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Analysis of Dissolved Oxygen and Nutrients in Zhanjiang Bay and the Adjacent Sea Area in Spring

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Abstract: As a semi-closed bay with narrow bay mouths, the distribution of nutrients in Zhanjiang Bay was different from bays with open bay mouths and rivers with large flows. It is important to study the water quality of Zhanjiang Bay to determine the impact of human activities on this semi-closed bay. Based on field survey data in spring, the spatial distribution of nutrients and other physico-chemical parameters was investigated, in order to study the geochemical characteristics of nutrients in semi-closed bays. Higher nutrient concentrations were observed in the inner and outer bays, but lower concentrations were observed at the bay mouth. With other analyses of physico-chemical parameters, the higher nutrient concentrations in the inner bay originated mainly from the diluted freshwater input from local developments and rivers. With the strong flow that exists along the western coast of Guangdong Province, the higher dissolved inorganic nitrogen (DIN) and SiO_3–Si concentrations along the outer bay may be influenced by discharge from local cities in western Guangdong Province. There was stronger phytoplankton assimilation at the bay mouth, which resulted in reduced nutrient concentrations in this area. Although the hydrographic characteristics between the inner bay and outer bay were significantly different, the distribution of chlorophyll-a (Chla) levels was similar. However, we found significantly low dissolved oxygen (DO) and high apparent oxygen utilisation (AOU) consumption levels in the inner bay, and high DO and low AOU levels in the outer bay, which suggested that decomposition was more important than photosynthesis in the closed bay, even in spring during the phytoplankton bloom.

Keywords: Dissolved Oxygen; Nutrients; Zhanjiang Bay

1. Introduction

The marine ecosystem in the coastal zone is complex and changeable, where various environmental factors affect and restrict each other. Trace elements necessary for the growth of phytoplankton (i.e., N, P, and Si) in seawater affect the level of marine primary productivity and the structure of the ecological environment. However, those human-induced elements in the environment are becoming a serious problem for coastal areas around the world [1–3]. Anthropogenic inputs have resulted in a series of adverse effects that include eutrophication, harmful algal blooms, and seasonal hypoxia [4–6]. Particularly in coastal bay areas, eutrophication is serious because of poor hydrodynamic conditions [2,7]. Strong public concerns about eutrophication have resulted in increasing levels of scientific study to evaluate it.

In coastal China, many urban centers and industries are located in a watershed, and a high human population, domestic waste, and the extensive use of chemical fertilizers have led to the coastal marine environment receiving a significant loading of anthropogenic nutrients in recent decades [3,7,8]. Thus, eutrophication has become increasingly serious, and noxious algal blooms have been more frequent

in the coastal areas of China [8]. For example, a quarter of recorded algal blooms occurred in the coastal East China Sea, particularly in the Yangtze River Estuary and adjacent sea [6,8,9]. In addition, eutrophication and associated hypoxic conditions induced by high inputs of anthropogenic nutrients from coastal cities have also become a serious problem in the northern South China Sea [3,10,11].

Over the past few decades, many investigations have focused on bays with large river flows and wide estuaries, such as the Pearl River and the Yangtze River, but we still have little understanding of small-watershed, semi-closed bays. Zhanjiang Bay is a semi-closed bay that is located in southern mainland China. It is connected to the northwestern part of the South China Sea, which is affected by the strong flow along the western coast of Guangdong Province. The bay is influenced significantly by frequent and intensive human activity, such as industry, agriculture, mariculture, and shipping. Furthermore, heavy metals in soils can be obtained by the weathering of natural rocks or by pollution generated by human activities [12]. Zhanjiang City is dominated by laterite, which is rich in iron and manganese ions. Under the influence of intensive human activity and soil properties, a large number of terrestrial heavy metals in land are discharged into Zhanjiang Bay through freshwater and impact the growth of phytoplankton deeply. With increased urbanization, pollutants accumulate gradually in the bay, due to the poor hydrodynamic conditions [13]. The nutrients in this coastal area are now derived mainly from manure from local areas, despite the westward flow of diluted Pearl River water [3]. Shi [14] and Jiang [15] have reported that even with spatial and seasonal variation in the degree of eutrophication in Zhanjiang Bay, there is still a lack of integrated research on the eutrophication of the semi-closed bays due to rapid urbanization.

In this study, which was based on field survey data in spring, the spatial distribution of nutrients, dissolved oxygen (DO), and chlorophyll-a (Chla) were studied in Zhanjiang Bay and the adjacent sea area. The relationship of these variables with temperature, salinity, and other related factors was analyzed so that we could determine the geochemical characteristics of nutrients in the semi-closed bays.

2. Materials and Methods

2.1. Study Area and Field Sampling

Zhanjiang Bay is a semi-closed bay that is surrounded by Zhanjiang City, Nansan Island, and Donghai Island. Suixi river flows into the bay from the northern bay to the inner bay, which is the main source of fluvial freshwater for the bay. There are three bay mouths in the bay, such as the eastern bay mouth between Nansan Island and Donghai Island, the western bay mouth between Donghai Island and Zhanjiang City, and the northern bay mouth between Nansan Island and Potou Zone (Figure 1). Because the western bay mouth is intersected by the East Levee, and the northern bay mouth is too narrow and shallow, most of the interaction between estuary and sea occurs in the eastern bay mouth. Although the inner bay is about 160 km^2, the width of the eastern bay at the mouth is only about 2 km. At high tide, the average vertical velocity from the south of the Maxie slope to the bay mouth (i.e, from sampling station S36 to S19) was 41.5–77.2 cm/s, and the maximum residual current was 29.0 cm/s, which were less than at the eastern bay mouth [16]. The slow velocity of the inner bay causes the interaction of freshwater and seawater to become slow and inadequate, which leads the time of water semi-exchange to decrease from 85 to 25 days, from the Maxie slope to the bay mouth, and makes it difficult to discharge pollutants outwards [17]. Furthermore, the inner bay is subject to a high terrestrial pollution burden, and is used for harbor and fisheries aquaculture like farming shrimp and oysters. It provides enough time and nutrients to decompose nutrients and incubate phytoplankton biomass. The interaction between freshwater and seawater, and the distribution of nutrients in particular, divides the bay into three distinct regions: the inner bay (i.e., from sampling stations S24 to S38), the bay mouth (i.e., from sampling stations S13 to S23), and the outer bay (i.e., from sampling stations S1 to S12) (Figure 1). The salinity and pH in the inner bay (i.e, sampling stations S33, S29, and S25) and the outer bay (i.e, sampling stations S10 and S4) were distributed throughout the water layers evenly, and the surface salinity was slightly lower than that on the bottom, indicating that the layers were

well-mixed (Figure 2). Combined with their salinity, the inner bay water body was considered to be mainly affected by freshwater hydrodynamics, such as river discharge (brackish water mixing with freshwater with relatively low salinity), and the outer bay would be dominated by seawater with tidal movement. The seawater from the outer bay would sink to the bottom, due to its density when two water masses meet at the bay mouth (i.e, sampling stations S21, S19, and S16), which causes salinity at the bay mouth to increase from the surface to the bottom layer. The flow velocity at the eastern bay mouth was highest in the bay, and the time of water semi-exchange was less than 5 days [16,17], which would lead to the rapid exchange of seawater and accelerate the biochemical coupling process. The distribution of pH also indicates this. The high values at the bay mouth suggests that there may be stronger phytoplankton assimilation at the bay mouth (Figure 2). Therefore, there are three different conditions for these regions, which represent three different states of water. The inner bay water body is considered to be mainly brackish water, with relatively longer residence time than outer bay water, where nutrient and hydrodynamics in the brackish water from the inner bay are dominated by freshwater discharge from the northern Suixi river. The bay mouth contains three estuaries, which exchange river and seawater strongly. The eastern bay mouth is the main water exchange pathway, the western Levee construction prohibits the water exchange in western bay mouth, and the northern bay mouth is too narrow and shallow, which could contribute to the minor water exchange compared to the eastern bay mouth. We mainly discuss the eastern bay mouth as the main bay mouth in this paper. The water outside the bay is dominated by seawater, which is influenced by the westward flow of the diluted Pearl River water throughout the year [11,13]. We conducted a cruise in May 2016 across Zhanjiang Bay to the adjacent territorial waters. The cruise was conducted in four days during the daylight. The sampling process was arranged to progress from the inner bay to the outer bay, and each sampling time was controlled within 8 h. The sampling stations were selected along eight transects that ran across the area outside the bay from north to south, between the bay mouth and the adjacent waters (Figure 1). Water samples were collected by Niskin bottles every five meters. Salinity, temperature, and depth of water samples were measured using a maestro multiparameter water quality monitor (Canada RBR. Ltd.). For the analysis of nutrients, water samples were filtered through membrane filters (47 mm diameter, 0.45 μm AR membrane; Hangzhou Huoju. Ltd.), and the filtrate was then transferred into acid-washed polyethylene bottles and stored at −20 °C for laboratory analysis. For Chla, water samples were filtered using a glass-fibre filter (Whatman, 0.7 μm, GF/F) and stored at −20 °C before further processing and analysis.
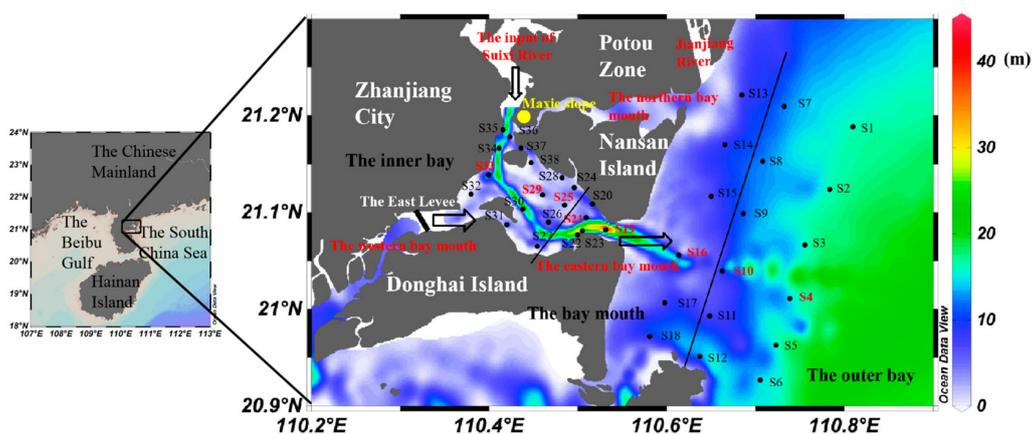

Figure 1. Water depth and sampling stations of the study area from Zhanjiang Bay, China.
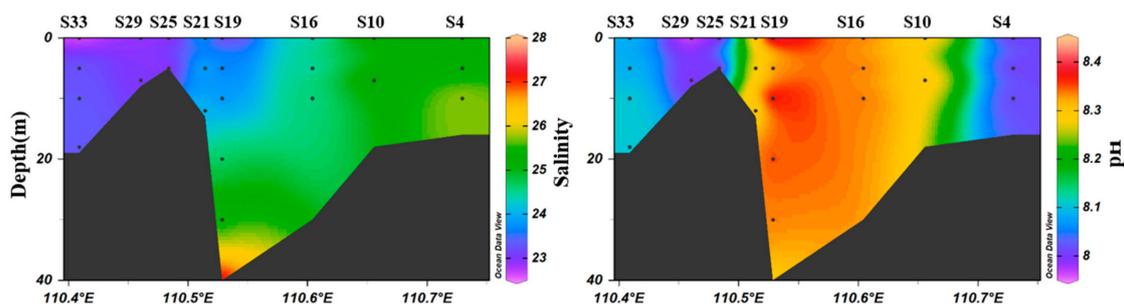
Figure 2. The profile of salinity and pH from the inner bay to the outer bay in Zhanjiang Bay.

The black arrow indicates the direction of residual currents about seawater in the bay. The sampling site marking red represents the sampling station shown in Figure 2.

2.2. Sample Processing

Before sailing, the sensors of RBR maestro multiparameter water quality monitor, such as temperature, salinity, and pH sensors, must be calibrated by reversing the thermometer, salinity meter, and standard solution with pH values of 7 and 9, in accordance with the requirements of the marine survey code. We kept the RBR instrument on the surface water for 1–2 min to stabilize sensors before measurement, and cleaned the sensor with distilled water at the end. The DO was analyzed by Winkler titration. Chla in the GF/F filter was extracted using 90% acetone and analyzed by the fluorometric method [18]. NO_3^- was determined by the cadmium–copper reduction method. Nutrients, which included NO_3^-, NO_2^-, SiO_3^{2-}, and PO_4^{3-}, were determined by a San++ continuous flow analyser (Skalar, Netherlands). The data quality was monitored by intercalibration, and the detection limits for NO_2^-, NO_3^-, SiO_3^{2-}, and PO_4^{3-} were set to 0.01 μmol L^{-1}. NH_4^+ was set to 0.1 μmol L^{-1}, and NH_4^+ concentrations were determined by spectrophotometry. The figures in the paper were interpolated by the Data Interpolating Variational Analysis (DIVA) gridding method in Ocean Date View software.

3. Results

3.1. The Spatial Distribution of Salinity, Temperature, pH, Chlorophyll-A and Dissolved Oxygen

Salinity in the bay ranged from 20.62 to 27.56 and exhibited an increasing trend from the inner bay to the outer bay (Figure 3). The salinity in the outer bay was significantly higher than that in the inner bay (Figure 3). The distribution pattern of salinity in surface water was similar to the bottom water in the inner bay and outer bay.

The temperature of the water at the surface and the bottom was 27.23–29.04 °C and 26.90–29.09 °C, respectively, with an average value of 28.33 ± 0.81 °C and 28.04 ± 0.6 °C. The temperature of surface seawater was slightly higher than the bottom layer, due to solar radiation. Similar to the distribution pattern of salinity, there was a significant difference in temperature between the inner bay and the outer bay, where the inner bay exhibited higher values.

The pH was 7.86–8.49, which showed a trend of first increasing and then decreasing from the inner bay to the outer bay. The pH reached its maximum value at the bay mouth, and decreased sharply in the outer bay. The distribution pattern of pH levels in the surface water was similar to that in the bottom water.
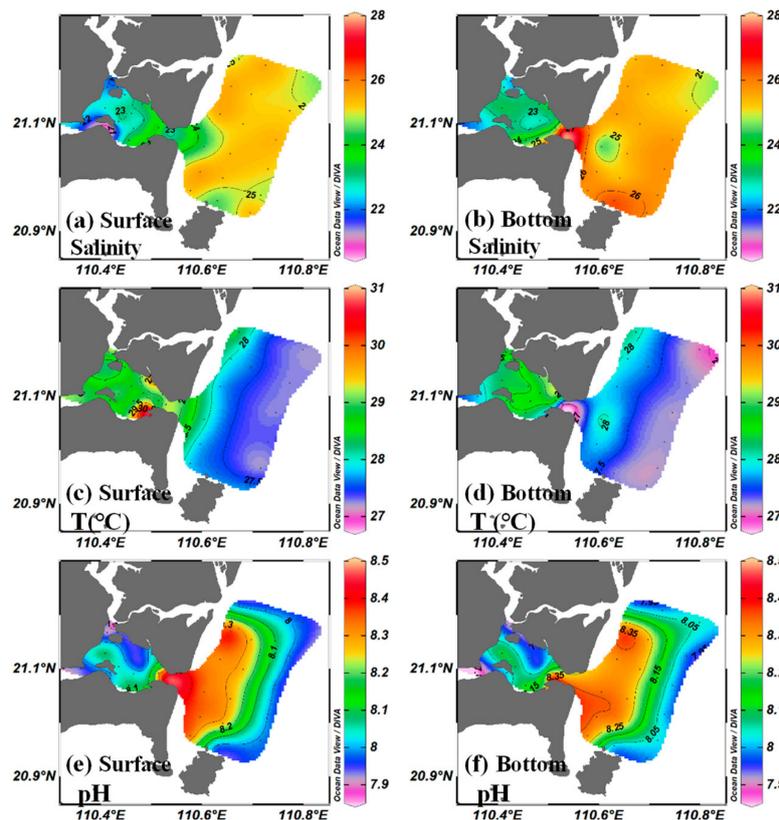
Figure 3. The distribution of salinity, temperature, and pH in Zhanjiang Bay, China in spring.

The concentrations of Chla were 0.68–26.28 ug/L, with an average value of 4.80 ± 4.67, and exhibited a relatively high level on the whole. The distributions of Chla in the surface and bottom water were similar, but the spatial distribution of Chla was different from the temperature and salinity. There was a higher concentration of Chla at the bay mouth, and the Chla levels in the outer bay were similar to the inner bay during spring. This suggested that the degree of photosynthesis by phytoplankton in the inner bay and the outer bay was similar.

DO in the surface and bottom water of the survey area was 5.39–10.99 mg/L and 5.52–10.10 mg/L, respectively, and the mean values were 7.24 ± 1.24 mg/L and 6.83 ± 0.94 mg/L, respectively, with a high level overall. The concentration of DO in surface water was higher than the bottom water. However, in contrast to the distribution of Chla levels, the DO level showed a significant spatial distribution pattern, with higher levels in the outer bay and lower levels in the inner bay. The distribution of DO saturation was similar to DO. DO saturation in the surface and bottom layer were 79.65%–163.21% and 81.49%–149.75%, with a mean of 106.81% and 101.44%, respectively. The DO in the inner bay was unsaturated, while that in the outer bay and bay mouth were the opposite. Apparent oxygen utilisation (AOU) in the surface and bottom water of the survey area were −4.25–1.38 mg/L and −3.31–1.30 mg/L, respectively, and the mean values were −0.46 mg/L and −0.01 mg/L. AOU was generally positive in the inner bay and negative in the outer bay (Figure 4). In addition, the consumption of oxygen in the bottom water was higher than in the surface water. This suggested there were obvious processes of oxygen consumption in the inner bay.
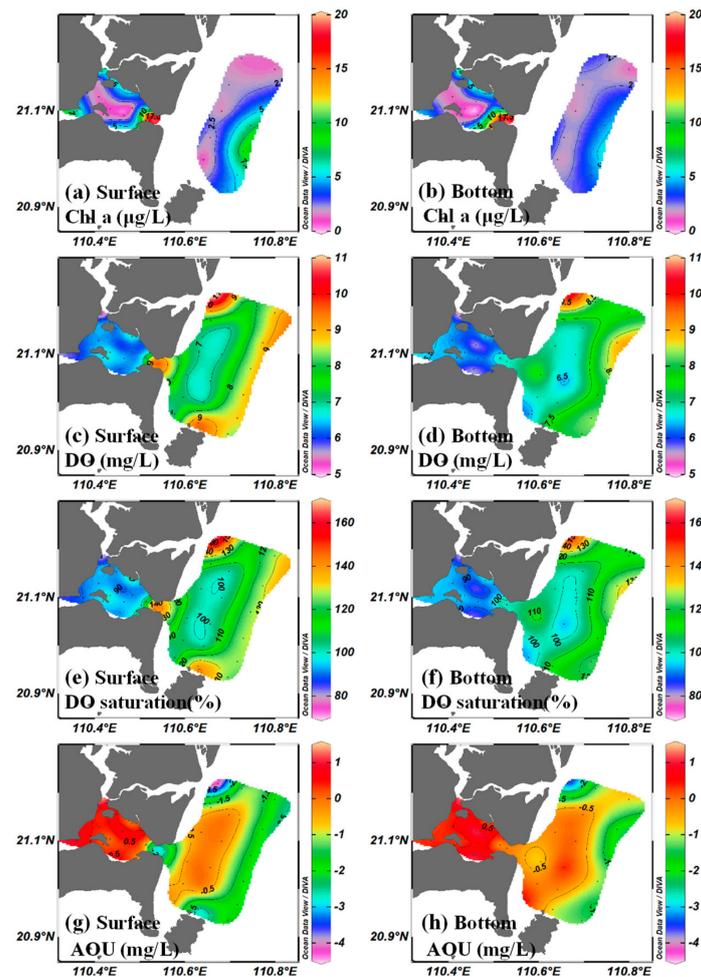
Figure 4. The distribution of cholorphll-a (Chla), dissolve oxygen (DO), DO saturation, and apparent oxygen utilisation (AOU) in Zhanjiang Bay, China in spring. The data for Chla (i.e., from sampling stations S13 to S18) was invalid, due to the operation error during the experiment.

3.2. The Spatial Distribution of Nutrients

Concentrations of NO_3–N and NH_4–N in the surface and bottom waters of the survey area were 6.37–25.45 umol/L and 0.68–10.14 umol/L, respectively, and the mean values were 17.35 μmol/L and 3.30 μmol/L, respectively, which means that the dissolved inorganic nitrogen (DIN) content was lower than the third national seawater quality standard. Concentrations of SiO_3–Si and PO_4–P were 0.64–14.87 μmol/L and 0.19–7.07 μmol/L, with mean values of 7.00 μmol/L and 1.82 μmol/L, respectively, which suggests that the concentration of PO_4–P in the inner bay was higher than the fourth national seawater quality standard; in addition, the concentration of PO_4–P in the outer bay was lower than the first national seawater quality standard. It was clear that NO_3–N was the dominant nutrient, which was consistent with the results of others [9,14]. In general, nutrient levels in the surface water were slightly higher than that of bottom water. Concentrations of SiO_3–Si and NO_3–N in the inner and outer bays were higher than that at the bay mouth. Concentrations of PO_4–P and NH_4–N were significantly higher in the inner bay and lower at the bay mouth and the outer bay.

4. Discussion

4.1. Sources and Geochemical Characteristics of Nutrients in Zhanjiang Bay

The salinity of seawater during the spring in the bay increased seaward, and temperature decreased seaward. The inner bay exhibited higher temperatures and lower salinity, while the outer bay exhibited

lower temperatures and higher salinity. We believe that these water conditions in the inner bay originated mainly from the diluted freshwater from the local area and rivers. Because of its location at the junction between the subtropics and tropics, air temperature starts to increase in Zhanjiang during the spring. Therefore, it is easy to lead to a faster rise in water temperature in the inner bay. Thus, the temperature in the inner bay during that season was higher than in the outer bay. Freshwater mainly affects the inner bay, but it has some influence on the distribution pattern of temperature and salinity in the outer bay. Furthermore, there was similar salinity between the surface and the bottom layer in the inner bay and outer bay (Figures 2 and 3), which means the seawater of these areas was well mixed. The depth of the inner bay was between 3 and 10 m mostly, and that of the outer bay was between 10 and 20 m. The water under these depths was usually well mixed. In addition, the temperature in Zhanjiang Bay was not too high to cause water stratification during the spring.

The highest concentration of nutrients appeared in the region with the lowest salinity, which was typically inside the bay; this indicated that the terrestrial sources may be the main sources of nutrients in the surface and bottom water of the bay (Figures 2, 5 and 6). The distribution of nutrients was uniform, due to the influence of a longer residence time and the mixing of water in the inner bay. However, sampling station S31 had high nutrients with low salinity, due to the fact that there was input from a small river near there, and the freshwater from the river diluted the seawater. The tidal pattern of Zhanjiang Bay is an irregular, semidiurnal tide. The tidal movement will control the transport process from inner bay to the outer bay, with a continuous process of diluting, mixing, and transporting. The residence time for nutrients and water in the inner part of the bay is considered relatively long. Previous studies in this area have also suggested that the rapid human population growth and economic development in the local cities in west Guangdong Province have brought high loads of manure and sewage to coastal waters [3,14,15]. NO_3–N, which originates from manure and sewage in those areas [3], was the dominant form of DIN in the bay during the spring. With the exception of spring, nitrates accounted for >74% of DIN in the inner bay and >86% in the outer bay. Influenced by domestic activity, the highest ammonia concentration occurred in the inner bay and accounted for 19% of the DIN.

Although the higher concentrations of DIN and PO_4–P were observed in the inner bay, the N/P ratios in the inner bay and outer bay were significantly different. The average value of N/P was 7 in the inner bay, but 95 in the outer bay. However, the average concentration of DIN in the inner bay was similar to that in the outer bay, which indicates that PO_4–P in the inner bay originated mainly from local discharge. In addition, the deviation of N/P (the Redfield ratio of 16 at which these nutrients are utilized by marine phytoplankton) [19] in the bay suggests that N limitation occurred in the inner bay, and P limitation occurred in the outer bay.

There were dramatic changes in SiO_3–Si and NO_3–N at the bay mouth, and the stratification of concentrations at the surface and bottom layer was obvious, due to an obvious estuary front. Generally, nutrients in the marine front can be replenished in time, and phytoplankton usually multiplies in large quantities. This may be responsible for the higher Chla level at the bay mouth. The higher Chla and DO levels and low nutrient concentrations in both the surface and bottom at the bay mouth suggest that stronger phytoplankton assimilation occurred at the bay mouth during the spring. In the process of phytoplankton assimilation, a large number of nutrient elements are absorbed, and photosynthesis is stronger under conditions of higher chlorophyll content, which absorbs carbon dioxide and releases oxygen. There may be several reasons for this distribution of phytoplankton. Firstly, the bay mouth water body was more clear due to the low suspended sediment (SS) water from the outer bay mixing here with tidal movement; however we did not monitor the SS data this time to support our hypothesis. The second reason is due to the nutrient conditions, especially for phosphorus, which controls the bloom of plankton; the phosphorus was high in the inner bay, decreasing towards the sea and staying low in outer bay (Figure 5K,I). However, the silicate, nitrate, and ammonium showed as high in the outer bay, and would be potential nutrient resources contributing to the bay mouth site. There also showed a decreasing trend in N/P ratios towards the sea in the inner bay

(Figure 5M,N), representing the supply of phosphorus from inner bay controlling the chlorophyll concentration in the bay mouth, although there was a sufficient silicate and N supply from the outer bay; due to the limiting of phosphorus in the outer bay, the chlorophyll concentration remained low with a relatively high N/P ratio. In addition, significantly higher pH levels occurred at the bay mouth (average of 8.26) compared with the inner bay (average of 7.98) and outer bay (average of 8.08), which supports our hypothesis.
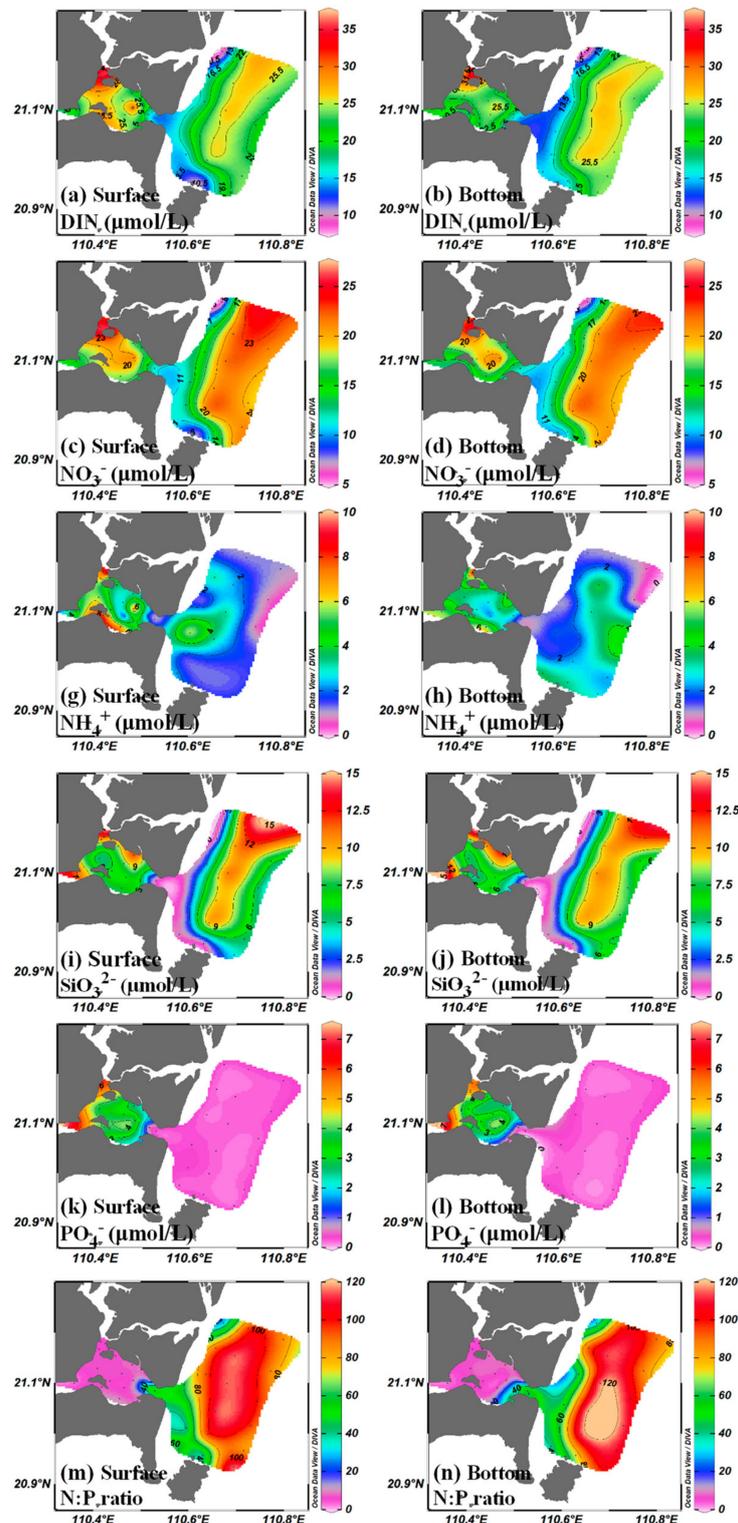

Figure 5. The distribution of nutrients and N/P ratio in Zhanjiang Bay, China in spring.
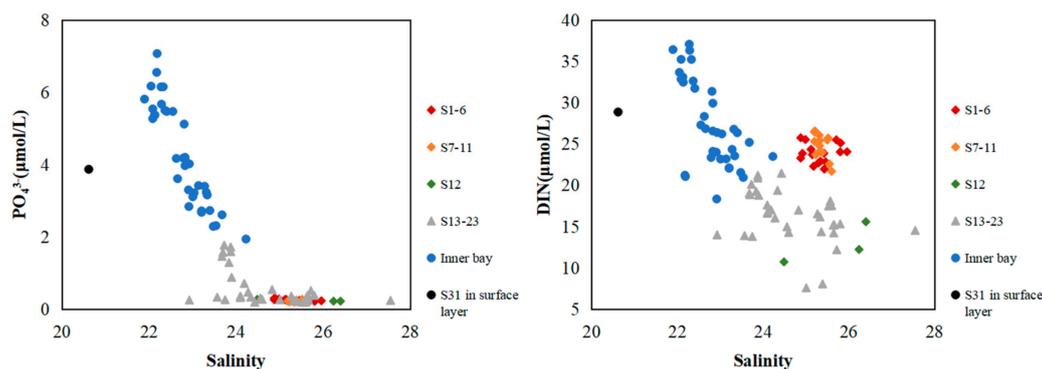
Figure 6. The relationship between nutrients and salinity in Zhanjiang Bay, China in spring. The prism represents the sampling in the inner bay, the triangle represents the bay mouth, and the circle represent the outer bay.

Figure 6 shows the relationship between DIN and salinity in all layers from all sampling stations. Different patterns are visible between the inner bay (marked as inner bay), bay mouth (marked as S13–23), and outer bay (marked as S1–6, S7–11 and S12). In the inner bay, a significant negative relationship between salinity and DIN is shown; DIN decreased dramatically towards the sea with increasing salinity, indicating that the nutrients are derived from freshwater sources and diluted by seawater via tidal exchange through bay mouth. Although the salinity increased and DIN decreased in the bay mouth, there is still a clear negative relationship between them, which demonstrates that the Zhanjiang Bay and coastal freshwater such as Jianjiang river still have clear impact on coastal nutrient (Figure 6). However, the outer bay (S1–11) did not show a clear relationship between DIN and salinity, which both showed high levels, providing evidence of the strong flow with excess nutrients that exists along the western coast of Guangdong Province. Furthermore, relatively higher DIN and SiO_3–Si concentrations in the outer bay were found compared with the bay mouth. The higher DIN and SiO_3-Si concentrations along the outer bay may be influenced by local discharge from cities [20]. The rapid development of the local economy in coastal Guangdong Province in recent years has led to excessive quantities of nutrients being discharged into coastal waters [21–23]. In addition, due to the effect of a geostrophic deflection force, strong coastal currents exist in the offshore waters of the western Guangdong Province, which would have carried a huge concentration of nutrients along the western coast of Guangdong Province [11,24]. Manure and sewage were the dominant sources of nutrients in the coastal area, and mainly originate from the discharge by local cities, due to the rapid development of local economies [20]. In addition, nitrogen fertilizer is applied heavily in the coastal cities in west Guangdong Province during the spring, and fertilizers could be the other nutrient source in this coastal area [23,25]. Sampling station S12 showed lower nutrients than other stations in the outer bay, because it was at a bend in the tide, leading to increased flow and strong waves that encouraged phytoplankton to consume more nutrients and grow rapidly [26].

In conclusion, the water flow from the inner bay met the strong coastal flow in the offshore waters of Western Guangdong Province at the bay mouth, where an estuary front of the nutrient salt was generated. Therefore, the water system inside the bay had a limited influence on the water outside the bay, and the eutrophic water inside and outside the bay were jointly caused by Zhanjiang City and nearby cities.

4.2. Strong Decomposition Occurred in the Inner Bay

Although the hydrographic characteristics between the inner bay and the outer bay were significantly different, Chla concentrations were similar. In addition, Chla concentrations during spring in the bay were significantly higher than those in the western coast of Guangdong Province during the same season (0.24~6.12 ug/L) [3]. This indicated that phytoplankton in the bay bloomed during that season, and the oxygen produced by photosynthesis was similar both in the inner and

outer bays. However, DO levels in the inner bay were significantly lower than in the outer bay, and the saturation of DO was less than 100%, which suggests that the consumption of oxygen in decomposition was more than that processed by photosynthesis in the semi-closed bay, even during the spring when phytoplankton bloomed. The lower DO levels in the inner bay was influenced by a strong decomposition process caused by a large amount of oxygen being consumed. The AOU is the difference between the measured DO and the ideal numerical value of the solubility of oxygen with the specified temperature and salinity, when the pressure is 1 ATM and the relative humidity is 100%. AOU primarily describes the consumption of biological oxygen. The water is in a state of hypersaturation of dissolved oxygen when the AOU < 0. The results in our study showed that the AOU values in the inner bay were generally higher than 0, which further confirmed that oxygen consumption indeed occurred in the inner bay. In addition, higher nutrient concentrations occurred in the inner bay, which may have originated partly from the degradation of organic matter. The degradation of organic matter in the water column and the underlying sediment porewaters have been proposed as important nutrient sources in coastal areas, and which mainly originate from local activity [27,28]. In addition, due to a relatively closed area in the inner bay, it is easier to accumulate organic matter emitted by local activity. In Zhanjiang City, the rainy season begins mainly in April, and rainfall increases significantly during that month [29]. During the sampling period in this study, heavy rainfall led to a relatively huge transport of organic matter from the local city into the bay, where organic matter could have been remineralised easily—due, perhaps, to the priming effect [30] to NH_4^+ and its subsequent nitrification to NO_3^- in the water column. This process would result in the concentration of NH_4^+ in the water to be less than that of NO_3^-, which is consistent with our observation in this area.

To reveal the control factors for nutrients and spatial distribution for DO in Zhanjiang Bay and the adjacent sea areas, bivariate correlation analysis was conducted on the environmental parameters of all sampling points. This study discusses the inner bay and outer bay, and we used correlations between environmental factors in the water, using all sampled water layers, to analyse the impact of land-source material input on the bay (Table 1).

Table 1. Correlation of environmental factors in the entire water layer in Zhanjiang Bay, China, in the spring.

		T	S	pH	DO	Chla	SiO_3^{2-}	PO_4^{3-}	DIN	AOU
	T	1	0.401	0.09	−0.181	0.288	0.321	−0.238	−0.438	0.053
	S		1	0.451	0.107	0.021	−0.207	−0.592 *	−0.543 *	−0.221
	pH			1	0.415	−0.386	−0.793 **	−0.635 *	−0.529 *	−0.458
The inner bay	DO				1	−0.559 *	−0.560 *	−0.527 *	−0.335	−0.989 **
	Chla					1	0.722 **	0.363	0.082	0.528 *
	SiO_3^{2-}						1	0.564 *	0.365	0.545 *
	PO_4^{3-}							1	0.565 *	0.595 *
	DIN								1	0.417
	AOU									1
	T	1	−0.151	0.574 **	−0.522 **	−0.494 **	0.269	−0.389 *	−0.012	0.507 **
	S		1	0.263	−0.546	0.267	0.419	−0.537	0.671 *	0.540
	pH			1	−0.932 **	−0.411	0.382	−0.365	0.363	0.934 **
The outer bay	DO				1	0.320	−0.578 *	0.416	-0.622 *	−1.000 **
	Chla					1	−0.352	−0.353	0.093	−0.316
	SiO_3^{2-}						1	0.233	0.784 **	0.581 *
	PO_4^{3-}							1	−0.105	−0.407
	DIN								1	0.627 *
	AOU									1

Note: * significance level $p < 0.05$; ** significance level $p < 0.01$. DIN means dissolved inorganic nitrogen.

The relationship between nutrients showed significant positive correlations between the inner bay and the outer bay, which suggested that they had similar sources. It could also provide the evidence that can support the difference in nutrient supply conditions between the inner and outer bays. In addition, the phosphorus showed a significantly negative relationship with salinity, which indicates that the nutrients in the seawater were affected by the local discharge. The DIN showed a significantly negative relationship with the salinity in the inner bay, but a positive relationship in outer bay, implying

a freshwater source of DIN in the inner bay and a marine source in the outer bay. This also supports the hypothesis mentioned above of a nitrogen limiting condition in inner bay but phosphorus limiting in outer bay. The relationship between temperature and DO both showed negative correlations in the inner and outer bay, implying different situations for the inner and outer bay. High temperatures and sufficient nutrients in the inner bay resulted in strong consumption of oxygen in decomposition, more so than the process by photosynthesis in the semi-closed bay, where the water was clearer due to a strong mixing process, and more than the relatively cold water in the outer bay. The relationship between Chla and DO showed a significant negative correlation in the inner bay, but no relationship was found in the outer bay. This suggested that the respiration of organisms and decomposition of organic matter (oxygen consumption process) in seawater were more important than photosynthesis (oxygen release process) by phytoplankton; that is, the dissimilation process played a leading role in the inner bay, which is consistent with the discussion above. In addition, the positive correlation between Chla and AOU and the negative correlation between pH and nutrients were found in the inner bay, which also indicates that the dissimilation process was dominant in the inner bay. Photosynthesis by phytoplankton produced organic matter, which was oxidized and decomposed, consumed a significant quantity of oxygen, and produced a higher concentration of nutrients.

5. Conclusions

Combined with the analysis of other physico-chemical parameters, the higher nutrient concentrations in the inner bay originated mainly from the diluted freshwater from the local environment, mariculture, and rivers. We found significantly low DO and AOU levels in the inner bay, and high DO and low AOU levels in the outer bay and the bay mouth, which suggests that decomposition was more important than photosynthesis in the semi-closed bay, even during the spring when the phytoplankton was blooming. Different biochemical coupling processes were observed in the inner bay and outer bay with similar concentrations of Chla and nutrients. Therefore, unlike the bays with open bay mouths and a large flow of rivers, the higher levels of nutrients in the semi-closed bay could deplete the dissolved oxygen, due to the dominant dissimilation process, and inhibit the growth of phytoplankton. Restricted by topography and tidal prism, the aquatic ecosystems of semi-closed bays are more fragile and influenced by human activities than we thought.

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