIC. The TA value was highest in the northeastern
298 area with low DIC and increased gradually to the mouth area. In March, the TA value ranged from
299 2290 $\mu\text{mol/kg}$ to 2347 $\mu\text{mol/kg}$. Spatial distribution of TA was similar to that of DIC, and the TA
300 values increased from the northern area to the mouth area. However, the change gradient of TA was
301 larger than that of DIC, and the TA values in the northern area were ~40 $\mu\text{mol/kg}$ lower than those
302 in the mouth.

303 **4. Discussion**

304 **4.1 The temperature effect on variation in surface $p\text{CO}_2$ in the JZB during winter**

305 Temperature is an important thermodynamic parameter affecting seawater $p\text{CO}_2$. For example,
306 the relationship between seawater temperature and $p\text{CO}_2$ proposed by Takahashi et al. (1993) shows
307 that $p\text{CO}_2$ decreases by approximately 4.23% for every 1 $^\circ\text{C}$ decrease in water temperature. To
308 assess the temperature effect on the $p\text{CO}_2$ distribution for each cruise, this study calculated $np\text{CO}_2$
309 by normalizing the surface $p\text{CO}_2$ at each station to the average seawater temperature in the
310 corresponding cruise (see Section 2.3.3 Methodology). As shown in Figure 7a-g, in December (13th
311 and 21st), early January (8th), mid-January (21st), and late January (26th), the $p\text{CO}_2$ in the upper end
312 of the bay with lower temperatures increased by 20~65 μatm after normalization, while the $p\text{CO}_2$ in
313 the mouth area of the bay with higher temperatures decreased by 15~30 μatm . This indicated that
314 surface $p\text{CO}_2$ in the nearshore area was relatively low due to the cooling effect of land, whereas that
315 in the mouth area was higher due to the frequent water exchange with the Yellow Sea where water
316 temperature was relatively higher. In March (25th), the $p\text{CO}_2$ in the upper end of the bay with higher
317 temperature decreased by ~12 μatm after normalization, while the $p\text{CO}_2$ in the mouth area with
318 lower temperature increased by ~12 μatm , suggesting that land warming resulted in higher $p\text{CO}_2$ in
319 the upper end area. All these results indicated the temperature effect on the spatial distribution of
320 $p\text{CO}_2$ in certain periods of winter. However, combined with the distribution of *in situ* $p\text{CO}_2$ in each

321 cruise (Figure 4), in mid-January and late January, the *in situ* $p\text{CO}_2$ value in the northeastern area
322 was lower than that in the mouth area by about $\sim 80 \mu\text{atm}$, which was larger than the contribution of
323 $p\text{CO}_2$ ($\sim 50 \mu\text{atm}$) caused by the difference in water temperature. In March, the *in situ* $p\text{CO}_2$ value
324 in the northeastern was higher than that in the mouth area by about $50 \mu\text{atm}$, which was also larger
325 than the contribution of $p\text{CO}_2$ ($\sim 24 \mu\text{atm}$) caused by the difference in water temperature. This
326 indicated that the spatial distribution of $p\text{CO}_2$ was still largely affected by other factors. Even in
327 some cruises, temperature may not be the main factor controlling $p\text{CO}_2$ distribution. For example,
328 in December, *in situ* $p\text{CO}_2$ was the lowest in the mouth area with higher temperatures and the highest
329 in the northeastern waters with lower temperatures. In late February, the difference between the
330 highest and lowest seawater temperature was only $0.9 \text{ }^\circ\text{C}$, but the difference in *in situ* $p\text{CO}_2$ was
331 more than $160 \mu\text{atm}$ (Figures 4, 7).

332 The seawater surface temperature in the JZB experienced a pattern of first decrease and then
333 increase from December to March. To assess the temperature effect on the $p\text{CO}_2$ variation between
334 cruises, the $Np\text{CO}_2$ was calculated by normalizing the average seawater $p\text{CO}_2$ in each cruise to the
335 average seawater temperature of all cruises ($5.2 \text{ }^\circ\text{C}$) (see Section 2.3.3 Methodology) (Figure 8).
336 After normalization, the $p\text{CO}_2$ decreased by $33 \mu\text{atm}$ and $51 \mu\text{atm}$ in December and March,
337 respectively, when the temperatures were relative higher; the $p\text{CO}_2$ increased by $20 \mu\text{atm}$, $21 \mu\text{atm}$,
338 $47 \mu\text{atm}$, and $12 \mu\text{atm}$ in early January, mid-January, late January and late February, respectively,
339 when the temperatures were relative lower. The difference of $p\text{CO}_2$ between cruises decreased by
340 74% from December to early January and 52% from late February to March, but it only decreased
341 by 8% from early January to late February. Moreover, the overall the temporal pattern of $p\text{CO}_2$ kept
342 stable. The highest and lowest $p\text{CO}_2$ values still appeared in December and late February,
343 respectively, and the difference between months was up to $130 \mu\text{atm}$. It indicated that the
344 temperature effect may play an important but not a dominant role in the whole intra-winter $p\text{CO}_2$
345 variation. Based on the method proposed by Takahashi et al. (2002) (see Section 2.3.3 Methodology),
346 the relative contributions of temperature (T) and non-temperature effect (B) to $p\text{CO}_2$ variation
347 throughout the winter were calculated. It is noteworthy that this method was originally designed for
348 open oceanic systems and the non-temperature effect could be attributed almost entirely to the “net

349 biology effect". However, it had been widely used by other authors to assess the role of temperature
 350 versus biological factors in the control of $p\text{CO}_2$ dynamics in coastal areas (de la Paz et al., 2009;
 351 Ribas et al., 2011). The non-temperature term for coastal waters includes all the biogeochemical
 352 processes acting on CO_2 . In this study, the T/B ratio was 0.81, indicating the main role of the non-
 353 temperature effect in intra-winter $p\text{CO}_2$ variation.

354 **4.2 The non-conservative behaviour of DIC and TA and variation in the JZB during winter**

355 In coastal waters, the non-temperature processes influencing $p\text{CO}_2$ mainly includes terrestrial
 356 input, biological processes (production/respiration), CaCO_3 processes (precipitation/dissolution),
 357 CO_2 sea-air exchange (evasion/invasion) and others. The occurrence of these processes often
 358 changes DIC and TA. Therefore, the analysis of DIC and TA non-conservative behaviour is helpful
 359 for identifying the main non-temperature factors for $p\text{CO}_2$ (Jiang et al., 2013; Li et al., 2017; Zhai
 360 et al., 2015). In some nearshore bays with no obvious runoff input, the ocean end-member can be
 361 used as a standard value to evaluate the effects of terrestrial input and biogeochemical processes,
 362 that is, the deviation of the measured DIC or TA from the ocean end-member. Thus, according to
 363 the approach of Jiang et al. (2013), the values for the addition or removal of DIC and TA in each
 364 cruise were obtained using the station data in the mouth area, which could represent the DIC and
 365 TA levels of the Yellow Sea, as the seawater end-member values (Li et al., 2017, Yang et al., 2018).
 366 In the specific calculation in late January, considering that the DO% in the mouth area was
 367 approximately 110% and a certain primary production existed (Figure 5e), this study chose the ocean
 368 end-member in mid-January, which was only 5 days apart. The calculation method is as follows:

$$369 \quad \Delta\text{DIC} = \text{DIC}_i - \frac{S_i}{S_{\text{ocean}}} \times \text{DIC}_{\text{ocean}} \quad (8)$$

$$370 \quad \Delta\text{TA} = \text{TA}_i - \frac{S_i}{S_{\text{ocean}}} \times \text{TA}_{\text{ocean}} \quad (9)$$

371 where ΔDIC and ΔTA represent the addition and removal of DIC and TA, respectively; and S_i (S_{ocean}),
 372 DIC_i ($\text{DIC}_{\text{ocean}}$), and TA_i (TA_{ocean}) are the salinity, DIC and TA of station i (the ocean end-member),
 373 respectively. This study used the average values of DIC and TA from the two stations, which had
 374 the highest salinity and were near the Yellow Sea, as the ocean end-member. The specific values are
 375 shown in Table 2.

376 As shown in Figure 9, the non-conservative behaviours of DIC and TA in the JZB presented
377 three stages. First, Δ DIC and Δ TA maintained an addition status in the two cruises in December.
378 The maximum addition values were observed in the northeastern area with low salinity and
379 exceeded 200 $\mu\text{mol/kg}$, showing the effect of terrestrial DIC and TA input. The altered ratio of Δ DIC
380 and Δ TA from terrestrial input was generally close to 1:1 (Cai et al., 2008), but the Δ DIC in the JZB
381 was obviously larger than Δ TA in this period. Moreover, the difference between Δ DIC and Δ TA was
382 the largest in the northeastern area (more than 90 $\mu\text{mol/kg}$), indicating that in addition to terrestrial
383 input, other factors influenced DIC. Second, in the four cruises from early January to late February,
384 Δ TA values also presented an addition status. However, there was a phenomenon that Δ DIC was
385 less than Δ TA. In early January, this situation only occurred in the western area. In mid-January,
386 this situation expanded to the entire bay. In late January and late February, the DIC showed partial
387 or complete removal in different stations. The results indicated that DIC experienced an obvious
388 consumption in this period. Finally, in March, both DIC and TA showed a removal status, and the
389 removal of TA was greater than that of DIC. The maximum removals of TA and DIC were close to
390 30 $\mu\text{mol/kg}$ and 20 $\mu\text{mol/kg}$, respectively. This suggested that the processes consuming DIC and TA
391 existed in the meantime. Thus, the influences of non-temperature processes on $p\text{CO}_2$ were discussed
392 in each period separately.

393 **4.3 Aerobic respiration caused the bay to act as a CO_2 source in early winter**

394 The biogeochemical processes that cause the non-conservative behaviour of DIC and TA could
395 alter Δ DIC and Δ TA in fixed ratios. By comparing the ratio of Δ TA to Δ DIC at each station with the
396 fixed ratios of the various processes that alter Δ TA and Δ DIC, the main processes causing the non-
397 conservative behaviour of DIC and TA can be further clarified (Cai et al., 2004; Li et al., 2017; Liu
398 et al., 2014). Throughout the winter in the low water period, the rivers flowing into the JZB had no
399 natural runoff and the salinity in the northeastern area of the JZB was always the lowest. Therefore,
400 the sewage discharge from the three wastewater treatment plants became the main source of
401 terrestrial input, and the impact ratio of Δ DIC to Δ TA was approximately 1.03:1 (Li et al., 2017).
402 For the production/respiration, the phytoplankton preferred $\text{NH}_4\text{-N}$ as a nitrogen source in the JZB
403 (Jiao, 1993). According to the Redfield equation with $\text{NH}_4\text{-N}$ as the nitrogen source (Redfield, 1963),

404 the fixed ratio of Δ DIC to Δ TA altered by this process was 106:15. The fixed ratio of TA to DIC
405 altered by the CaCO_3 process was 2:1, and CO_2 evasion/invasion did not change TA while affected
406 DIC. Thus, the Figure 10 can be obtained.

407 The Δ TA/ Δ DIC values in December were all located in the first quadrant, between the ratio
408 lines of direct treated sewage input and aerobic respiration (Figure 10 a, b). This indicated that the
409 DIC and TA additions were mainly caused by direct treated sewage input and aerobic respiration.
410 The total amount of daily treated sewage from the three wastewater treatment plants near the
411 northeastern area was 510,000 tons, and the DIC and TA concentrations of discharged sewage were
412 as high as 2554~5173 $\mu\text{mol/kg}$ and 2326~4570 $\mu\text{mol/kg}$, respectively. Obviously, the direct input
413 of sewage was an important factor for the addition of DIC and TA in the northeastern area (Liu et
414 al., 2019; Yang et al., 2018). The impact of sewage on aquatic environment has been widely reported
415 in China (Yang et al., 2008; Yang et al., 2012). Meanwhile, the DO in the entire bay was unsaturated,
416 and the DO% was the lowest in the northeastern area with the highest $p\text{CO}_2$, which confirmed the
417 existence of an aerobic respiration process. Moreover, since aerobic respiration had little effect on
418 TA while increased DIC according the Redfield ratio, Δ DIC values were obviously larger than Δ TA
419 values in December. In addition, the influence of perennial urbanization and long water residence
420 time (~60 days, Liu et al., 2004) allowed the northeastern area of the bay to accumulate large
421 amounts of terrestrial materials (high DIC and TA input, organic matter, and others). Under the
422 strong vertical mixing in winter, the upwelling of bottom water would increase the DIC and TA in
423 surface seawater, and the organic matter carried from bottom would further promote aerobic
424 respiration and increase DIC.

425 After identifying that the main non-temperature processes which caused DIC and TA addition
426 in December were treated sewage input and aerobic respiration, the DIC/TA value was introduced
427 to explain their impacts on $p\text{CO}_2$. The DIC/TA value can directly indicate the relative abundance of
428 carbonate species (e.g., HCO_3^- and CO_3^{2-}) in seawater. As such, for a specific temperature and
429 pressure, seawater surface $p\text{CO}_2$ is correlated with this ratio (Wang et al., 2013). The DIC/TA value
430 of treated sewage (1.03) was higher than that of the seawater (0.92~0.97) in the JZB. Therefore,
431 direct treated sewage input could increase the DIC/TA and $p\text{CO}_2$ of seawater in the northeastern

432 area. Meanwhile, aerobic respiration increased DIC by producing CO₂ directly and had a stronger
433 increase effect on DIC/TA and *p*CO₂. The significant negative correlation between the *np*CO₂ (the
434 temperature effect was removed) and DO% (*p* < 0.05) (Figure 11a) indicated that aerobic respiration
435 had a dramatic effect on *p*CO₂ in the entire bay and it caused the bay to act as a CO₂ source in
436 December. In the northeastern area with the lowest salinity, the degree of DO unsaturation was
437 largest and the effects of treated sewage input were superimposed, so the *p*CO₂ was highest. As the
438 sea area extended to the mouth area, the degree of DO unsaturation decreased gradually. The decline
439 of aerobic respiration caused a gradual decrease in *p*CO₂ (Figure 11b). The dominant of aerobic
440 respiration in December may be related to that the strengthened vertical mixing brought organic
441 matters and the moderate temperature favoured the degradation activity of heterotrophic bacteria.
442 The similar phenomenon was reported in the continental shelf off Georgia (USA) and the northern
443 Yellow Sea (Jiang et al., 2010; Xu et al., 2016).

444 **4.4 Primary production promoted the strength of CO₂ sink in winter**

445 The distributions of Δ TA/ Δ DIC in the four cruises from early January to late February are
446 shown in Figure 10c-f. In the northeastern area in early January, Δ TA/ Δ DIC values were similar to
447 those in December, between the ratio lines of aerobic respiration and treated sewage input. This
448 suggested that the DIC additions in this area were still mainly caused by these two processes.
449 However, in the western area in early January and the entire bay in mid-January, all Δ TA/ Δ DIC
450 values were larger than 0.97 (the ratio of the treated sewage-altered Δ TA and Δ DIC), moving toward
451 the ratio line of primary production. Considering the oversaturated DO in these periods and regions,
452 the data indicated that primary production obviously consumed DIC, while the treated sewage input
453 directly added DIC and TA. It is worth noting that the Δ TA/ Δ DIC in these periods and regions were
454 also close to the ratio lines of CaCO₃ dissolution and CO₂ evasion. This resulted from the coupled
455 effects of direct treated sewage input and primary production because the possibility of CaCO₃
456 dissolution and CO₂ evasion were very low based on the high $\Omega_{\text{arag@situ}}$ (>1.80) and appearance of
457 a CO₂ sink (Figures 4, 12). In late January and late February, the degree of DO oversaturation was
458 higher and the Δ TA/ Δ DIC values were closer to the ratio line of primary production, indicating the
459 stronger consumption of DIC from primary production.

460 Obviously, the non-temperature processes affecting $p\text{CO}_2$ changed from aerobic respiration
461 in December to primary production during January and February, which caused an obvious decrease
462 in $p\text{CO}_2$ in the JZB (Figure 4). In the northeastern area of the JZB in early January, DO remained
463 unsaturated and aerobic respiration dominated and the region still acted as a CO_2 source. However,
464 in the western area in early January and the entire bay during mid-January, late January and late
465 February, DO was oversaturated and primary production dominated. The good correlations of
466 npCO_2 vs. DO% and Chl *a* vs. DO% (Figure 13) indicated that absorption of CO_2 by primary
467 production played an important role in the performance of the CO_2 sink in these periods and regions.
468 In the western area in early January, the DO was slightly oversaturated, and the primary production
469 began to dominate and turned the sea area from a CO_2 source in December into a sink. From mid-
470 January to late January, both DO supersaturation and Chl *a* concentration increased (Figure 5h), and
471 the correlation coefficients (r^2) of npCO_2 vs. DO% and DO% vs. Chl *a* also increased. The
472 enhancement of primary production continuously strengthened the CO_2 sink in the period (Figure
473 4h). In terms of the direct input of treated sewage, the increase in $p\text{CO}_2$ caused by this process was
474 persistent. However, the DO% was always the highest and the $p\text{CO}_2$ was always the lowest in the
475 northeastern area from mid-January to late February (Figures 4, 5), indicating that strong CO_2
476 consumption from primary production covered the increase in $p\text{CO}_2$ caused by direct input of treated
477 sewage.

478 The dominant of primary production in this period may be related to the relatively low
479 seawater temperature. The average seawater temperature had decreased obviously and was below
480 $4\text{ }^\circ\text{C}$ since early January and even below $2\text{ }^\circ\text{C}$ in late January, which suppressed the activities of
481 aerobic respiration. Meanwhile, under stable hydrologic conditions and nutrient accumulation in
482 winter, the cold algae community, which had strong photosynthetic activity and was acclimatized to
483 low temperatures, often exhibited a vigorous growth in the JZB in January and February (Li and
484 Sun, 2014; Sun et al., 2011a; Wu et al., 2004). This is also the reasons for the vigorous growth of
485 phytoplankton in the nearshore areas of Hokkaido (Japan) and Blanca (Argentina) (Popovich et al.,
486 2008; Sakamoto et al., 2008). The weakening of feeding pressure caused by low temperatures may
487 be another reason. In Narragansett Bay, Oviatt et al. (2002) noted that the feeding effect from

488 zooplankton and filter feeders was inhibited and algal blooms usually occurred when the seawater
489 temperature was below 3 °C. In Massachusetts Bay, Keller et al. (2011) found a good negative
490 correlation between average Chl *a* concentration and seawater temperature during winters from
491 1995 to 1999 and they emphasized the control of zooplankton feeding on algal blooms.

492 **4.5 The coupled effects of primary production and CaCO₃ precipitation on the *p*CO₂ in March**

493 In March, all $\Delta\text{TA}/\Delta\text{DIC}$ values fell in the third quadrant, basically between the ratio lines of
494 primary production and CaCO₃ precipitation (Figure 10g). Combined with oversaturated DO and
495 high $\Omega_{\text{arag@situ}}$ (2.28~2.53, Figure 12g), it could be inferred that the removal of DIC and TA was
496 mainly caused by primary production and CaCO₃ precipitation. Compared to late February, both the
497 DO oversaturation and the Chl *a* concentration decreased obviously in this period (Figure 5h). Thus,
498 the weakening of primary production was an important factor causing the increase in *p*CO₂ in March.
499 Meanwhile, *np*CO₂ showed no correlation with DO% (Figure 14a), indicating the reduced influence
500 of primary production on the spatial distribution of *p*CO₂. In terms of CaCO₃ precipitation, this
501 process consumed twice TA of DIC, and it further increased the *p*CO₂ levels in March. Considering
502 that primary production consumed DIC but hardly affected TA, the degree of TA removal (ΔTA)
503 could indicate the strength of CaCO₃ precipitation in the period. As shown in Figure 14b, *np*CO₂
504 was the highest in the northern area, where the TA removal was the largest (~25 $\mu\text{mol}/\text{kg}$). As the
505 sea area extended to the mouth area, TA removal and *p*CO₂ showed a decreasing trend. Obviously,
506 the release of CO₂ from CaCO₃ precipitation had a certain influence on the spatial distribution of
507 *p*CO₂ in March. Despite this, the losses of DIC and TA in March were all < 30 $\mu\text{mol}/\text{kg}$, indicating
508 the small intensity of primary production and CaCO₃ precipitation. Moreover, due to the opposite
509 effects on *p*CO₂ from the above two processes, the *np*CO₂ differences between the stations in this
510 period were small, less than 30 μatm . In summary, in March, primary production and CaCO₃
511 precipitation together affected the concentration and spatial distribution of *p*CO₂ in the JZB.

512 The primary production may be constrained by the insufficient supply of nutrients in the bay
513 in March. According to the observation between 2004 and 2008 (Sun et al., 2011b), the nutrient
514 concentration in the JZB showed a gradual decrease from December to March and reached the
515 minimum of < 0.2 mg/L in March. Meanwhile, the increase of feeding pressure caused by higher

516 seawater temperature also reduced the phytoplankton biomass (Zhang et al., 2005). The appearance
517 of CaCO₃ precipitation in March may be related to the previously strong primary production in
518 January and February. This is because large amounts of CO₂ consumption from primary production
519 can increase the concentration of CO₃²⁻ and promote the rise of Ω_{arag} , which could increase the
520 possibility of CaCO₃ precipitation (Kim et al., 2013; Xue et al., 2017). Meanwhile, the seawater
521 temperature rose, and clams began to grow in spring (Zhang et al., 2005). The northern area of the
522 JZB, where TA removal is the greatest, is an important breeding area for shellfish (*Ruditapes*
523 *philippinarum*) in Qingdao, indicating that the appearance of CaCO₃ precipitation may be associated
524 with human shellfish farming activities.

525 In summary, from aerobic respiration in December to primary production during January and
526 February, and then to the weaken of primary production and the presence of CaCO₃ precipitation in
527 March, the transition of non-temperature processes changed the JZB from a CO₂ source to sink and
528 then to a weak sink throughout the winter. At the same time, the water temperature gradually
529 decreased from December to late January and then increased until March, which suggested that the
530 direction of temperature effect on $p\text{CO}_2$ was consistent with the non-temperature effect in most
531 periods and temperature variation further expanded the $p\text{CO}_2$ variation range. Finally, according to
532 the climatological mean wind speed in Qingdao from December to March (5.6 m/s, Yuan et al., 1996)
533 and the average atmospheric CO₂ concentration (408 μatm) in the Tae-ahn Peninsula station from
534 December 2015 to March 2016, the gas transfer velocity formula of Sweeney et al. (2007) was used
535 to calculate the sea-air exchange fluxes of CO₂ (FCO_2). Overall, the JZB appeared as a sink of
536 atmospheric CO₂ throughout the winter, with the average FCO_2 of $-3.8 \text{ mmol m}^{-2} \text{ d}^{-1}$. In December,
537 the average FCO_2 of the two cruises was $3.0 \text{ mmol m}^{-2} \text{ d}^{-1}$. Then the bay turned into an atmospheric
538 CO₂ sink and the strength of sink continued to increase, from $-6.4 \text{ mmol m}^{-2} \text{ d}^{-1}$ in early January to
539 $-15.5 \text{ mmol m}^{-2} \text{ d}^{-1}$ in late February. In March, the sink strength decreased obviously and the FCO_2
540 came to $-1.1 \text{ mmol m}^{-2} \text{ d}^{-1}$.

541 **5. Conclusions**

542 In the JZB from December to March, the mutual effect of non-temperature processes among
543 aerobic respiration, primary production and CaCO₃ precipitation were the main intrinsic driving

544 forces for the $p\text{CO}_2$ variation. Meanwhile, the direction of temperature effect on $p\text{CO}_2$ was
545 consistent with the non-temperature effect in most periods. In December, the higher seawater
546 temperature and the dominance of respiration resulted in the bay acting as a CO_2 source. From early
547 January to late January, with the decrease in $p\text{CO}_2$ caused by cooling, primary production of cold
548 algae increased obviously and the Chl *a* concentration peaked in late February, with the consequence
549 that the JZB became a larger CO_2 sink. In March, the seawater temperature rose, and the strength of
550 CO_2 sink weakened obviously. In this period, with the decrease of primary production, the release
551 of CO_2 from CaCO_3 precipitation appeared. The offsetting of these two processes resulted in a minor
552 difference of the distribution of $p\text{CO}_2$. The strong biogeochemical process occurred widely in the
553 mid-latitude coasts in winter, and its marked impact on seawater $p\text{CO}_2$ should not be ignored. To
554 further improve our understanding of CO_2 sink/source change process and the influence factors in
555 coastal waters, more field studies are still largely needed.

556 **Acknowledgements**

557 This work was supported by the National Natural Science Foundation of China (NSFC) (Grant
558 No. 41376123), the National Natural Science Foundation of China - Shandong Joint Fund for
559 Marine Science Research Centres (NSFC) (Grant No. U1406403) and the Science and Technology
560 Foundation of Shanxi Agricultural University (Grant No. 2018YJ21). We thank Qianqian Jiang,
561 Xiangyu Liu and Ping Han for the sampling and measuring work.

562 **References**

- 563 Bauer J E, et al, 2013. The changing carbon cycle of the coastal ocean. *Nature*, 504, 61-70.
- 564 Bianchi A A, et al, 2009. Annual balance and seasonal variability of sea-air CO_2 fluxes in the
565 Patagonia Sea: Their relationship with fronts and chlorophyll distribution. *Journal of*
566 *Geophysical Research Oceans*, 114(C03018).
- 567 Borges A V, 2011. Present day carbon dioxide fluxes in the coastal ocean and possible feedbacks
568 under global change. *Oceans and the Atmospheric Carbon Content*, 47-77.
- 569 Bozec Y, et al, 2012. Seasonal dynamics of air-sea CO_2 fluxes in the inner and outer Loire estuary
570 (NW Europe). *Estuarine Coastal and Shelf Science*, 100(1), 58-71.
- 571 Cai W J, et al, 2004. The biogeochemistry of inorganic carbon and nutrients in the Pearl River

572 estuary and the adjacent Northern South China Sea. *Continental Shelf Research*, 24(12), 1301-
573 1319.

574 Cai W J, et al, 2008. A comparative overview of weathering intensity and HCO_3^- flux in the world's
575 major rivers with emphasis on the Changjiang, Huanghe, Zhujiang (Pearl) and Mississippi
576 rivers. *Continental Shelf Research*, 28(12), 1538-1549.

577 Cai W J, 2011. Estuarine and coastal ocean carbon paradox: CO_2 sinks or sites of terrestrial carbon
578 incineration? *Annual Review of Marine Science*, 3(3), 123-145.

579 Chen C, et al, 1999. Influences of physical processes on the ecosystem in Jiaozhou Bay: a coupled
580 physical and biological model experiment. *Journal of Geophysical Research Oceans*, 104,
581 29925-29949.

582 Chen C-T A, et al, 2013. Air-sea exchanges of CO_2 in the world's coastal seas. *Biogeosciences*, 10,
583 6509-6544.

584 Cohen J E, et al, 1997. Estimates of coastal populations, *Science*, 278, 1209-1213.

585 de la Paz M, et al, 2009. Surface $f\text{CO}_2$ variability in the Loire plume and adjacent shelf waters: High
586 spatio-temporal resolution study using ships of opportunity. *Marine Chemistry*, 71(1), 55-64.

587 Dickson A G and Millero F J, 1987. A comparison of the equilibrium constants for the dissociation
588 of carbonic acid in seawater media. *Deep Sea Research Part A Oceanographic Research Papers*,
589 34(10), 1733-1743.

590 Gao Z, et al, 2008. The land-sourced pollution in the Jiaozhou Bay. *Chinese Journal of Oceanology*
591 and *Limnology*, 26(2), 229-232.

592 Gruber N, 2015. Ocean biogeochemistry: Carbon at the coastal interface. *Nature*, 517, 148-149.

593 Guillaud J F, et al, 2008. Seasonal variation of riverine nutrient inputs in the northern Bay of Biscay
594 (France), and patterns of marine phytoplankton response. *Journal of Marine Systems*, 72(1-4),
595 309-319.

596 Heike L, et al, 2004. The $p\text{CO}_2$ variability in the midlatitude North Atlantic Ocean during a full
597 annual cycle. *Global Biogeochemical Cycles*, 18, GB3023.

598 Jiang L Q, et al, 2010. Pelagic community respiration on the continental shelf off Georgia, USA.
599 *Biogeochemistry*, 98(1), 101-113.

600 Jiang L Q et al, 2013. Influence of terrestrial inputs on continental shelf carbon dioxide.
601 Biogeosciences, 10(2), 839-849.

602 Jiao N, 1993. Interactions between ammonium uptake and nitrate uptake by natural phytoplankton
603 assemblages. Chinese Journal of Oceanology and Limnology, 11(2), 97-107.

604 Keller A A, et al, 2011. Phytoplankton production patterns in Massachusetts Bay and the absence of
605 the 1998 winter-spring bloom. Marine Biology, 138(5), 1051-1062.

606 Kim D, et al, 2013. Biologically mediated seasonality of aragonite saturation states in Jinhae Bay,
607 Korea. Journal of Coastal Research, 29(6), 1420-1426.

608 Laruelle G G, et al, 2014. Regionalized global budget of the CO₂ exchange at the air-water interface
609 in continental shelf seas. Global Biogeochemical Cycles, 28, 1199-1214.

610 Lewis E and Wallace D W R, 1998. Program developed for CO₂ systems calculations.
611 ORNL/CDIAC 105, Carbon Dioxide Information Analysis Center, Oak Ridge National
612 Laboratory US Department of Energy, Oak Ridge, Tennessee.

613 Li J L and Sun X X, 2014. Photosynthetic characteristics of phytoplankton in winter in the Jiaozhou
614 Bay. Oceanologia et Limnologia Sinica, 3(45), 468-479. (in Chinese).

615 Li N, et al, 2006. Natural environment and geological evolution of Jiaozhou Bay. Ocean Press,
616 Beijing (in Chinese).

617 Li X, et al, 2007. Role of the Jiaozhon Bay as a source/sink of CO₂ over a seasonal cycle. Scientia
618 Marina, 71(3), 441-450.

619 Li Y, et al, 2017. Controlling mechanisms of surface partial pressure of CO₂ in Jiaozhou Bay during
620 summer and the influence of heavy rain. Journal of Marine Systems, 173, 49-59.

621 Liu Z, et al, 2004. Simulation of water exchange in Jiaozhou Bay by average residence time
622 approach. Estuarine Coastal and Shelf Science, 61(1), 25-35

623 Liu Z, et al, 2014. Removal of dissolved inorganic carbon in the Yellow River Estuary. Limnology
624 and Oceanography, 59(2), 413-426.

625 Liu X Y, et al, 2019. Variations in dissolved inorganic carbon species in effluents from large-scale
626 municipal wastewater treatment plants (Qingdao, China) and their potential impacts on coastal
627 acidification. Environmental Science and Pollution Research, 26, 15019-15027.

628 Ljubimir S, et al, 2017. Interannual (2009-2013) variability of winter-spring phytoplankton in South
629 Adriatic Sea: effects of deep convection and lateral advection. *Continental Shelf Research*, 143,
630 311-321.

631 Mehrbach C, et al, 1973. Measurement of the apparent dissociation constants of carbonic acid in
632 seawater at atmospheric pressure. *Limnology and Oceanography*, 18(18), 897-907.

633 Millero F J, 1979. The thermodynamics of the carbonate system in seawater. *Geochimica Et*
634 *Cosmochimica Acta*, 43(10), 1651-1661.

635 Miyazawa Y, et al, 2017. Assimilation of high-resolution sea surface temperature data into an
636 operational nowcast/forecast system around Japan using a multi-scale three-dimensional
637 variational scheme. *Ocean Dynamics*, 67(6), 713-728.

638 Mucci A, 1983. The solubility of calcite and aragonite in seawater at various salinities, temperatures,
639 and one atmosphere total pressure. *American Journal of Science*, 283(7), 14-27.

640 Nakaoka S I, et al, 2006. Temporal and spatial variations of oceanic $p\text{CO}_2$ and air-sea CO_2 flux in
641 the Greenland Sea and the Barents Sea. *Tellus* 58B, 148-161.

642 Oviatt C, et al, 2002. Annual primary production in Narragansett Bay with no bay-wide winter-
643 spring phytoplankton bloom. *Estuarine Coastal and Shelf Science*, 54(6), 1013-1026.

644 Popovich C A, et al, 2008. Dissolved nutrient availability during winter diatom bloom in a turbid
645 and shallow estuary (Bahía Blanca, Argentina). *Journal of Coastal Research*, 24(1), 95-102.

646 Redfield A C, 1963. The influence of organisms on the composition of seawater. In: Hill, M.N. (Ed.),
647 *The Sea*. vol. 2. Interscience, pp. 26-77.

648 Ribas-Ribas M, et al, 2011. Air-sea CO_2 fluxes in the north-eastern shelf of the Gulf of Cádiz
649 (southwest Iberian Peninsula). *Marine Chemistry*, 123(1-4), 56-66.

650 Sakamoto A, et al, 2008. Time series of carbonate system variables off Otaru coast in Hokkaido,
651 Japan. *Estuarine Coastal and Shelf Science*, 79(3), 377-386.

652 Sun X, et al, 2011a. Long- term changes of chlorophyll a concentration and primary productivity in
653 the Jiaozhou Bay. *Oceanologia et Limnologia Sinica*, 42(5), 654-661. (in Chinese).

654 Sun X, et al, 2011b. Long- term changes in nutrient concentration and structure in the Jiaozhou Bay.
655 *Oceanologia et Limnologia Sinica*, 42(5), 662-669. (in Chinese).

656 Sweeney C, et al, 2007. Constraining global air-sea gas exchange for CO₂ with recent bomb ¹⁴C
657 measurements. *Global Biogeochemical Cycles*, 21, GB2015.

658 Takahashi T, et al, 1993. Seasonal variation of CO₂ and nutrients in the high-latitude surface oceans:
659 a comparative study. *Global Biogeochemical Cycles*, 7(4), 843-878.

660 Takahashi T, et al, 2002. Global sea-air CO₂ flux based on climatological surface ocean pCO₂ and
661 seasonal biological and temperature effects. *Deep Sea Research Part II: Topical Studies in*
662 *Oceanography*, 49(9-10), 1601-1622.

663 Tin H C, et al, 2016. Satellite-derived estimates of primary production during the Sargasso Sea
664 winter/spring bloom: Integration of in-situ time-series data and ocean color remote sensing
665 observations. *Regional Studies in Marine Science*, 3, 131-143.

666 Thomas H, et al, 2005. Controls of the surface water partial pressure of CO₂ in the North Sea.
667 *Biogeosciences*, 2(4), 323-334.

668 Wang B and Wang Z, 2011. Long-term variations in chlorophyll a and primary productivity in
669 Jiaozhou Bay, China. *Journal of Marine Biology*, 1-6.

670 Wang Y J, et al, 2015. Temporal and spatial variations of chlorophyll a and environmental factors
671 in Jiaozhou Bay in 2010–2011. *Acta Oceanologica Sinica*, 37 (4), 103–116 (in Chinese).

672 Wang Z A, et al, 2013. The marine inorganic carbon system along the Gulf of Mexico and Atlantic
673 coasts of the United States: Insights from a transregional coastal carbon study. *Limnology and*
674 *Oceanography*, 58(1), 325-342.

675 Wanninkhof R, et al, 2013. Global ocean carbon uptake: magnitude, variability and trends.
676 *Biogeosciences*, 10(3), 1983-2000.

677 Wesslander K, et al, 2010. Inter-annual variation of the air-sea CO₂ balance in the southern Baltic
678 Sea and the Kattegat. *Continental Shelf Research*, 30, 1511-1521.

679 Wu Y, et al, 2004. Quantitative study in long-term variation of phytoplankton in Jiaozhou Bay.
680 *Oceanologia et Limnologia Sinica*, 35 (6), 518-523 (in Chinese).

681 Xu X, et al, 2016. Monthly CO₂ at A4HDYD station in a productive shallow marginal sea (Yellow
682 Sea) with a seasonal thermocline: Controlling processes. *Journal of Marine Systems*, 159, 89-
683 99.

684 Xue L, et al, 2012. Surface partial pressure of CO₂, and air–sea exchange in the northern Yellow
685 Sea. *Journal of Marine Systems*, 105-108(12), 194-206.

686 Xue L, et al, 2017. Sea surface aragonite saturation state variations and control mechanisms at the
687 Gray’s Reef time-series site off Georgia, USA (2006–2007). *Marine Chemistry*, 195, 27-40.

688 Yang H, et al., 2008. Carbon source/sink function of a subtropical, eutrophic lake determined from
689 an overall mass balance and a gas exchange and carbon burial balance. *Environmental*
690 *Pollution*, 151, 559-568.

691 Yang H, et al., 2012. Pollution in the Yangtze. *Science*, 337, 410.

692 Yang W, et al, 2007. Preliminary study on effects of scallop cultivation on water quality in Jiaozhou
693 Bay. *Transactions of Oceanology and Limnology*, (2), 86-93 (in Chinese).

694 Yang X, et al, 2018. Treated wastewater changes the export of dissolved inorganic carbon and its
695 isotopic composition and leads to acidification in coastal oceans. *Environmental Science and*
696 *Technology*, 52, 5590-5599.

697 Zang H, et al, 2018. The contribution of low temperature and biological activities to the CO₂ sink
698 in Jiaozhou Bay during winter. *Journal of Marine Systems*, 186, 37-46.

699 Zhang J H, et al, 2005. Clearance rate, ingestion rate and absorption efficiency of cultivated clam
700 *ruditapes philippinarum* in Jiaozhou Bay, China. *Oceanologia et Limnologia Sinica*, 36 (6),
701 548-555. (in Chinese)

702 Zhang L, et al, 2012. Distribution and seasonal variation in the partial pressure of CO₂ during
703 autumn and winter in Jiaozhou Bay, a region of high urbanization. *Marine Pollution Bulletin*,
704 64(1), 56-65.

705 Zhai W, et al, 2015. Occurrence of aragonite corrosive water in the North Yellow Sea, near the Yalu
706 River estuary, during a summer flood. *Estuarine Coastal and Shelf Science*, 166, 199-208.

707 Zhao Q, et al, 2004. Winter and summer chlorophyll a and nutrient distribution and characteristics
708 in the Bohai Sea. *Marine Sciences*, 28 (4), 34–39 (in Chinese).

709

710 **Figure captions**

711 **Figure 1.** Study area and survey stations. Solid black circles represent the sampling stations and
712 white stars represent wastewater treatment plants. The gray scale shows water depth.

713

714 **Figure 2.** Variations in seawater surface salinity and temperature during the seven cruises in the
715 JZB. The solid black and open blue squares represent the average seawater surface temperature and
716 salinity. The upper and lower error bars represent the maximum and minimum of seawater surface
717 temperature (salinity) in the cruise. The thick gray line represents the daily average seawater
718 temperature in the JZB from December to April during the period of 2008-2016. The daily seawater
719 temperature data were from FRA-JCOPE2 reanalysis data in Japan
720 (<http://www.jamstec.go.jp/jcope/htdocs/e/home.html>) and were calculated using the JCOPE2 model
721 according to satellite data (for more method details, please refer to Miyazawa et al. (2017)).

722

723 **Figure 3.** Spatial distributions of seawater surface salinity and temperature during the seven cruises
724 in the JZB. The isoline represents salinity and the color scale shows temperature.

725

726 **Figure 4.** Spatial distributions of seawater surface $p\text{CO}_2$ during the seven cruises in the JZB (a-g).
727 Mean $p\text{CO}_2$ during the seven cruises and the upper and lower error bars represent the maximum and
728 minimum of $p\text{CO}_2$ in each cruise (h).

729

730 **Figure 5.** Spatial distributions of seawater surface DO% and Chl *a* during the seven cruises in the
731 JZB (a-g). The isoline represents Chl *a* and the color scale shows DO%. The mean DO% and Chl *a*
732 during the seven cruises and the upper and lower error bars represent the maximum and minimum
733 of DO% (Chl *a*) in each cruise (h).

734

735 **Figure 6.** Spatial distributions of seawater surface DIC and TA during the seven cruises in the JZB.
736 The isoline represents DIC and the color scale shows TA.

737

738 **Figure 7.** Spatial distributions of $\Delta p\text{CO}_2$ during the seven cruises in the JZB. $\Delta p\text{CO}_2$ represents the
739 difference between $np\text{CO}_2$ and *in situ* $p\text{CO}_2$. The $np\text{CO}_2$ represents the *in situ* $p\text{CO}_2$ normalized to
740 the average seawater temperature for each cruise.

741

742 **Figure 8.** Variations in $p\text{CO}_2$ (solid circle) and $Np\text{CO}_2$ (open circle) during the seven cruises.
743 $Np\text{CO}_2$ represents the average $p\text{CO}_2$ for each cruise normalized to the average seawater temperature
744 of all seven cruises.

745

746 **Figure 9.** Scatterplot of ΔDIC (red triangle) and ΔTA (black circle) with salinity in the JZB during
747 the seven cruises. ΔTA and ΔDIC are deviations calculated using Equations. 8 and 9.

748

749 **Figure 10.** Scatterplot of ΔTA vs. ΔDIC in the JZB during the seven cruises. The four lines represent
750 the theoretical ratio lines altered the ΔTA and ΔDIC by the direct treated sewage input, CaCO_3
751 precipitation/dissolution, biological process (primary production or respiration) and CO_2
752 evasion/invasion, respectively. The stations in northeastern area and western area were located in
753 the solid and dotted line circles in c, respectively. Color scale shows $\text{DO}\%$.

754

755 **Figure 11.** Scatterplot of $np\text{CO}_2$ vs. $\text{DO}\%$ (a) and $\text{DO}\%$ vs. salinity (b) on 13 December (solid
756 circles, y_1) and 21 December (open squares, y_2).

757

758 **Figure 12.** Spatial distributions of seawater surface $\Omega_{\text{arag}@\text{situ}}$ during the seven cruises in the JZB.

759

760 **Figure 13.** Scatterplot of $np\text{CO}_2$ vs. $\text{DO}\%$ (a) and $\text{DO}\%$ vs. $\text{Chl } a$ (b) in western area in early January
761 (solid triangles, y_1) and the entire bay in mid-January (open circles, y_2), late January (solid squares,
762 y_3) and late February (stars, y_4).

763

764 **Figure 14.** Scatterplot of $np\text{CO}_2$ vs. $\text{DO}\%$ (a) and $np\text{CO}_2$ vs. ΔTA (b). The open circles represent
765 the stations in northern area of the JZB.

766

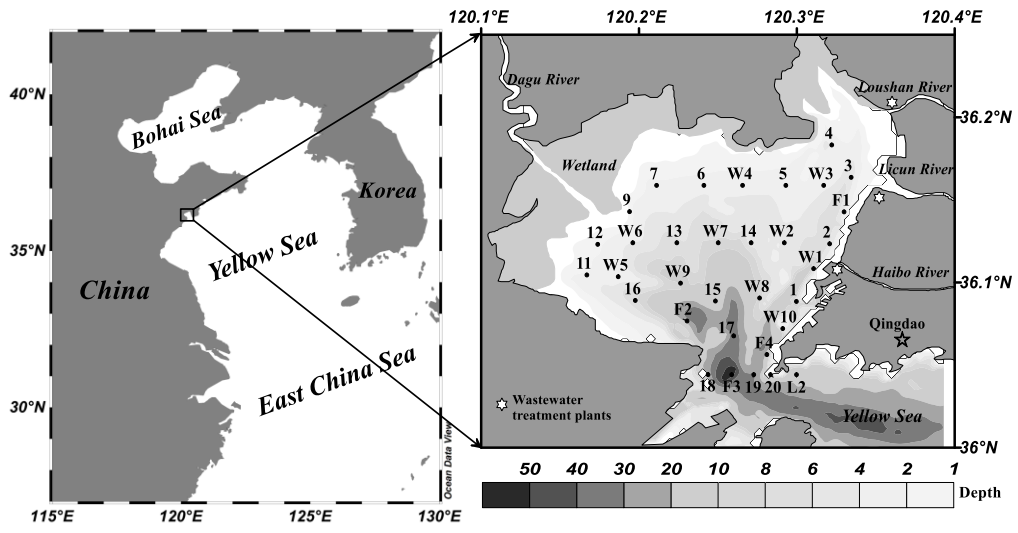
767 **Table. 1.** Summary of the sampling cruises. In late February, we only referenced the data covering
768 our research stations.

769

770 **Table. 2.** The values of salinity, DIC and TA of ocean end-member in each cruise during winter in
771 the JZB.

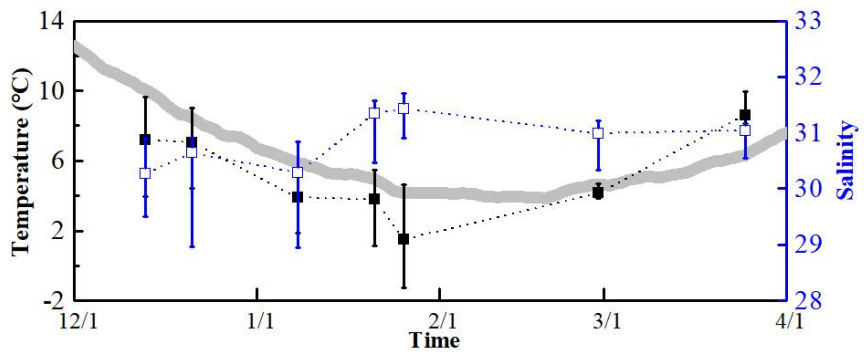
772 Figures

773 Figure 1.



774

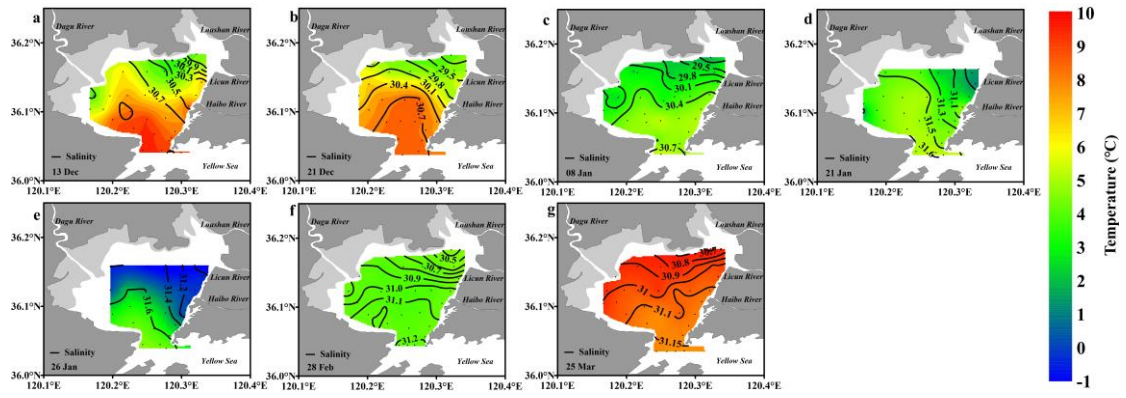
775 **Figure 2.**



776

777

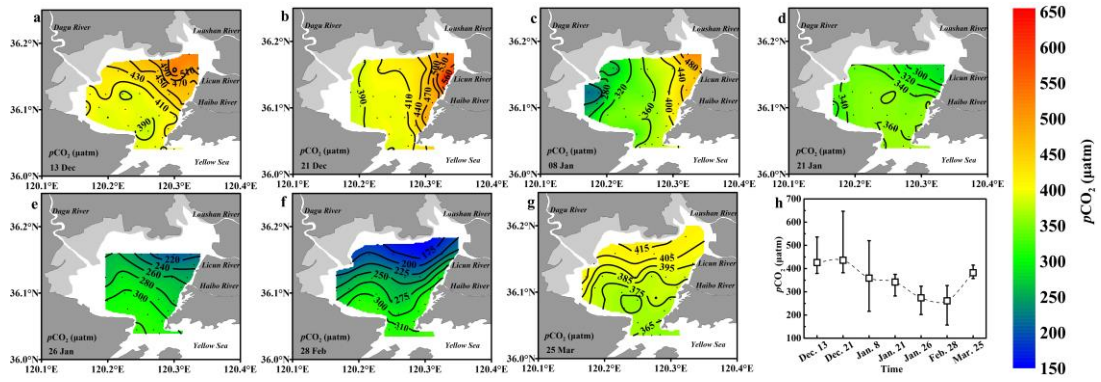
778 **Figure 3.**



779

780

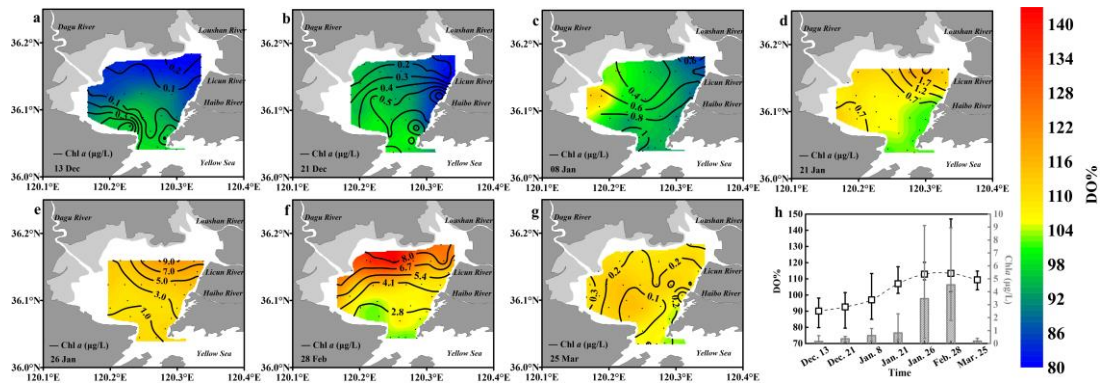
781 **Figure 4.**



782

783

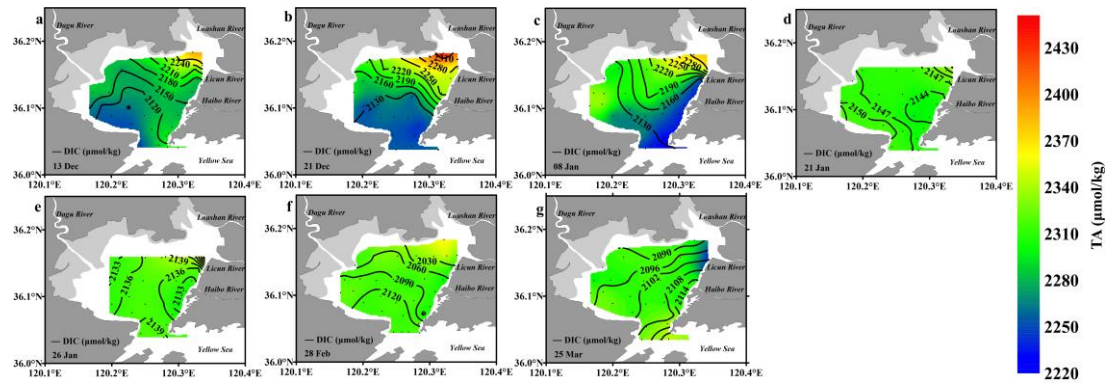
784 **Figure 5.**



785

786

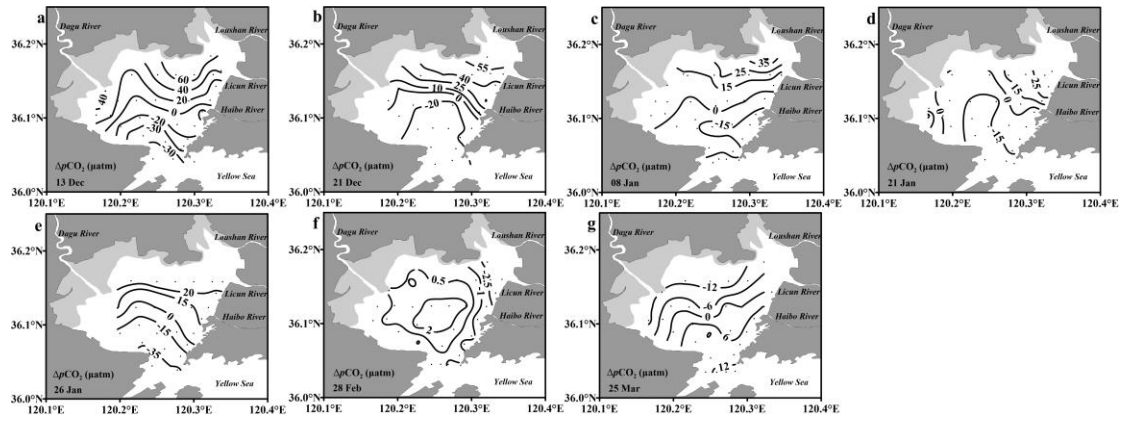
787 **Figure 6.**



788

789

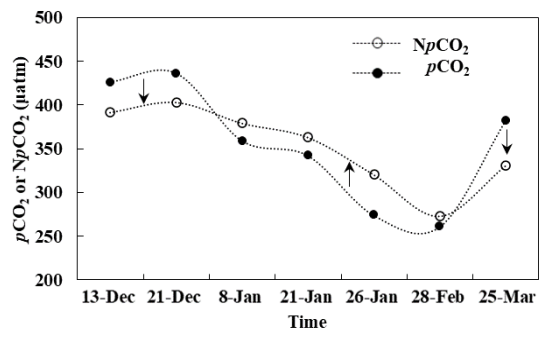
790 **Figure 7.**



791

792

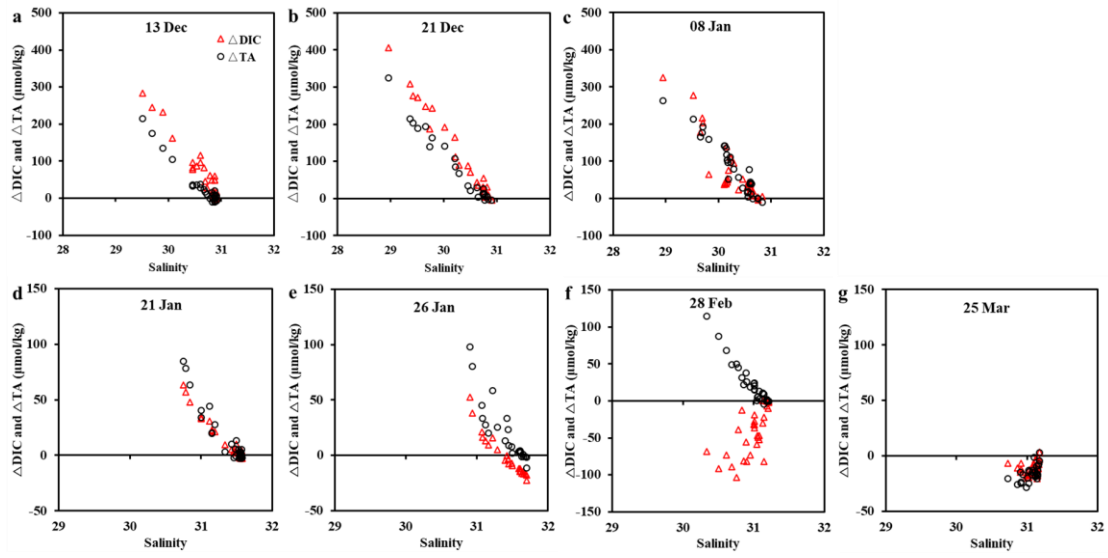
793 **Figure 8.**



794

795

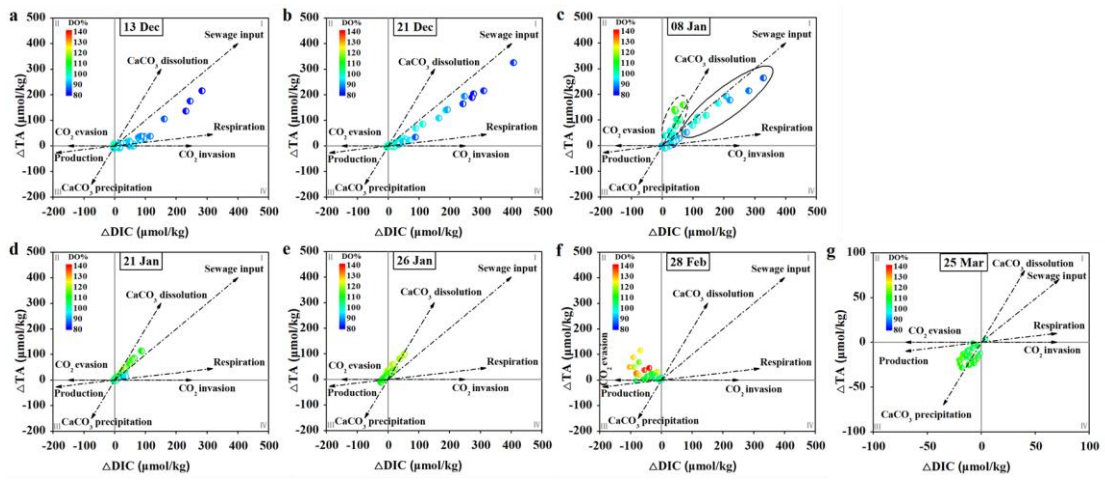
796 **Figure 9.**



797

798

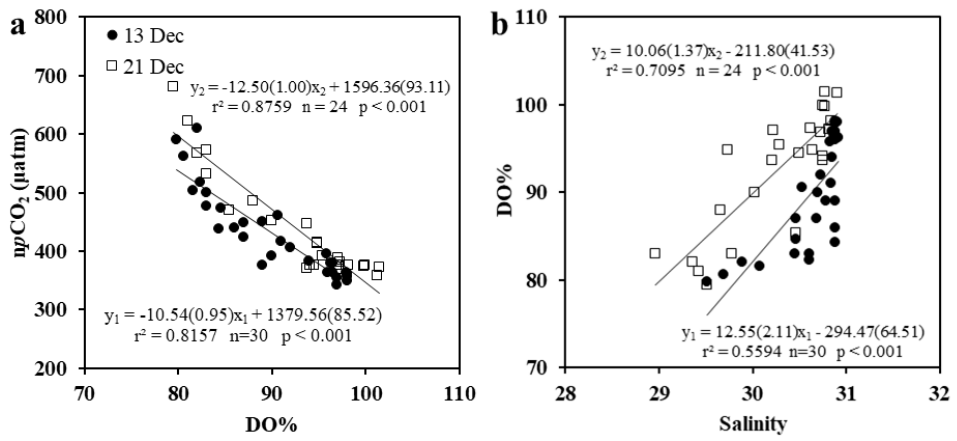
799 **Figure 10.**



800

801

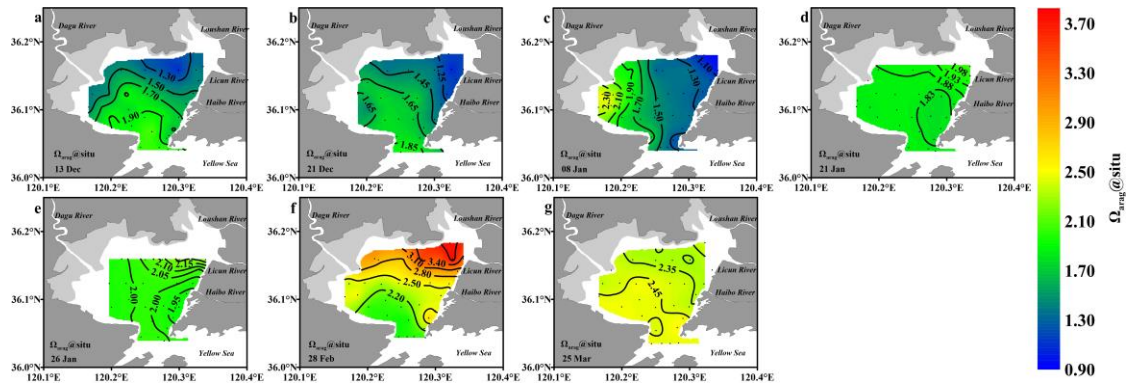
802 **Figure 11.**



803

804

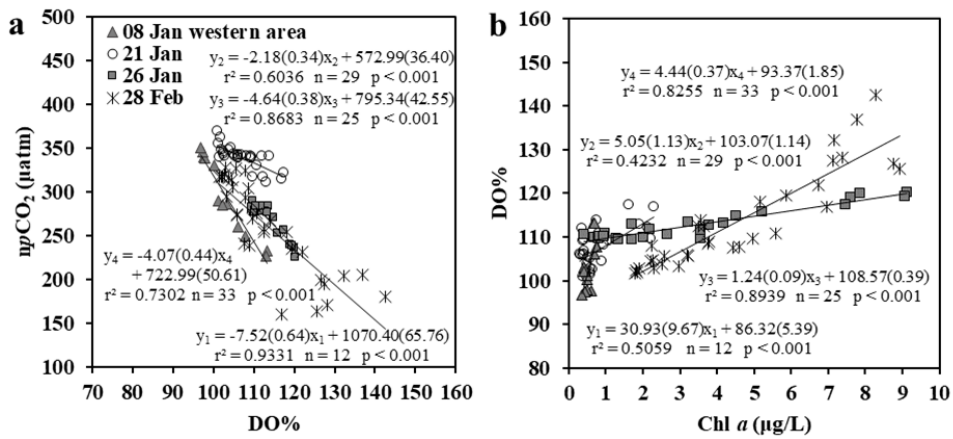
805 **Figure 12.**



806

807

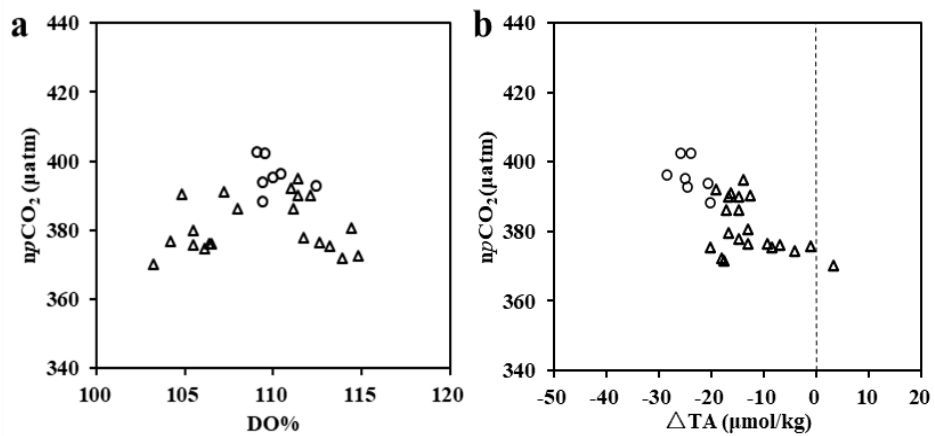
808 Figure 13.



809

810

811 Figure 14.



812

813

814 **Table. 1.**

Cruise	Surveying time	Number of stations	Reference/data source
December	13 Dec. 2014	30	This study
	21 Dec. 2011	24	This study
Early January	08 Jan. 2012	33	This study
Mid-January	21 Jan. 2016	29	Zang et al. (2018)
Late January	26 Jan. 2016	25	Zang et al. (2018)
Late February	28 Feb. 2008	33	Zhang et al. (2012)
March	25 Mar. 2014	30	This study

815

816 **Table. 2.**

Cruise	S _{ocean}	DIC _{ocean}	TA _{ocean}
13 Dec	30.88±0.00	2102±2	2277±1
21 Dec	30.84±0.07	2088±1	2255±1
08 Jan	30.75±0.00	2117±4	2240±0
21, 26 Jan	31.55±0.00	2147±1	2310±0
28 Feb	31.21±0.00	2140±2	2314±1
25 Mar	31.17±0.00	2122±0	2344±0

817