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# Spatial Variation in Aragonite Saturation State and the Influencing Factors in Jiaozhou Bay, China

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**Abstract:** Both natural processes and human activities affect seawater calcium carbonate saturation state ( $\Omega_{\text{arag}}$ ), while the mechanisms are still far from being clearly understood. This study analysed the seawater surface  $\Omega_{\text{arag}}$  during summer and winter in Jiaozhou Bay (JZB), China, based on two cruises observations performed in January and June 2017. The ranges of  $\Omega_{\text{arag}}$  values were 1.55–2.92 in summer and 1.62–2.15 in winter. Regression analyses were conducted to identify the drivers of the change of  $\Omega_{\text{arag}}$  distribution, and then the relative contributions of temperature, mixing processes and biological processes to the spatial differences in  $\Omega_{\text{arag}}$  were evaluated by introducing the difference between total alkalinity (TA) and dissolved inorganic carbon (DIC) as a proxy for  $\Omega_{\text{arag}}$ . The results showed that biological processes were the main factor affecting the spatial differences in  $\Omega_{\text{arag}}$ , with relative contributions of 70% in summer and 50% in winter. The contributions of temperature (25% in summer and 20% in winter) and the mixing processes (5% in summer and 30% in winter) were lower. The increasing urbanization in offshore areas can further worsen acidification, therefore environmental protection in both offshore and onshore is needed.

**Keywords:** aragonite saturation state; temperature; mixing processes; biological processes; Jiaozhou Bay

## 1. Introduction

Ocean acidification (OA) not only causes physical and chemical changes in the ocean but is also of widespread concern due to its serious impact on marine ecosystems and calcifying organisms [1–4]. Coastal waters are the most active areas for fishery production and shellfish farming, and studies related to OA mechanisms are a top priority in the region [5–7]. Unlike the open ocean, nearshore acidification is not only affected by global OA caused by increasing atmospheric CO<sub>2</sub> levels but also by the coupled effects of various processes, such as upwelling, organic matter degradation, primary production of phytoplankton and river input, due to the strong interaction between land and ocean, making the acidification mechanism in coastal waters more complicated [8–11]. In bays, which are highly affected by human disturbance, the mutual enhancement, interference and superimposition of the effects of the above processes are especially prominent. Therefore, clarifying the OA mechanism in this region will be helpful for understanding the OA process in coastal waters under

the coupled influence of natural processes and human activities, and will be of great significance for predicting the developing trend and impact of OA and formulating appropriate mitigation measures in coastal waters.

Compared with pH and carbonate ion concentration ( $[\text{CO}_3^{2-}]$ ), calcium carbonate saturation ( $\Omega$ ) is more directly indicative of the effect of acidification on biocalcification [12,13].  $\Omega$  is defined as the product of calcium and carbonate ion concentrations divided by the apparent solubility product ( $K_{sp}^*$ ) of calcium carbonate, i.e.,  $\Omega = [\text{Ca}^{2+}] [\text{CO}_3^{2-}] / K_{sp}^*$  [14]. When  $\Omega < 1.0$ , waters are undersaturated with respect to carbonate minerals, and the outer shell and skeleton of the organism should dissolve [15,16]. Calcite and aragonite are the main existing forms of  $\text{CaCO}_3$  in the marine environment. The solubility of aragonite is about 50% higher than that of calcite at 25 °C [17], and aragonite is usually the most abundant carbonate mineral in the shallow sea area [18]. Therefore, the aragonite saturation state ( $\Omega_{\text{arag}}$ ) is often used as an indicator for assessing the effects of natural processes and human activities on marine calcareous organisms in coastal waters [5,19,20].

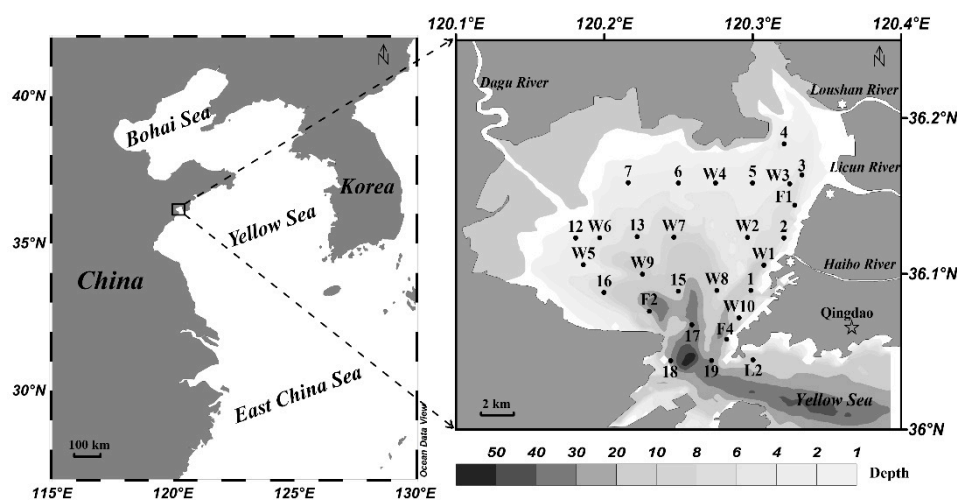
In recent years, marine  $\Omega_{\text{arag}}$  has attracted considerable attention, and analytical methods have gradually developed from qualitative identification of parameters to quantitative estimation in some shelf areas and estuary regions [10,21,22]. However, related studies in the bays which have been affected by serious human disturbance are still rare, and most analysis focus on the use of correlations between parameters or semi-quantitative methods. In the Jinhae Bay, South Korea, Kim et al. [23] found that biological activity was a major factor controlling  $\Omega_{\text{arag}}$  over four seasons according to the strong linear correlation between the  $\Omega_{\text{arag}}$  values and dissolved oxygen concentrations. In Tokyo Bay, Japan, the vertical distribution of salinity, dissolved oxygen (DO) and carbonate parameters showed that  $\Omega_{\text{arag}}$  was high at the surface as a result of photosynthesis and low at the bottom due to remineralization of organic matter. Moreover, researchers estimated the change of  $\Omega_{\text{arag}}$  since the preindustrial period and by the end of this century using the CO2SYS program and a high  $\text{CO}_2$  emission scenario Rcp8.5 in IPCC AR5 [24]. Cotoviz et al. [25] investigated the dynamics of  $\Omega_{\text{arag}}$  in Guanabara Bay, Brazil, which is dominated by phytoplankton bloom. The slope of the linear regression between  $\Omega_{\text{arag}}$  and the apparent utilization of oxygen (AOU) had a very close behavior with the Redfield ratio. They concluded that eutrophication controlled the variations of  $\Omega_{\text{arag}}$  in Guanabara Bay. Obviously, the quantitative approach has been increasingly applied in the recent studies on  $\Omega_{\text{arag}}$ . Similarly, the quantitative methods are used in the current study.

Jiaozhou Bay (JZB) (35°18'~36°18' N, 120°04'~120°23' E) is a typical semi-closed shallow bay in northern China and is highly affected by urbanization. Under the influence of urban domestic and aquaculture wastewater discharge, large amounts of N, P and chemical oxygen demand (COD) substances are imported into the bay through rivers such as the Haibo River, Licun River and Loushan River in the eastern area of the bay [26,27], resulting in a perennial eutrophication state in the entire bay. The reported chlorophyll *a* data from the past 20 years showed that the biomass of phytoplankton exhibits a clear bimodal pattern with peaks in summer and winter in the bay [28–30]. Furthermore, JZB is an important shellfish-farming area [31], where scallop, clam and others are vulnerable to low  $\Omega$ . In recent years, many researchers have conducted extensive studies on the changes in seawater surface dissolved inorganic carbon (DIC), total alkalinity (TA) and  $\text{CO}_2$  partial pressure in JZB [11,32,33], but there is little analysis and discussion of  $\Omega_{\text{arag}}$ , especially its controlling processes. Therefore, through two cruise-based investigations in JZB during summer and winter when biological activity is strongest, this study analyses the spatial distribution characteristics of  $\Omega_{\text{arag}}$  in detail and reveals the main processes that cause the spatial distribution difference in  $\Omega_{\text{arag}}$  by qualitative analysis and quantitative calculation. The results of this study can offer a reference for understanding the control mechanism of  $\Omega_{\text{arag}}$  in coastal waters under the influence of human activities.

## 2. Study Area and Methods

### 2.1. Study Area

JZB is located on the southern side of the Shandong Peninsula in China (Figure 1). The city of Qingdao encloses the bay on three sides, and seawater exchange occurs only through the southern part of the bay. JZB covers a water area of 302.9 km<sup>2</sup>, and the average water depth is 7 m. The climate is dominated by the East Asian Monsoon, with northerly wind in winter and southerly wind in summer. The tidal current in JZB is a regular semi-diurnal tide that induces strong vertical mixing, resulting in nearly homogeneous vertical profiles in term of seawater temperature and salinity [34]. Most of the rivers that enter JZB have no natural runoff under most conditions except for significant heavy rainfall. In the eastern area of the bay adjacent to the downtown of Qingdao, a wastewater treatment plant (WWTP) is located beside each of the major estuaries (Licun River, Haibo River and Loushan River). Therefore, the estuaries have become conduits for wastewater [27]. In the western area of the bay, which has an ecological wetland with an area over 50 km<sup>2</sup>, the seawater is relatively cleaner [35].



**Figure 1.** Study area and sampling stations. Solid circles represent the sampling stations, and solid white stars represent wastewater treatment plants (WWTPs). The grey scale shows the bottom seawater depth.

## 2.2. Survey Stations and Sample Processing

The basic data included those collected at 28 stations on 28 June 2017 during summer [35] and on 17 January 2017 during winter (Figure 1). All seawater samples were collected from the seawater surface at a depth of approximately 1.5 m because of the homogeneous vertical profiles in the JZB water column [34]. In addition to basic hydrological parameters, such as seawater temperature and salinity, dissolved oxygen saturation (DO%), dissolved inorganic carbon (DIC) and pH were also measured. Among the measured parameters, seawater temperature, salinity and DO% were automatically recorded each second and averaged over 1 min, while DIC was measured within one week after the seawater sample was transferred to the laboratory.

Surface temperature and salinity were measured using an SBE 45 Micro TSG (Sea-Bird, Inc., Bellevue, WA, USA), with a nominal precision of 0.002 °C for temperature and 0.005 for salinity. The DO% was measured with a YSI-5000 oxygen analyser (YSI Corporation, Yellow Spring, OH, USA), which was calibrated using the Winkler titration method (nominal precision: 0.1%). The DIC samples were directly collected from the Niskin bottles using a syringe and filtered through a 0.45 µm disposable syringe filter to avoid exchange with the air. The DIC samples were all poisoned with saturated mercury chloride (final concentration: c. 0.02% by volume) and measured by acid extraction using a DIC analyser (AS-C2, Apollo SciTech, Newark, DE, USA). In the process of DIC measurements, Certified Reference Materials (CRMs) from Scripps Institution of Oceanography were used for quality control, and the precision and accuracy level were 0.1%. pH was determined *in situ* using an Orion Star-A211 Plus pH Benchtop Meter with a Ross pH electrode (Thermo Fisher Scientific Inc., Beverly, MA, USA), calibrated according to standards from the National Bureau of Standards (NBS Standard) with values of 4.00, 6.86 and 9.18 at 25 °C. The precision of pH measurement was

0.01. Additionally, pH samples were also transferred to the laboratory and measured at a constant temperature of 25 °C for calibration.

### 2.3. Calculation of $\Omega_{\text{arag}}$ and TA

Considering the possible effects of organic acids on TA, the calculation of  $\Omega_{\text{arag}}$  avoided using TA. The  $\Omega_{\text{arag}}$  values at *in situ* temperature were calculated from the DIC, pH, *in situ* temperature and *in situ* salinity values using the CO<sub>2</sub> program [36] and the CO<sub>2</sub> system coefficients of Mehrbach et al. [37] as refitted by Dickson and Millero [38]. The  $K_{\text{sp}}^*$  values for aragonite were taken from Mucci [17], and the Ca<sup>2+</sup> concentrations were assumed to be proportional to salinity, as presented in Millero [39]. Additionally, TA was also obtained in the above calculation process.

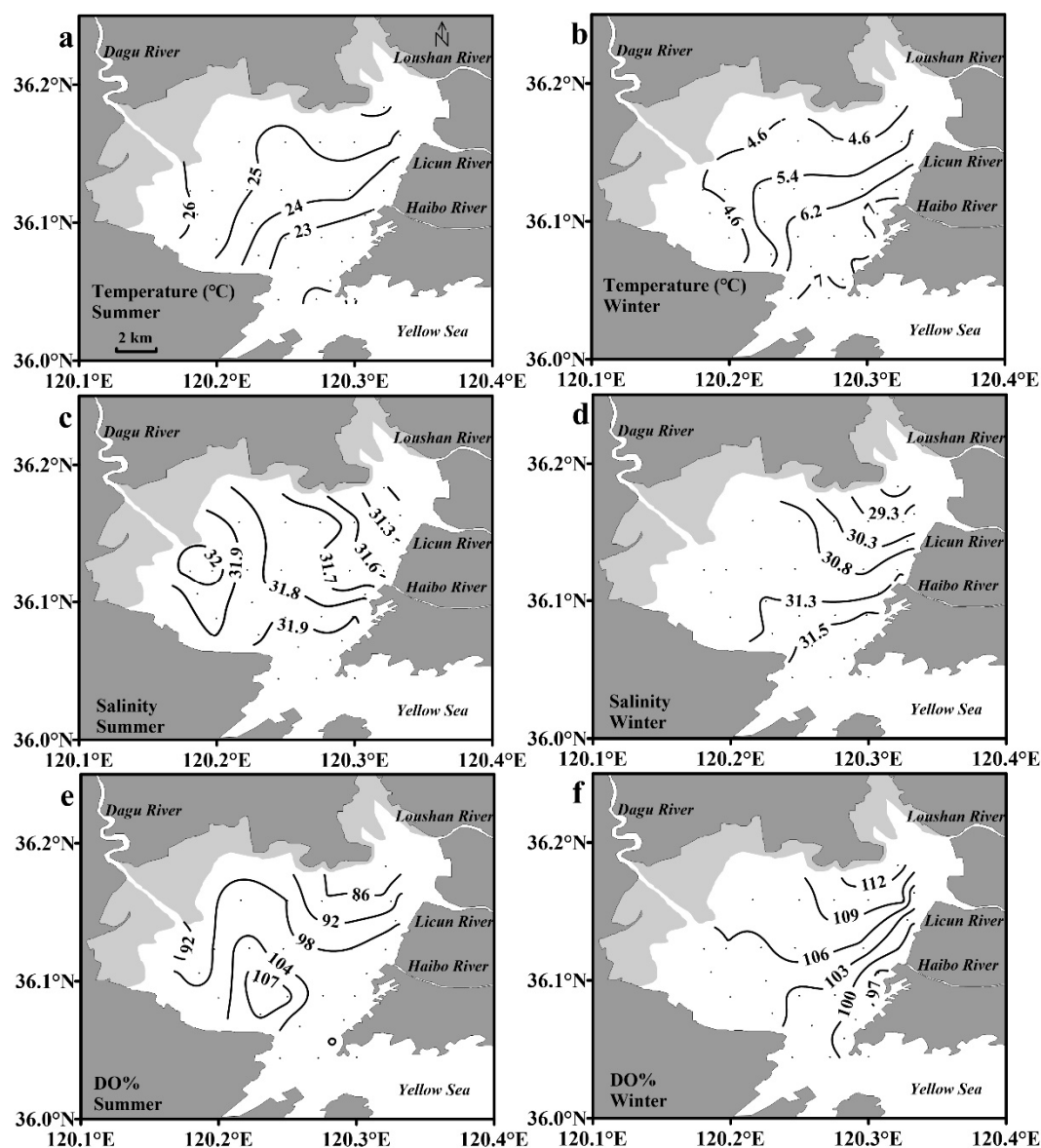
### 2.4. Statistical Analyses

The correlations between  $\Omega_{\text{arag}}$  and environmental variables were analysed using Excel (Office 2016, Microsoft, Redmond, WA, USA). All statistical analyses were at significance level of 0.05.

## 3. Results and Discussion

### 3.1. Variations in Seawater Surface Temperature, Salinity and DO%

The seawater surface temperature was between 21.8 °C and 26.2 °C, with an average of 24.0 °C, in JZB during the summer, showing a decreasing trend from the upper end of the bay to the mouth of the bay. The highest temperature value appeared in the western area of the bay with the shallowest water depth. The temperature variation range in winter was 3.8~7.8 °C, and the average value was 5.8 °C. Due to the effects of land cooling, the temperature increased from the upper end of the bay to the mouth area, and the lowest value appeared in the western area. The ranges of seawater surface salinity were 31.0~32.1 in summer and 27.8~31.6 in winter, with average values of 31.8 and 30.9, respectively. The salinity variation gradient in winter was great and may have been related to the strong exchange of seawater between the Yellow Sea and the bay. In terms of distribution, the salinity showed an increasing trend from the northeastern area to the mouth area in the two periods. The salinity was the lowest and the gradient changed drastically in the northeastern area. Most of the rivers that enter JZB have no natural runoff at most of the time of a year and the estuaries have become conduits for wastewater discharge [27]. The total amount of wastewater treated by the three WWTPs located near the northeastern area of JZB is up to ~510,000 tons per day (Figure 1). Therefore, the direct input of treated wastewater was the main reason for the low salinity in this region [11,33]. Additionally, a high-salinity area with a value higher than 30.9 was found in the nearshore area of the western area in summer. Considering the shallow water depth (< 2 m) and the long water residence time (~100 d) in this region, it may be caused by strong evaporation. The range of seawater surface DO% was 81.1%~108.6% in summer, with an average of 98.7%. The DO values were unsaturated in the northeastern area and the area near the estuary of the Dagū River, while those in other areas were supersaturated. The lowest DO% value appeared in the northeastern area of the bay, and the highest value was observed in the southwestern area. The DO% values in winter were higher than those in summer, ranging from 96.5% to 113.8%, with an average of 103.9%. Except for the area near the estuary of the Haibo River, the DO in the entire bay was supersaturated, with the highest value (> 110%) appearing in the northeastern area. In addition, the DO% distribution roughly showed a reverse pattern of the summer, and the DO% values decreased from the northeastern area to the mouth area (Figure 2).

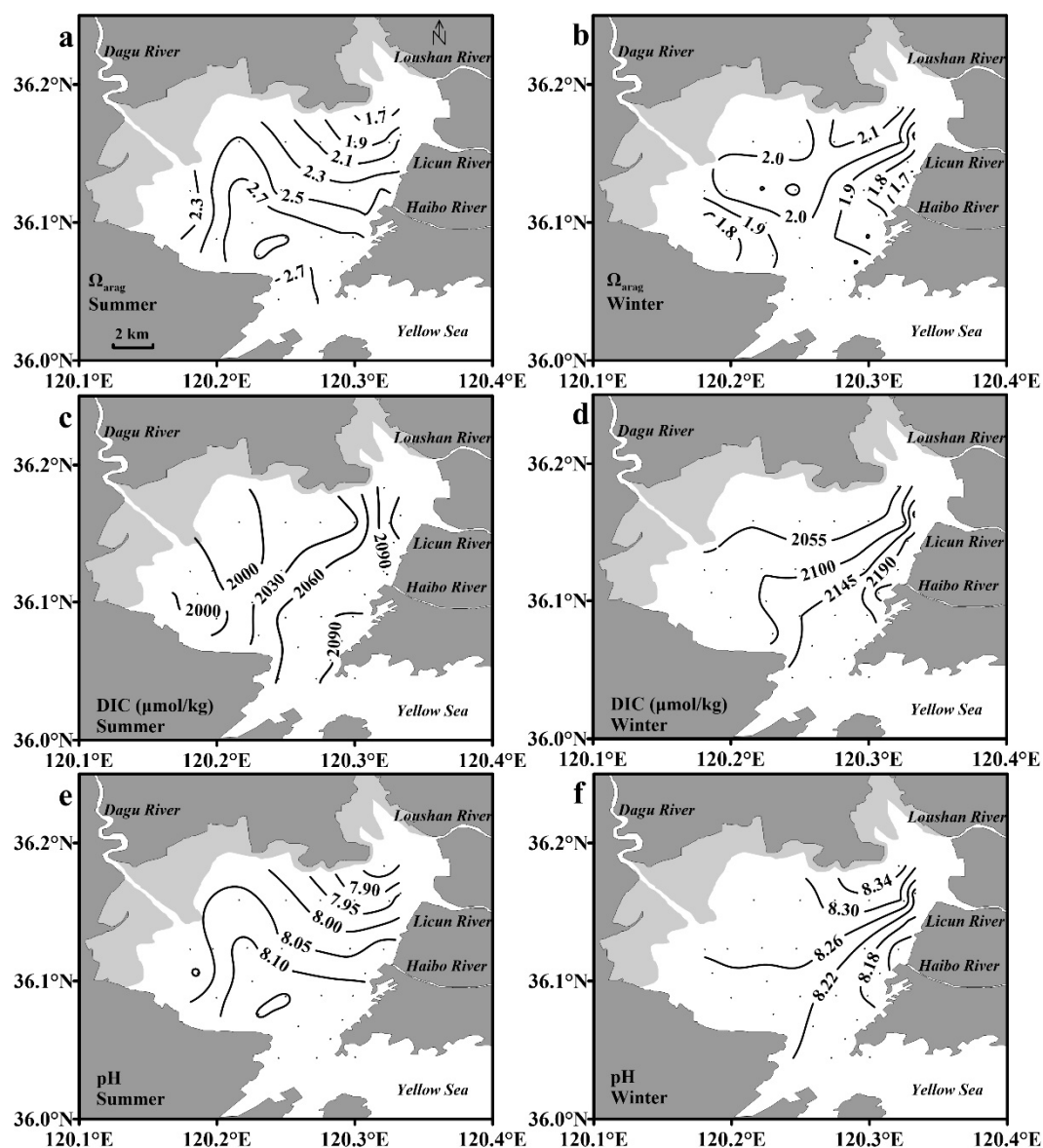


**Figure 2.** Distributions of seawater surface temperature (a,b), salinity (c,d) and dissolved oxygen saturation (DO%) (e,f) in Jiaozhou Bay (JZB) during summer (a,c,e, on 28 June 2017) and winter (b,d,f, on 17 January 2017).

### 3.2. Variations in Seawater Surface $\Omega_{\text{arag}}$ , DIC and pH

The seawater surface  $\Omega_{\text{arag}}$  was supersaturated in JZB during summer and winter. The  $\Omega_{\text{arag}}$  values in summer ranged from 1.55 to 2.92, with an average of 2.47, and the gradient variation was great. The lowest  $\Omega_{\text{arag}}$  value ( $< 2.10$ ) was in the northeastern area, while values in most other areas exceeded 2.50, and the highest value ( $> 2.70$ ) appeared in the nearshore area of the southwestern area. The  $\Omega_{\text{arag}}$  values in winter were between 1.62 and 2.15, with an average of 1.93. The  $\Omega_{\text{arag}}$  gradient variation in this period was obviously more gradual than that in summer, and the  $\Omega_{\text{arag}}$  value in most areas of JZB was approximately 1.90. The surface DIC ranged from 1979  $\mu\text{mol/kg}$  to 2135  $\mu\text{mol/kg}$ , with an average of 2057  $\mu\text{mol/kg}$ , and the value showed a trend of increasing from the western area to the mouth area in summer. In winter, the DIC was in the range of 2027–2249  $\mu\text{mol/kg}$ , with an average of 2122  $\mu\text{mol/kg}$ , and generally increased from the northern area to the mouth area. The highest DIC value appeared in the area near the estuary of the Haibo River. The surface pH value ranged from 7.81 to 8.16, with an average of 8.06, and showed an increasing trend from the northeastern area to the mouth area in summer with high water temperature. In the winter with low water temperatures, the pH level was obviously higher, ranging from 8.12 to 8.37, with an average of

8.24. Moreover, the pH distribution trend was opposite that in summer and showed a trend of decreasing from the northeastern area to the mouth area (Figure 3).



**Figure 3.** Distributions of seawater surface  $\Omega_{\text{arag}}$  (a,b), DIC (c,d) and pH (e,f) in JZB during summer (a,c,e, on 28 June 2017) and winter (b,d,f, on 17 January 2017).

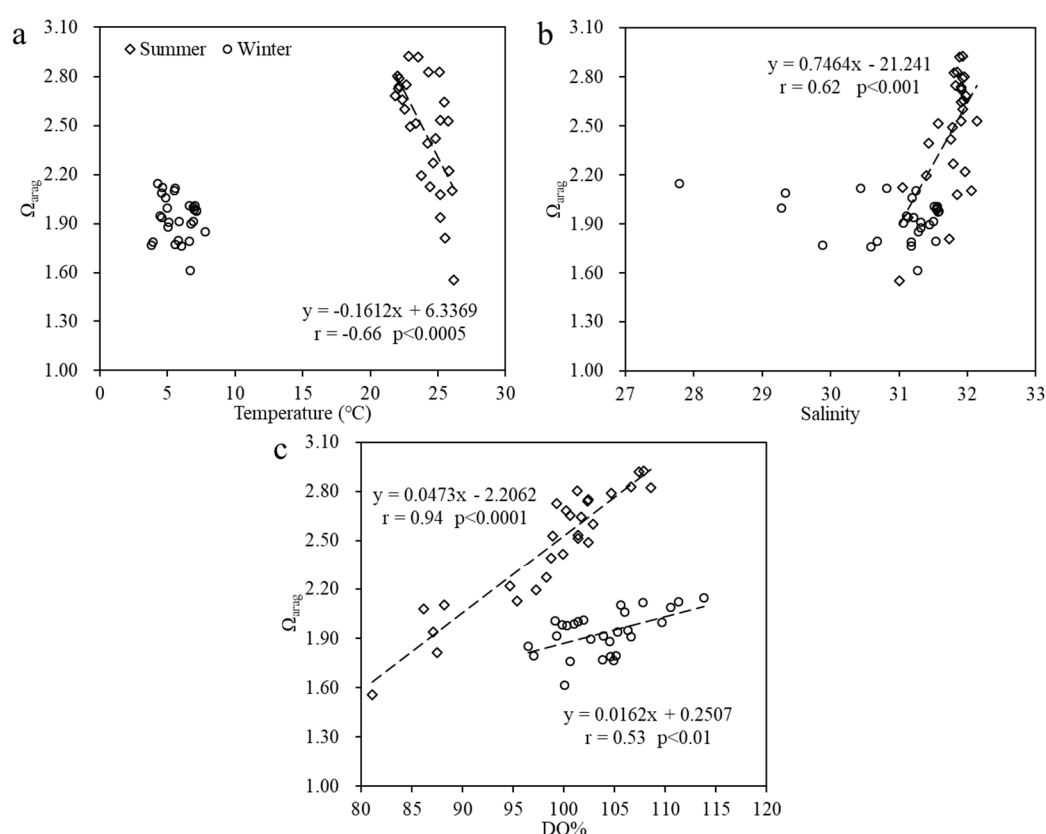
### 3.3. Qualitative Identification of the Main Factors Controlling the Spatial Distribution of Surface $\Omega_{\text{arag}}$

In coastal waters, seawater surface  $\Omega$  is mainly controlled by temperature, mixing processes (mixing between terrestrial input and seawater) and biological processes [8,20,40,41]. The influence of temperature on  $\Omega$  is mainly manifested in two aspects. On the one hand, without changing TA and DIC, an increase in seawater temperature can increase the first and second carbonic acid dissociation constants ( $k_1$  and  $k_2$ ) of carbonic acid and decrease the  $K_{sp}^*$  of calcium carbonate [17,37], thereby promoting an increase in  $\Omega$ . The difference between highest and lowest seawater temperatures for each investigated cruise were small: 4.4 °C in summer and 4.0 °C in winter. By normalizing the  $\Omega_{\text{arag}}$  of each station at *in situ* seawater temperatures to the average seawater temperature (24.01 °C for the summer and 5.76 °C for the winter) of the corresponding cruises, it is found that the change of  $\Omega_{\text{arag}}$  before and after the normalization was very small:  $\leq 0.04$  in summer and  $\leq 0.02$  in winter. The variation in difference between highest and lowest  $\Omega_{\text{arag}}$  values for each investigated cruise did not exceed 4% after normalization. This indicated that this process had little effect on the spatial



distribution of  $\Omega_{\text{arag}}$  difference. On the other hand, an increase in seawater temperature can reduce the DIC level by reducing the solubility of  $\text{CO}_2$  in seawater without changing TA [42], thereby increasing  $\Omega$ . Since the change in  $\text{CO}_2$  solubility in seawater often directly affects the  $\text{CO}_2$  exchange process at the sea-air interface, this effect is usually strong [20,41]. However, the  $\Omega_{\text{arag}}$  had no obvious correlation with seawater temperature in JZB during winter and a somewhat negative correlation in summer (Figure 4a). Obviously, temperature was not the main reason for the spatial distribution differences of  $\Omega_{\text{arag}}$  in these two cruises.

Terrestrial runoff usually has low pH and  $[\text{CO}_3^{2-}]$  values, which directly lead to a decrease in  $\Omega_{\text{arag}}$  in the receiving water body [21,43]. The rivers entering JZB have no natural runoff, but the daily discharges of the Licun River WWTP, the Lushan River WWTP and the Haibo River WWTP, which are located at the three estuaries in the eastern area of the bay, are up to 250,000, 100,000 and 160,000 tons, respectively [11,44]. The direct input of treated wastewater has become the main form of terrestrial input, and unlike natural rivers affected by seasonal changes, treated wastewater input is a persistent process. The pH values of the treated wastewater from the three WWTPs were 7.16–7.33 in January and 7.44–7.50 in June [44]. The wastewater input with low pH values would directly reduce the  $\Omega_{\text{arag}}$  in the northeastern area of JZB. In summer, the  $\Omega_{\text{arag}}$  values in the northeastern area were just significantly lower than those in the central and mouth areas with high salinity values (Figure 3c). However, the  $\Omega_{\text{arag}}$  in the northeastern area was relatively high in winter, indicating that the effect of treated wastewater input was masked by other factors (Figure 3b).



**Figure 4.** Scatterplots of seawater surface  $\Omega_{\text{arag}}$  vs. temperature (a), salinity (b) and DO% (c) in JZB during summer (28 June 2017) and winter (17 January 2017). Diamonds and circles represent the summer cruise and winter cruise, respectively.

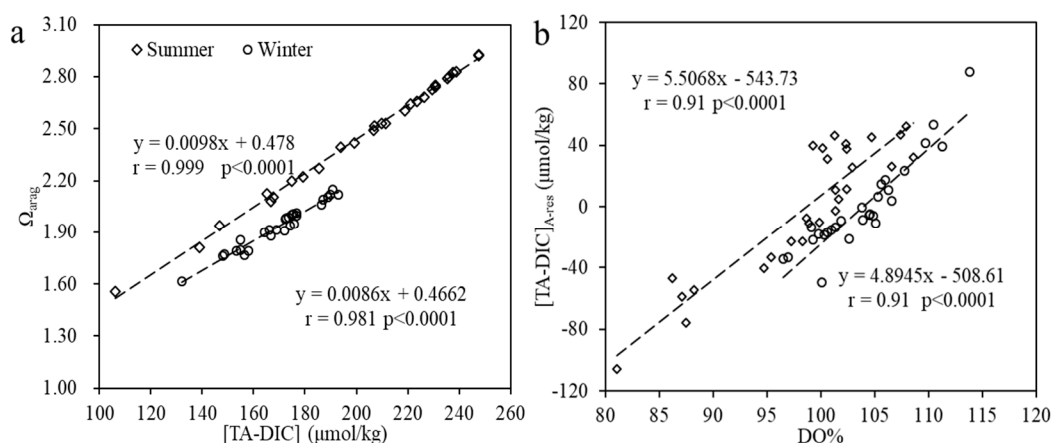
Biological processes mainly include primary production and aerobic respiration. Primary production produces oxygen and consumes  $\text{CO}_2$ , thus increasing  $\Omega_{\text{arag}}$  [45]. Conversely, aerobic respiration consumes oxygen and reduces  $\Omega_{\text{arag}}$ . During the summer,  $\Omega_{\text{arag}}$  had an excellent positive correlation with DO% (Figure 4c) ( $r = 0.94$ ,  $p < 0.0001$ ), suggesting that biological processes were the main factor affecting the distribution of  $\Omega_{\text{arag}}$  in JZB and might explain the main differences in the

spatial distribution of  $\Omega_{\text{arag}}$ . According to the unsaturated DO levels, the dominance of aerobic respiration resulted in the lowest  $\Omega_{\text{arag}}$  in the northeastern area of JZB. However, in most other areas of JZB, the DO was supersaturated, and primary production was dominant, which led to higher  $\Omega_{\text{arag}}$  levels. During the winter, the oversaturated DO values in most areas of the entire bay meant that primary production was dominant, but the relationship between DO% and  $\Omega_{\text{arag}}$  only showed a relatively weaker negative correlation (Figure 4c) ( $r = 0.53$ ,  $p < 0.01$ ), indicating that the control of biological processes on the spatial distribution of  $\Omega_{\text{arag}}$  in winter was weaker than that in summer. Despite this, considering that  $\Omega_{\text{arag}}$  had no significant correlations with seawater temperature and salinity (Figure 4a,b), primary production may still be the main factor affecting the  $\Omega_{\text{arag}}$  distribution in winter, and the weak negative correlation between DO% and  $\Omega_{\text{arag}}$  may be the result of the effects of the mixing processes and regional temperature variation. For example, treated wastewater input with low pH values could decrease the  $\Omega_{\text{arag}}$  levels in the northeastern area where the DO% (> 107%) values were highest, the low seawater temperature could cause a decrease in  $\Omega_{\text{arag}}$  in the western area where the DO% values were approximately 105%, and the strong external seawater exchange could cause an increase in  $\Omega_{\text{arag}}$  in the mouth area where the DO% values were near 100% (Figure 2b,f and Figure 3b).

The regression analysis indicates that biological processes may be the main factor affecting the spatial difference of  $\Omega_{\text{arag}}$  in JZB during summer and winter, while the influence of temperature and mixing processes is relatively smaller. However, the specific contributions of the above three processes could not be calculated if only using the regression analysis, and the correlation between parameters may even obscure the important role of certain processes in some cases. For example, direct input of the treated wastewater had the most significant impact in the northeastern area with the lowest DO% values and the strongest degradation of organic matter during summer, and the excellent positive correlation between  $\Omega_{\text{arag}}$  and DO% (Figure 4c) partly included the contribution of the treated wastewater input. Therefore, a further quantification analysis involving the contributions of the above three processes to the spatial distribution of  $\Omega_{\text{arag}}$  is still necessary.

### 3.4. Processes Controlling the Spatial Distribution of Surface $\Omega_{\text{arag}}$ Revealed by Quantitative Evaluation

In the carbonate system, the change in  $\Omega_{\text{arag}}$  with salinity is nonlinear and non-conservative, so  $\Omega_{\text{arag}}$  is not convenient for quantitative calculations. The  $\Omega_{\text{arag}}$  in seawater is essentially determined by the  $[\text{CO}_3^{2-}]$  value, and the difference between TA and DIC ( $[\text{TA-DIC}]$ ) can reflect the levels of  $[\text{CO}_3^{2-}]$  well, thereby acting as a good proxy for  $\Omega_{\text{arag}}$  [20,46]. As shown in Figure 5a, a significant positive correlation (with  $r$  values close to 1) was observed between  $\Omega_{\text{arag}}$  and  $[\text{TA-DIC}]$  in JZB in both summer and winter. Thus, the effects of the temperature, mixing processes and biological processes on  $\Omega_{\text{arag}}$  could be converted to  $[\text{TA-DIC}]$ . To quantify the contribution of each factor to  $[\text{TA-DIC}]$ , the  $[\text{TA-DIC}]$  and salinity of each station were subtracted from the average  $[\text{TA-DIC}]$  and salinity values of the corresponding cruises, and then  $[\text{TA-DIC}]_A$  and  $S_A$  were obtained. Accordingly, the above evaluation problem was transformed into the calculation of the contribution to  $[\text{TA-DIC}]_A$  from temperature variation, the mixing processes and biological processes.



**Figure 5.** Scatterplots of seawater surface  $\Omega_{arag}$  vs. [TA-DIC] (a) and [TA-DIC]<sub>A-res</sub> vs. DO% (b) in JZB during summer (28 June 2017) and winter (17 January 2017). [TA-DIC] represents the difference between TA and DIC. [TA-DIC]<sub>A-res</sub> represents the [TA-DIC]<sub>A</sub> values after the deduction of the effects from temperature and mixing processes according to Equation (4). [TA-DIC]<sub>A</sub> represents the difference between the [TA-DIC] value of the station and the average [TA-DIC] value during one cruise.

For the contribution of temperature variation, only the effect of temperature on the solubility of  $\text{CO}_2$  in seawater was evaluated in these two cruises, due to the negligible  $\Omega_{arag}$  changes caused by the variation of  $k_1$  and  $k_2$  of carbonic acid and  $K_{sp}^*$  of calcium carbonate from temperature (Section 3.3). In the calculation process, taking the average TA and salinity of the cruise as the starting values (the average TA and salinity were  $2260.1 \mu\text{mol/kg}$  and  $31.76$  in summer and  $2291.4 \mu\text{mol/kg}$  and  $30.93$  in winter, respectively) and assuming seawater  $\text{CO}_2$  reached equilibrium with the atmosphere at *in situ* temperature of each station, this research calculated the corresponding DIC ( $\text{DIC}_{eq}$ ) of each station at different temperatures and the DIC ( $\text{DIC}_{avg}$ ) at the average temperature of the corresponding cruise at this equilibrium state using the CO2SYS program [36]. Then, the difference between  $\text{DIC}_{avg}$  and  $\text{DIC}_{eq}$  was the contribution from the temperature of the corresponding station to [TA-DIC]<sub>A</sub> ([TA-DIC]<sub>A-tem</sub>) (Equation (1)).

$$[\text{TA-DIC}]_{A-tem} = \text{DIC}_{avg} - \text{DIC}_{eq} \quad (1)$$

where the  $\text{DIC}_{eq}$  and  $\text{DIC}_{avg}$  are the DIC value at *in situ* temperature of the station and at the average temperature of the corresponding cruise, respectively, when seawater  $\text{CO}_2$  reached equilibrium with the atmosphere. Atmospheric  $\text{CO}_2$  concentration data from flask measurements in the Tae-ahn Peninsula ( $126.13^\circ \text{E}$ ,  $36.73^\circ \text{N}$ ) adjacent to the southern Yellow Sea were used, with values of  $410 \mu\text{atm}$  in January 2017 and  $395 \mu\text{atm}$  in June 2017, respectively ([ftp://ftp.cmdl.noaa.gov/data/greenhouse\\_gases/co2/flask](ftp://ftp.cmdl.noaa.gov/data/greenhouse_gases/co2/flask)).

For the contribution of the mixing processes to [TA-DIC]<sub>A</sub>, considering that the direct input of treated wastewater is the main form of terrestrial input, this study used the [TA-DIC] values of the treated wastewater and the station in the mouth area of the bay with the highest salinity as the freshwater and seawater end-member, respectively. Thus, the change ratio of [TA-DIC] per unit salinity was obtained. The [TA-DIC] values of the treated wastewater were obtained from Liu et al. [44], and the [TA-DIC] value of the freshwater end-member was calculated according to the proportion of three WWTPs' discharge ( $\sum([\text{TA-DIC}]_i \times Q_i) / \sum Q_i$ ,  $Q$  was the charge, Table 1). The freshwater end-member values were  $-405 \mu\text{mol/kg}$  in January and  $-110 \mu\text{mol/kg}$  in June. The seawater end-member set to the L2 station, which was closest to the Yellow Sea, and the [TA-DIC] and salinity values were  $173 \mu\text{mol/kg}$  and  $31.6$  in January and  $236 \mu\text{mol/kg}$  and  $32.0$  in June, respectively. Then, the contribution of the mixing processes to the [TA-DIC]<sub>A</sub> ([TA-DIC]<sub>A-mix</sub>) were calculated by multiplying by  $S_A$  (Equation (2)).

$$[\text{TA-DIC}]_{A-mix} = ([\text{TA-DIC}]_{tw} - [\text{TA-DIC}]_{sea}) / (-S_{sea}) \times S_A \quad (2)$$

where the  $[TA-DIC]_{tw}$  and  $[TA-DIC]_{sea}$  are the  $[TA-DIC]$  values of the treated wastewater and seawater end-member, respectively;  $S_{sea}$  is the salinity of the seawater end-member.  $S_A$  is the difference between salinity of station and average salinity of the corresponding cruise.

**Table 1.** Discharge of three WWTPs in January and June, and their corresponding temperature, TA, DIC and  $[TA-DIC]$  [44]. HBR, LCR and LSR were Haibo River, Licun River and Loushan River, respectively. The end-member values of  $[TA-DIC]$  were calculated by  $[TA-DIC]$  values of three WWTPs according to the proportion of discharge.

Month	WWTP	Temperature (°C)	Discharge (10 <sup>4</sup> m <sup>3</sup> /d)	TA (μmol/kg)	DIC (μmol/kg)	$[TA-DIC]$ (μmol/kg)	$[TA-DIC]$ End-Member Value
January	HBR	11.4	4.60	2257	2675	−418	−405
	LCR	11.3	5.25	2809	3311	−502	
	LSR	11.0	2.67	2752	2943	−191	
June	HBR	22.0	4.30	3627	3742	−115	−110
	LCR	21.7	5.82	3541	3643	−102	
	LSR	22.6	2.67	3568	3688	−120	

Meanwhile, compared with seawater, the treated wastewater had different temperatures, indicating that mixing term may include some bias from temperature changes. Temperature mixes linearly, so this component can be estimated if the proportion of treated wastewater in seawater can be obtained. According to mass balance, the sample salinity of a station can be calculated as follows [11]:

$$S_i = S_{sea}/(1 + y) \quad (3)$$

where  $y$  is the proportion of wastewater in seawater and  $S_i$  is the salinity of the station  $i$ .

In January and June, the lowest salinity value in the eastern area of the bay was 27.8 and 31.0, respectively. According to the Equation (3), the  $y$  values were calculated as 0.13 and 0.03, respectively. The temperature difference between treated wastewater and seawater in the eastern area did not exceed 7.6 °C in January and 4.5 °C in June, indicating that the temperature changes caused by this mixing process were  $\leq 1.0$  °C in January and  $\leq 0.14$  °C in June. Therefore, the effect of this process on  $\Omega_{arag}$  could be ignored in the current study.

The  $[TA-DIC]_A$  value after the deduction of the effects from temperature and mixing processes was the contribution of other processes ( $[TA-DIC]_{A-res}$ ) (Equation (4)).

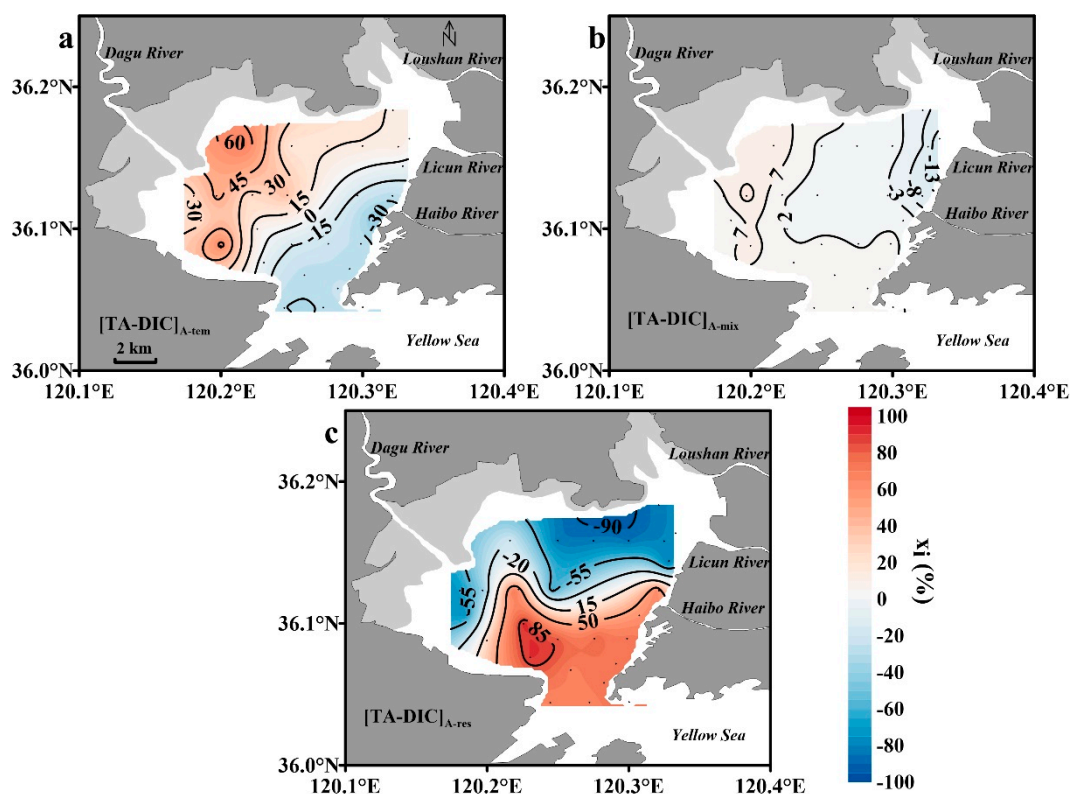
$$[TA-DIC]_{A-res} = [TA-DIC]_A - [TA-DIC]_{A-tem} - [TA-DIC]_{A-mix} \quad (4)$$

where the  $[TA-DIC]_{A-tem}$  and  $[TA-DIC]_{A-mix}$  are the contribution of temperature and mixing processes to the  $[TA-DIC]_A$ , respectively.

After stripping off the effects of temperature and mixing processes,  $[TA-DIC]_{A-res}$  showed an excellent positive correlation with DO% ( $r = 0.91$ ,  $p < 0.0001$ ), indicating that  $[TA-DIC]_{A-res}$  basically reflected the contribution of biological processes to  $[TA-DIC]_A$ . This further verified the rationality of this estimation method. Thus, the relative contribution percentage of the three processes to  $[TA-DIC]_A$  were evaluated.

The relative contributions of each process to  $[TA-DIC]_A$  in summer are shown in Figure 6. The relative contribution of temperature to  $[TA-DIC]_A$  was the largest in the northwestern area of the bay with the highest seawater temperature, exceeding 45%. However, in other areas, it was smaller, less than 30%. The mixing processes had the minimum relative contribution, and most of the regions featured values of less than 10%; however, the contribution reached 13% in the northeastern area, which had the strongest impact of treated wastewater input. The biological processes had the maximum relative contribution to  $[TA-DIC]_A$ , which was more than 50% in most regions. In the northeastern area with the lowest DO% ( $< 90\%$ ) and the southwestern area with the highest DO% ( $> 105\%$ ), the relative contribution of biological processes exceeded 85%. Overall, the average

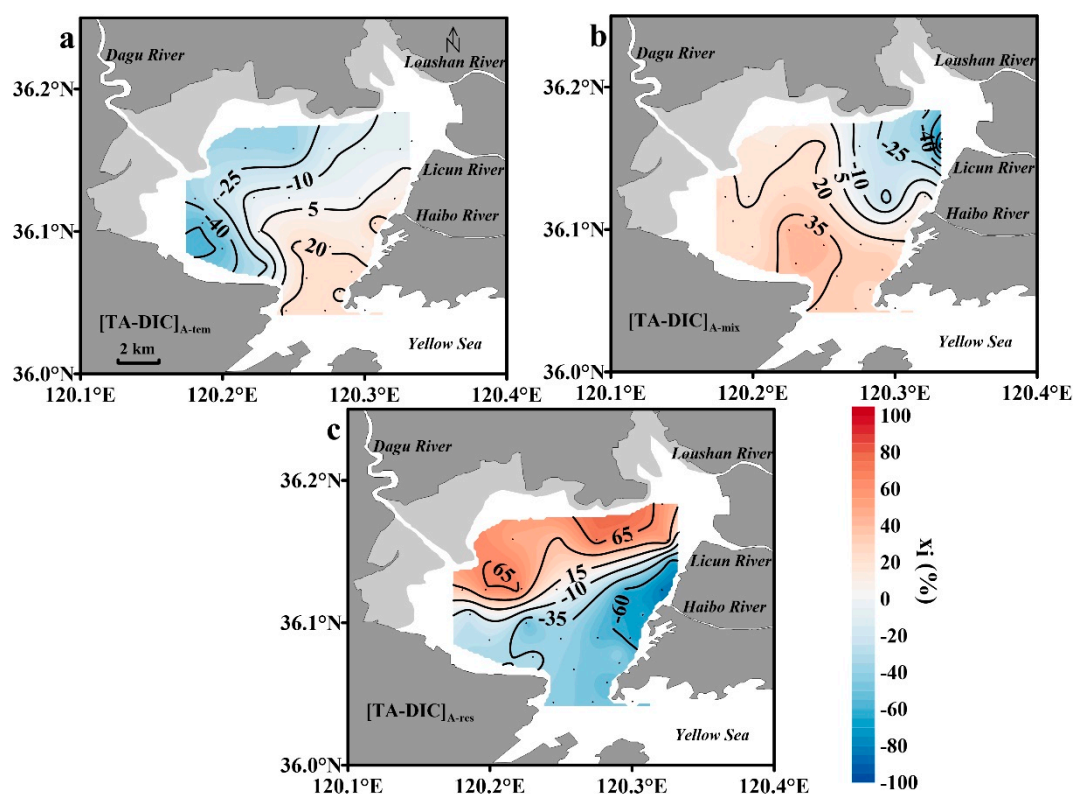
contributions of temperature, mixing processes and biological processes to  $[TA-DIC]_A$  were 25%, 5% and 70%, respectively. The biological processes were the main factor controlling the spatial distribution of  $\Omega_{arag}$  in JZB during summer. It is worth noting that the effects of temperature and mixing processes on  $[TA-DIC]_A$  were mutually reinforced with biological processes in most areas in this period. In the northeastern area with the minimum value of  $\Omega_{arag}$ , the main effect was that treated wastewater input and aerobic respiration together caused the reduction of  $[TA-DIC]_A$ , and the contributions of the two were up to 90%. In the southwestern area with the maximum value of  $\Omega_{arag}$ , primary production and the higher seawater temperature lead to an increase in  $[TA-DIC]_A$ , and the combined contributions of the two reached approximately 90%. As such, there were marked difference in  $\Omega_{arag}$  among the various regions of JZB in summer.



**Figure 6.** Relative contribution percentages of temperature (a), mixing processes (b) and other processes (c) to  $[TA-DIC]_A$  in JZB during summer (28 June 2017).

In winter (Figure 7), the relative contribution of temperature to  $[TA-DIC]_A$  was largest and exceeded 45% in the western area where the seawater temperature was lowest; in the other regions, the contribution was less, below 25%. The relative contribution of the mixing processes to  $[TA-DIC]_A$  was much higher in winter than in summer and was more than 30% in the northeastern area with the lowest salinity ( $< 30.0$ ) and the mouth area with the highest salinity ( $> 31.5$ ). This may be related to enhanced exchange of seawater between the bay and the Yellow Sea caused by the low seawater temperatures and high wind speeds in winter. The biological processes contributed the most to  $[TA-DIC]_A$ , and the relative contribution was more than 60% in the northern area and the area near the estuary of the Haibo River. During this period, DO values in most areas of the entire bay were supersaturated, and primary production was dominant, which corresponds to the growth peak of phytoplankton in JZB in winter [25–27]. Overall, the average relative contributions of temperature, mixing processes and biological processes to  $[TA-DIC]_A$  were 20%, 30% and 50%, respectively. The biological processes were also the main processes contributing to spatial differences in  $\Omega_{arag}$  in winter in JZB, but the total contribution of temperature and mixing processes was similar to that of the biological processes in this period. Furthermore, different from the situation in summer, the effects of the above three processes on  $[TA-DIC]_A$  showed mutual cancellation in most areas. In the

northeastern area where DO% values exceeded 109%, the low seawater temperature and treated wastewater input had a negative effect on  $[TA-DIC]_A$ , while the strong primary production had a positive effect on  $[TA-DIC]_A$ , resulting in a net increase in  $[TA-DIC]_A$  of only approximately 10%. In the western area, the relative contribution of the mixing processes and primary production, corresponding to an increase in  $[TA-DIC]_A$ , was approximately 60%, whereas the remaining 40% contribution corresponded to a decrease in  $[TA-DIC]_A$  caused by low seawater temperatures. Therefore, the differences in  $\Omega_{arag}$  among the various regions in JZB were markedly reduced in winter.



**Figure 7.** Relative contribution percentages of temperature (a), mixing processes (b) and other processes (c) to  $[TA-DIC]_A$  in JZB during winter (17 January 2017).

In the open ocean, physical transport in the horizontal and vertical directions is a key factor causing differences in the distribution of  $\Omega$  [47–49], while the increasing human disturbance has affected the biological processes more prominently in coastal waters. In ocean shelf regions, the effect of biological processes on  $\Omega$  mainly appears in the summer. Due to the stratification of seawater, the surface water body often features strong primary production, which increases  $\Omega$  under the appropriate illumination and nutrient supply conditions, while organic matter deposited from the upper water body often leads to strong aerobic respiration in the subsurface water body, resulting in low  $\Omega$  and pH [8,50,51]. However, in nearshore bays where the impact of human activities is more significant, the situation is slightly different. The urbanization process affects biological processes in certain areas. For example, in the JZB, the eastern area of the bay, which is adjacent to downtown Qingdao, receives large amounts of terrestrial pollutants brought by wastewater all the year round and is dominated by aerobic respiration. This situation can weaken the living environment of calcified organisms in the region and does not change even after heavy rain [33,35]. In contrast, in the western area, which is far from the urban area and adjacent to the wetland, primary production produces an increase in  $\Omega$ , and this region is an important area for shellfish farming in JZB [52]. A similar phenomenon was also observed in Fujian, Southeast China [53,54] and Guanabara Bay in Brazil [25]. Moreover, perennial eutrophication often causes algal blooms and produces strong primary production even under the low temperatures in winter in some waterbodies [55,56], offsetting the decrease in  $\Omega$  caused by the low temperatures. In addition, bays often have a shallow

water depth, and strong turbulence might cause full mixing of the seawater vertically, making the effect of biological activity on  $\Omega$  extend through the entire water column [23]. With the rapid urbanization and worsening climate change in coastal areas, the effects of strong heterotrophic bacteria activity and vigorous plankton growth on  $\Omega$  will become increasingly prominent. Thankfully, environmental protection has been received increasing attention in China. Central and local governments have accelerated efforts to tackle environmental pollution by raising environmental protection standards and revising laws [57,58]. However, strict enforcement of environmental protection laws is urgently needed to conserve the aquatic environment, particularly the effective treatment of wastewater which brought large amounts of organic matters and nutrients to coastal environment [59]. In the future, collaboration between government, industry and environmental non-governmental organizations (NGO) will be of great importance to mitigate ocean acidification and other problems in coastal areas.

### 3.5. Uncertainty Analysis of the Quantitative Estimate

Here the uncertainty associated with key terms in the quantitative evaluation method in Section 3.4 was analysed. First, the uncertainty of TA and  $\Omega_{\text{arag}}$  calculated from the pH and DIC were estimated to be  $\sim 7 \mu\text{mol/kg}$  and  $\sim 0.05$ , respectively, via the CO2SYS program (without considering the uncertainty induced by carbonate acid dissociation constants during calculations) [60], given the uncertainty of  $\sim 2 \mu\text{mol/kg}$  for DIC and the uncertainty of 0.01 for pH measurement. The TA uncertainty will lead to an uncertainty of  $\sim 7.3 \mu\text{mol/kg}$ , or  $(7^2 + 2^2)^{0.5}$ , for [TA-DIC]. This uncertainty will propagate into [TA-DIC]<sub>A</sub> ( $\sim 7.4 \mu\text{mol/kg}$ , or  $(7.3^2 + 7.3^2/28)^{0.5}$ ), Xi-tem and Xi-mix ( $< 5.5\%$ ) and Xi-res ( $< 8\%$ ). Second, [TA-DIC] has some limitations as a proxy for *in situ*  $\Omega_{\text{arag}}$ . In the current study, [TA-DIC] may not accurately reflect the influence of temperature. The effect of temperature only refers to its impact on thermodynamic constants or internal allocation of carbonate system species by temperature driven acid-base equilibrium under conditions of constant TA and DIC, which is called “internal temperature effect” [20]. For instance, for one unit increase in temperature,  $\Omega_{\text{arag}}$  will increase by  $\sim 0.60\% \text{ } ^\circ\text{C}^{-1}$  based on our data. Fortunately, the thermal influence is relatively minor due to the small spatial variation in seawater temperature for each investigated cruise. Meanwhile, to calculate the effects of temperature on the solubility of  $\text{CO}_2$  in seawater, it is assumed that seawater  $p\text{CO}_2$  can reach an equilibrium state with the atmospheric  $\text{CO}_2$  quickly. In fact, it is almost impossible to reach transient air-sea  $\text{CO}_2$  equilibrium due to the slow air-sea  $\text{CO}_2$  exchange [61], which will lead to overestimation or underestimation of  $\text{DIC}_{\text{eq}}$ . However, this influence on [TA-DIC]<sub>A-tem</sub> may be minor since this overestimated or underestimated part offset, to a large extent, each other after subtraction as shown from Equation (1). Third, to separate mixing effects, the slope values of [TA-DIC]-Salinity between the composite treated wastewater and seawater in January and June were estimated from end-members values. Treated wastewater end-member values were calculated by the [TA-DIC] values and discharge of three WWTPs in corresponding months which were reported by Liu et al. [44]. Though their studies showed that changes in DIC and TA were generally same in the two years, the uncertainties brought by the treated wastewater end-member in our cruises still exist in [TA-DIC]<sub>A-mix</sub>. Despite some uncertainties in our methods which are also widely applied in other studies, the current study provides some quantitative findings on the control mechanism of  $\Omega_{\text{arag}}$  in the bays under the influence of human activities.

### 3.6. Limitation and Future Research

Similar to many studies, some limitations exist in the current research. First,  $\Omega_{\text{arag}}$  and TA were calculated based on pH and DIC. The uncertainty of pH measurements made with electrodes calibrated on the NBS scale may cause a certain level of inaccuracy [62,63]. Thankfully, the spatiotemporal changes of pH in JZB were large enough, and the conclusions were valid based on these data. Second, this study focused the contributions of three factors (temperature, biological processes and mixing processes) to the distribution of  $\Omega_{\text{arag}}$ . However, the effects of other factors, for

example, mineral precipitation, vertical mixing of water column, nitrification processes, may also exist, although their contributions may be minor in our research area. Additionally, the effects of urbanization on  $\Omega_{\text{arag}}$  include sewage input and other factors. Third, the seasonal changes of  $\Omega_{\text{arag}}$  is unavailable due to the data limitation. Obviously, more cruise investigations and related studies are still needed to improve our understanding of the complex ocean acidification under the impact of climate change and human activities.

#### 4. Conclusions

Seawater surface aragonite saturation state ( $\Omega_{\text{arag}}$ ) during summer and winter in Jiaozhou Bay, China, was analysed in this study. The seawater surface  $\Omega_{\text{arag}}$  was supersaturated, and the ranges were 1.55–2.92 in summer and 1.62–2.15 in winter, respectively. In addition to the analysis of the effects of temperature, mixing processes and biological processes on the spatial difference of  $\Omega_{\text{arag}}$  based on regression analysis with surface temperature, salinity and DO%, the relative contributions of these three processes were quantified by introducing the difference between TA and DIC as a proxy for  $\Omega_{\text{arag}}$ . The results showed that the biological processes were the main processes affecting the spatial difference of  $\Omega_{\text{arag}}$ , and the relative contribution was 70% in summer and 50% in winter. The contributions of temperature (25% in summer and 20% in winter) and mixing processes (5% in summer and 30% in winter) were smaller. Moreover, the interaction among the three factors that influence  $\Omega_{\text{arag}}$  exhibited mutual promotion in summer and mutual cancellation in winter, causing the regional distribution of  $\Omega_{\text{arag}}$  to show marked difference in summer and a relatively uniform change in winter.

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