Seasonal and Spatial Controls on the Eutrophication-Induced Acidification in the Pearl River Estuary

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Abstract Our understanding of eutrophication-induced acidification in estuaries and coastal oceans is complicated by the seasonally and spatially changing interactions between physical and biochemical drivers. By combining the conservative mixing method and a physical-biogeochemical model, we present the seasonal and spatial dynamical analysis of eutrophication-induced acidification in the Pearl River Estuary in the northern South China Sea. In summer, the widespread eutrophication-induced acidification is regulated by two distinct physical drivers, which are the strengthened stratification in the hypoxia zone and the high turbidity in the Lingdingyang Bay. In the hypoxia zone, eutrophication-induced acidification is controlled by the combined effect of benthic remineralization and stratification, while it is dominantly regulated by local biochemical processes (nitrification and respiration) of the whole water column in other regions of the estuary. In winter with the enhanced vertical mixing, the eutrophication-induced acidification is still active in the Lingdingyang Bay, and its strength has largely decreased compared with summer condition. While for the hypoxia zone, the eutrophication-induced acidification peaks in summer and disappears in winter.

Plain Language Summary Eutrophication in estuaries has accelerated the ocean acidification, which induced a negative impact on marine ecosystem. In the estuary, physical and biochemical processes lead to difficulties in understanding and evaluating the impact of eutrophication-induced acidification. High-resolution and coupled oceanographic models can reproduce the biogeochemical cycles in the marine system and present an integrated framework to understand ocean acidification. We revealed two distinct types of eutrophication-induced acidification in the estuary by using an oceanographic model. The model results show that these two types of eutrophication-induced acidification are regulated by different physical processes that are water stratification and turbidity, which result in their unique seasonal evolution patterns.

1. Introduction

Ocean acidification (OA) is an increasingly serious threat to marine ecosystems (Doney et al., 2009; Hofmann et al., 2010; Sillig & Sorte, 2018; Sunday et al., 2017). Since the industrial era, the ocean has absorbed about one third of anthropogenic CO₂ emissions, which leads to a pH decrease of ∼0.1 in global ocean (Caldeira & Wickett, 2003; Feely et al., 2004; Orr et al., 2005). In coastal areas, organic matter oxidation and the decreased buffering capacity further aggravate acidification in the subsurface by another ∼0.34 pH (Cai et al., 2011). With combined climatic and anthropogenic influences, coastal ecosystems are facing more severe and complex OA that may be intensified in the future (Cai et al., 2011).

The estuary receives a large amount of freshwater discharge, terrestrial nutrients and organic materials from upstream (Doney, 2010; Levin et al., 2015; Rabouille et al., 2001), which results in a more active biogeochemical reaction system in coastal areas. The strong terrestrial nutrients influx can cause eutrophication in estuaries (Cai et al., 2011; Feely et al., 2010; Hagens et al., 2014; Sunda & Cai, 2012) with elevated primary production that increases pH levels through biological CO₂ removal in the upper water column (Borges & Gypens, 2009; Cai et al., 2020; Jiang et al., 2019). The benthic aerobic respiration of the organic matter (both marine and terrestrial origin) reduces the dissolved oxygen (DO) concentration (Rabouille...
et al., 2008) and returns CO₂ to the water column, which lowers pH levels in the subsurface water (Altieri & Gedan, 2014; Breitburg et al., 2015; Laurent et al., 2017; Xiong et al., 2020).

The ratio of DO change to dissolved inorganic carbon (DIC) change (Δ /ΔDO DIC) induced by aerobic respiration generally matches with the Redfield ratio, which is widely used to quantify OA in global oceans. In the estuary, however, the Redfield stoichiometry could break down under oxygen-depleted conditions (e.g., Cai et al., 2017). Moreover, the estuary is a complex system affected by dynamical processes across different interfaces. Previous studies have shown that shorter equilibrium time of oxygen (O) than CO₂ also makes Δ /ΔDO DIC deviate from the Redfield ratio at surface (Jiang et al., 2019). At the land-ocean interface, the chemical characteristics of the river runoff strongly influence OA distribution in the estuary (Aufdenkampe et al., 2011; Baumann & Smith, 2017; Guo et al., 2012; Moore-Maley et al., 2018; Lowe et al., 2019), which essentially decouples from the one-dimensional framework. Vertical mixing can bring bottom acidic water into the surface layer and affect coastal chemistry (Salisbury et al., 2008). While hypoxia in the coastal ocean has received significant attention, the decoupling between DO and carbon dynamics in the estuary makes it challenging to quantify OA by simply linking it with Oxygen consumption.

The Pearl River is the largest river discharging into the northern South China Sea. It transports a large amount of freshwater (∼3.3 × 10¹¹ m³ yr⁻¹) and terrigenous materials (∼9.2 × 10⁵ t yr⁻¹ organic matter) through its eight outlets into the coastal area (Figure 1), and nearly 80% of the river discharge occurs from April to September. Among the eight outlets, Modaomen contributes the largest estuarine freshwater flux (∼25% of the total amount), and the second to the fourth contributions are from Humen (∼24%), Jiaomen (∼18%) and Hengmen (∼13%), respectively (Hu et al., 2011). Eutrophication has been reported in the Pearl River Estuary (PRE) and adjacent shelf (Dai et al., 2008) under the increasing anthropogenic nutrients influxes from watershed (Qian et al., 2018). The imbalance of urban development and diverse watershed features in the PRE result in different biochemical reaction systems between the western and eastern estuary, leading to the increasingly recognized eutrophication and associated seasonal hypoxia in the bottom water (Su et al., 2017). In summer, the Humen outlet (eastern estuary) is affected by nitrification (Nitr) and aerobic respiration. The runoff from upstream is characterized by low DO concentration (<5 mg L⁻¹, Cai et al., 2004; Zhai et al., 2005) and low pH (~7.0, Zhai et al., 2005). The upstream runoff at Modaomen outlet
(western estuary) also presents low pH (<7.3), while the DO concentration is relatively high (>6 mg L\(^{-1}\), Wang et al., 2017). In the Lingdingyang Bay located at the downstream of Humen outlet, bottom hypoxia defined as DO < 3 mg L\(^{-1}\) is mainly caused by aerobic respiration of marine sourced organic matter (Su et al., 2017). In the coastal transition zone (Li et al., 2020; Yu et al., 2020) of Modaomen outlet, sediment O demand plays a key role in hypoxia generation (Wang et al., 2017).

In winter, the amount of freshwater and terrigenous material input into the estuary are significantly reduced compared with that in summer. With the weakened vertical stratification (Hong et al., 2016), hypoxia area disappears in the PRE, but eutrophication still exists (Qiu et al., 2010). A previous study has shown that the organic carbon accumulated in the sediment of the PRE in summer will continue to affect the carbon system in the water column through mineralization in autumn and winter (Liang et al., 2020).

By excluding mixing-induced pH change, eutrophication-induced surface pH increase and bottom acidification in summer have been recently reported in the PRE, which demonstrates strong spatial variability of DIC and pH (Zhao et al., 2020). However, the seasonal evolution of eutrophication-induced acidification in the PRE still remains largely unknown. In this study, by using a coupled physical-biogeochemical model and the conservative mixing method, we examine the seasonal generation and elimination mechanisms of eutrophication-induced acidification downstream the eight outlets in the PRE.

2. Model and Method

2.1. The Coupled Physical-Biogeochemical Model

The physical model is a three-dimensional hydrodynamical model coupled with a one-dimensional river network model (Hu & Li, 2009), which captured freshwater and suspended sediment fluxes (SFs) from Pearl River Delta to the estuary. The biogeochemical model is the extended Row-Column Advanced Ecological Systems Modeling Program model (RCA; HydroQual Inc., 2004) that includes cycles of nitrogen, phosphorus, O, silicon, and carbon between aquatic and sediment (see details in Liang et al., 2020 and Wang et al., 2017). RCA uses the transport fields that result from the physical model computation to compute the transport of water quality within the study domain. The inorganic carbon in the water column is affected by phytoplankton and bacterial metabolism, the carbon chemistry balance, and sediment-water flux and air-sea CO\(_2\) flux (Liang et al., 2020). The coupled model has been successfully used for the budget analysis of nutrients (Hu et al., 2011), simulation of hypoxia (Wang et al., 2017; H. Zhang & Li, 2010), simulation of distributions of DIC, total alkalinity (TA), CO\(_2\) partial pressure (pCO\(_2\)), and organic carbon, and the estimation of carbon fluxes (Liang et al., 2020) in the PRE.

The DIC, TA, pH (total scale) at in situ temperature, and pCO\(_2\) are parameterized and simulated in both aquatic and sediment based on previous studies (Borges et al., 2005; Fennel et al., 2008; Millero, 1995; Raymond & Cole, 2001). The biogeochemical processes can consume/produce DIC and TA according to the stoichiometric ratios in the corresponding reaction equation and further affect the modeled pH and pCO\(_2\) (Liang et al., 2020).

2.2. The Conservative Mixing Method

Under stable flow conditions after tidal cycle averaging, the concentration distribution of conservative tracers in relation to salinity can be expressed by the following three end-members conservative mixing (Álvarez-Salgado et al., 1997; Fry, 2002):

\[
F_r + F_b + F_s = 1
\]  
\[
\theta_r F_r + \theta_b F_b + \theta_s F_s = \theta_{simulation}
\]  
\[
S_r F_r + S_b F_b + S_s F_s = S_{simulation}
\]
\[ \theta_{r,b,s,\text{simulation}} = T_{r,b,s,\text{simulation}} \left( \frac{1000}{P} \right)^{0.286} \]  

(4)

where \( F_r, F_b \) and \( F_s \) are fractions of the three end-members, which are the upstream river discharge, the offshore bottom water and the offshore surface water, respectively. \( \theta_{r,b,s}, T_{r,b,s} \) and \( S_{r,b,s} \) are the potential temperature, temperature and salinity of the three end-members. \( T_{\text{simulation}} \) and \( S_{\text{simulation}} \) are the modeled temperature and salinity. \( P \) is the pressure.

The conservative mixing concentrations \( (C_{\text{Conservative Mixing}}) \) of DIC or TA resulting from the mixing of the three end-members can be calculated by:

\[ C_{\text{Conservative Mixing}} = C_r F_r + C_b F_b + C_s F_s \]  

(5)

where \( C_r, C_b \) and \( C_s \) are the concentrations of the three end-members. For the western PRE, freshwater end-member is selected in the upstream of Modaomen outlet. For the eastern PRE, freshwater end-member is selected in the upstream of Humen outlet. Their offshore subsurface water and offshore surface water end-members are similar (Figure 1; Appendix A).

The salinity-dilution curves for the calcite saturation state \( (\Omega_{\text{Calc}}) \) and pH are nonlinear (Rheuban et al., 2019). Therefore, their conservative mixing values \( (V_{\text{Conservative Mixing}}) \) are calculated by CO2SYS (Pierrot et al., 2006) using the \( (\text{DIC, TA})_{\text{Conservative Mixing}} \). CO2SYS is a widely used software that calculates and returns a detailed state of the carbonate system for oceanographic water samples. The differences \( (\Delta V) \) between modeled and conservative values of DIC, TA, pH and \( \Omega_{\text{Calc}} \), represent the change induced by biochemical processes (eutrophication-induced acidification) with positive values indicating addition and negative ones indicating removal:

\[ V_{\text{Biochemical}} = V_{\text{Simulation}} - V_{\text{Conservative Mixing}} \]  

(6)

3. Results and Discussions

3.1. Model Validation

In this study, summer and winter data-sets are used to examine the distribution of carbonate system and coastal acidification in the PRE and to validate the model results. The in situ data including salinity, temperature, nutrients, organic carbon, DO, pH and TA at different depths were collected by the State Oceanic Administration of China from July 15 to August 24, 2006 and from December 3, 2006 to January 20, 2007 in the PRE and its adjacent coastal area (Wang et al., 2017; H. Zhang & Li 2010). The carbon cycle component of our model has been extensively validated in previous studies (Liang et al., 2020; Ye et al., 2021), and the model skill in simulating key carbon cycle dynamics in PRE is comparable with the modeling studies conducted in other regions (Fitzpatrick, 2009; Kwiatkowski et al., 2014; Sohma et al., 2018). Therefore, this study focuses on the validation of the modeled distribution of DO, pH and TA. Modeled daily averaged pH, DO and TA in the PRE are compared with in situ observations (locations shown in Figure 1) in summer 2006 (Figures 2 and 3). The correlation coefficients between simulated results and observations of the three variables are higher than 0.68 (0.68–0.89), and the relative errors are lower than 13% (1.8%–20.37%). The root mean square errors of pH and TA are low (0.17 pH, 0.20 mmol L$^{-1}$), while that of DO is relatively higher (0.50 mg L$^{-1}$). The model reasonably reproduces the distribution patterns of pH, DO and TA of different water masses in the region (Zhao et al., 2020), that is, except in the hypoxia zone, low pH is often accompanied with low DO, salinity and TA (Figure 2), which is a typical feature in the PRE due to the strong summer runoff from upstream. The validation results for water quality variables, hydrodynamics and turbidity can be found in our previous studies (Wang et al., 2017; H. Zhang & Li, 2010). In winter, the model also can reasonably capture pH distributions with the correlation coefficient of 0.74, the root mean square error of 0.09, and the relative error of 0.98% (Figure S1). These comparisons indicate that the model can be used to examine seasonal dynamics in the PRE.
In addition, the vertical distributions of simulation results match with the observations (Figure 3). The model captures the distribution features of DO, pH (Figure 3), and TA (Figure S2) in different sub-regions of PRE. Low Oxygen condition (DO < 6 mg L$^{-1}$) coupled with low pH (<7.8) occurs in the entire water column near Humen outlets (Figure 3), while the low Oxygen area near Yamen outlet (Figure 3b) only appears at the bottom and it is accompanied with relatively high pH (>7.8, Figure 3g). Bottom DO consumption occurs downstream in the Lingdingyang Bay, which also induces a slight decrease in pH (Figures 3c and 3h). Modeled low TA distributes along with the spreading of the river plume at surface, which is consistent with observations (Figure S2).

3.2. Eutrophication-Induced Acidification in Summer

The inner Lingdingyang Bay is affected by runoff with low pH (pH < 7.65; Figure 4a) and low DO concentration (<6 mg L$^{-1}$). The area with low calcite saturation state ($\Omega_{Cal} < 1$) extends with a wide salinity range (Figure 5a), which reflects the effect of low pH runoff (Baumann & Smith, 2017; Salisbury et al., 2008). In the outer Lingdingyang Bay and Modaomen sub-estuary, pH at the bottom layer is significantly higher than that at the sea surface, and $\Omega_{Cal}$ at the bottom layer increases rapidly to ~4. Previous studies have reported that the bottom hypoxia zone in the Modaomen sub-estuary is accompanied by high DIC concentration (Liang et al., 2020), which is induced by the combined effects of water bottom respiration, benthic biochemical processes, and vertical stratification (Wang et al., 2017). Spatial distribution of pH is significantly affected by the biochemical processes (Figures 4a and 4b) compared with conservative mixing pH (Figures 4c and 4d), which indicates the importance of eutrophication-induced acidification. The $\Delta$ pH shows that vertical decoupling between surface eutrophication and subsurface acidification occurs in the hypoxia
zone (Figures 4e and 4f), which may imply the importance of bottom seawater intrusion with high pH and its mixing with low pH discharge.

According to the spatial distribution of $\Delta pH$ in summer, there are regions with 0.4–0.6 pH increase along the western shoreline of PRE and in the Shenzhen Bay (Figure 4e), which is consistent with the regions where surface chlorophyll concentrations are high (Figure S3). The production induced surface pH increase in summer is also reported by Zhao et al. (2020). As a consequence, the production-induced carbon assimilation appears to limit the spatial extent of the low $\Omega_{Cal}$ (<1) at surface caused by runoff (Figure 5b). The $\Omega_{Cal}$ of the eastward spreading plume reaches the value of 3–4, which is consistent with previous observations (Cao et al., 2011). Summer stratification leads to the decoupling between the surface primary production induced DIC consumption and bottom water DIC supplementation via mineralization (Liang et al., 2020), resulting in the generation of acidification at bottom in Lingdingyang Bay and Modaomen.
sub-estuary, with the pH reduction ranging from 0.1 to 0.4 units (Figure 4f). The location and magnitude of bottom pH decrease at the downstream region of Lingdingyang Bay match well with Zhao et al. (2020). Furthermore, this study shows a stronger and widespread pH decreasing region inside the Lingdingyang Bay (Figure 4f), while the hypoxia in this region has been shown not as significant as in the Modaomen sub-estuary (Su et al., 2017; Yu et al., 2020). Eutrophication-induced acidification of PRE is of great spatial variance with the range from 0.1 to 0.6 similar to the one in Chesapeake Bay (Cai et al., 2017) but more intensive when compared with open ocean acidification globally.

Eutrophication-induced acidification at bottom also leads to a decrease of $\Omega_{Cal}$ (Figure 5). However, sensitivities of $\Omega_{Cal}$ and acidification in different regions are not uniform (Figures 4 and 5). The $\Omega_{Cal}$ decreases by 0.5~1 in Lingdingyang Bay, where pH decreases about 0.2 pH. The $\Omega_{Cal}$ decrease in the hypoxia zone

**Figure 4.** Monthly averaged spatial distributions of (a and b) simulated pH, (c and d) conservative mixing pH and (e and f) eutrophication-induced $\Delta pH$ during August 2006. The white contours in (a–d) denote isolines of pH. The black contours in (e) denote isolines of salinity 5, 15, 25‰, respectively. The purple contours in (f) denote the hypoxia zone defined by $DO = 3$ mg L$^{-1}$. 
near the Modaomen sub-estuary can reach 2~4, while the pH only decreases 0.1–0.2 units. This regional difference may be due to the fact that DIC is close to TA in the strong estuarine acidification region (Cai et al., 2017) of Lingdingyang Bay, which leads to a tight correspondence of pH with Ω_{Cal} change there (Cai et al., 2011). Moreover, the ratio of the benthic fluxes of TA and DIC in different regions, and the buffer capacity of different rivers and seawater might also contribute to the different changes of pH and Ω_{Cal}. In the inner Lingdingyang Bay, high turbidity upstream runoff limits the surface production-induced pH decrease (basification) in summer (<0.1 pH), but it leads to the intense benthic eutrophication-induced acidification (up to 0.4 pH). These results reveal that local biogeochemical processes play a role in modifying eutrophication-induced acidification in different subregions. It also suggests that in some regions of PRE, eutrophication-induced acidification is more severe than in the open ocean and the plume area estimated by Cai et al. (2011).

### 3.3. Seasonal Evolution of Eutrophication-Induced Acidification

Extending the analysis to the seasonal cycle, the eutrophication-induced acidification in the hypoxia region (AS1 in Figure 5a) appears in June, peaks in August, and disappears in October (Figures 6 and 7a and Figure S4). The surface basification lasts from April to October, which covers the period of eutrophication-induced acidification occurring at bottom from June to September. In comparison, surface basification is not clear in the along shoreline section of Lingdingyang Bay (AS2 in Figure 5a) in summer when eutrophication-induced acidification reaches the maximum at bottom (Figure 7b and Figure S5). While in other seasons, the section is always associated with strong production-induced surface basification and relatively weak eutrophication-induced acidification at bottom (Figure S5).
Local hydrodynamic processes play important roles in the evolution of eutrophication-induced acidification in different subregions of the PRE (Figures 7a and 7b). Although with river discharge, the turbidity (represented by suspended sediment concentration (SSC)) of the water column is relatively low and the vertical stratification quantified by the potential energy anomaly (Burchard & Hofmeister, 2008; Appendix B) is at a high level (~60 J m\(^{-3}\)) of the year when eutrophication-induced acidification occurs in the hypoxia region of the Modaomen sub-estuary (AS1; Figure 7a). When the acidification reaches the peak in August, the stratification begins to weaken. In contrast, the eutrophication-induced acidification at the Lingdingyang Bay section (AS2) peaks accompanying with relatively weak stratification (~30 J m\(^{-3}\)) and high turbidity (SSC > 20 mg L\(^{-1}\)) due to river discharge in summer. When vertical stratification and the turbidity of water column decrease in spring and fall, strong basification (>0.5 pH) appears at the sea surface in the Lingdingyang Bay (Figures 6d and 6h), and eutrophication-induced acidification weakens at bottom.

3.4. Uncertainty Analysis of Conservative Mixing Method

The reliability of conservative mixing method largely depends on the choice of endmembers, which may lead to uncertainty in the estimation of eutrophication-induced acidification. In order to evaluate this uncertainty, we set the following endmember selection cases to examine the upper and lower limits and uncertainty of eutrophication-induced acidification in summer. The variation of pH is affected by temperature, salinity, DIC, and TA. The statistical results of those state variables at the endmembers of west four outlets (salinity < 2), east four outlets (salinity < 2), and the open sea (salinity > 32) at both surface and bottom in August are listed in Table 1.

Among them, when the salinity, temperature, DIC increase, and TA decrease at endmembers, the conservative mixing pH of the endmembers will decrease, resulting in overestimation of basification and under-estimation of eutrophication-induced acidification. Therefore, the numbers of Table 1 marked by one star (*) represent the selection of endmember with the weakest in eutrophication-induced acidification, and
the numbers with two stars (**) represent the strongest eutrophication-induced acidification case. For the water column, the strongest eutrophication-induced acidification of AS1 is $-0.08 \pm 0.13$ (negative indicates pH decrease; Figure 8a), the weakest is $0.01 \pm 0.17$ (Figure 8e), and the average is $-0.04 \pm 0.16$ (Figure 8c). The strongest acidification of AS2 is $-0.21 \pm 0.19$ (Figure 8b), the weakest is $-0.10 \pm 0.17$ (Figure 8f), and the average is $-0.16 \pm 0.18$ (Figure 8d). As shown in Figure 8, although variability exists in the intensity of bottom acidification and surface basification due to the selection of endmembers, the maximum eutrophication-induced acidification of AS1 in all the three cases can reach $-0.25$ and that of AS2 is $-0.45$.

It is noteworthy that endmember selection and mixing characteristics may lead to uncertainty in the calculation of eutrophication-induced acidification. The uncertainty may be reduced by selecting endmembers in a reasonable spatial range based on mixing characteristics of the study area. The endmember selection in this study is an optimized selection based on the prior knowledge of characteristics of upstream and the regional biogeochemical condition. The estimated eutrophication-induced acidification falls within the upper and lower limits and is close to the mean case.

3.5. Biochemical Processes of Eutrophication-Induced Acidification

The difference between DIC ($\Delta DIC$) and TA supplementation ($\Delta TA$) is a key indicator of pH and buffer capacity change (Cai et al., 2020). Take Nitr as an example, the reaction describing the complete Nitr process is:

$$\text{NH}_4^+ + 1.89 \text{O}_2 + 1.98 \text{HCO}_3^- \rightarrow 0.98 \text{NO}_2^- + 0.016 \text{C}_2\text{H}_3\text{O}_2\text{N}_4 + 1.90 \text{CO}_2 + 2.93 \text{H}_2\text{O}.$$  

The stoichiometric coefficients imply that 1 mole ammonium ($\text{NH}_4^+$) removal through Nitr requires 1.98 mole of TA and DIC consumption and produces 1.90 mole of free CO$_2$ (Dai et al., 2008). Then the difference between $\Delta DIC$ and $\Delta TA$ is 1.90 mole. The reaction equations of other processes are listed in Appendix C.
The biochemical induced differences between $\Delta DIC$ and $\Delta TA$ budgets are calculated for the four sections (AS1 and AS2 in Figure 9; CS1 and CS2 in Figure S6). The budget analysis shows that benthic DIC supplementation is higher than TA from June to September in the hypoxia region of Modoamen sub-estuary (AS1; Figure 9a). The period coincides with the timing of eutrophication-induced acidification occurred in this section. However, in the other three sections, benthic DIC supplementations are consistently higher than TA all year round (Figures 9b, Figures S6c and S6g), indicating a persistent bottom acidification enhanced by benthic biochemical processes.

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Analysis of the difference between DIC and TA supplementation of the entire water column further reveals diverse mechanisms of the generation and elimination of eutrophication-induced acidification in the PRE. In the hypoxia region of Modaomen sub-estuary (AS1), the budget analysis shows that the TA addition is greater than that of DIC, which results in the amount of hydrogen ion ([H+]\(^{+}\)) decrease in the entire water column from June to August (Figure 9c). Strong stratification in this section during summer results in the decoupling between the primary production in surface water and respiration in bottom water. Therefore, acidification is mainly supported by bottom water respiration and benthic biochemical processes. For the other three sections, their benthic and water column budgets are in a similar pattern. In the Lingdingyang Bay section (AS2, Figure 9d), the water column budget reveals that \(\Delta DIC - \Delta TA\) induced by community respiration (including autotrophic respiration (AR), heterotrophic respiration (HR), Nitr, denitrification (Denit) and SF) shows small variance (2.3 mmol C m\(^{-3}\) day\(^{-1}\)) during the whole year, while primary production changes significantly in different months (9.2 mmol C m\(^{-3}\) day\(^{-1}\)). When eutrophication-induced acidification peaks from June to August, primary production of the entire water column is weakest during the year, turbidity is highest, and stratification is at a relatively weak level than the Modaomen sub-estuary (Figure 9d). In other months, low water turbidity benefits for the increase of primary production, and with relatively stable and weak stratification, the eutrophication-induced acidification is sharply decreased in the Lingdingyang Bay. In addition, significant differences in biochemical contributions to the eutrophication-induced acidification are found in different regions of the PRE. In the hypoxia region of Modaomen sub-estuary (AS1), the eutrophication-induced acidification is mainly driven by AR, HR, sediment release, and Nitr (Figure 9a). The existence of strong water stratification highlights the importance of the sediment release process to eutrophication-induced acidification in this region. While for the sections in Lingdingyang Bay, Nitr, AR and HR (Figures 9b and 9d and Figure S6) are shown to be the driving factors for eutrophication-induced acidification. Moreover, the temporal evolution of eutrophication-induced acidification of AS1 is different from AS2, because the bottom water respiration and benthic remineralization play key roles at AS1 while water column biochemical processes dominate the eutrophication-induced acidification at AS2.

3.6. Conceptual Model of the Eutrophication-Induced Acidification in Pearl River Estuary

In the coastal area influenced by river plume, Cai et al. (2011) revealed the surface eutrophication and subsurface acidification and suggested that the subsurface acidification is induced by aerobic respiration. The PRE receives a large amount of terrestrial material input seasonally at eight outlets, which leads to the evolution of eutrophication-induced acidification largely different from the coastal plume area and the open ocean. The benthic respiration and remineralization are active during the whole year. The local physical dynamics result in two distinct types of eutrophication-induced acidification in the estuary (Figure 10).

In wet season (summer), river discharge strongly affects the entire estuary. The particulate matter carried by the discharge settles down to the
sediment at the inner side of the salinity front, forming a high turbidity area near the outlet (Figure 10) and leading to the benthic carbon accumulation in the sediment (Liang et al., 2020). The remineralization of settled organic matter causes the occurrence of eutrophication-induced acidification at bottom in the high turbidity area (Type I, turbidity enhanced). This process is clear in the alongshore section of Lingdingyang Bay (AS2). While the plume water with low salinity spreads away from the outlet and interacts with the open sea, stratification and light availability increase, which stimulates the algae bloom and results in the pH increase in the upper layer. When organic matters sink down from the salinity front, they will be remineralized and release DIC into bottom water, which will induce the acidification at bottom when strong stratification exists (Type II, stratification enhanced). This process occurs in the hypoxia region of Modaomen sub-estuary (AS1).

In dry season (winter), eutrophication-induced subsurface acidification reduced (Figure 10). The organic matter accumulated in the sediments from late spring to autumn are gradually remineralized. The released \( \text{NH}_4^+ \) from sediment affects the primary production of PRE in winter (L. Zhang et al., 2014). Due to the reduction of river discharge, the high turbidity zone and the salinity front shrink to the upstream region. The turbidity of the estuary water is low and vertical stratification is weakened, which benefits the vertical exchange. Therefore, for Type I (turbidity enhanced), although the benthic DIC supplementation via biochemical processes in winter is still higher than TA (Figure 9b), the strengthen of eutrophication-induced acidification is sharply decreased relative to summer. While for Type II (stratification enhanced), the physical environment can no longer support the decoupling between primary production and respiration, which leads to the disappearance of eutrophication-induced acidification in the hypoxia zone.

### 3.7. Comparison With Other Coastal Area

The stratification enhanced type of eutrophication-induced acidification in the PRE in summer is consistent with the formation mechanism proposed by previous studies in the north Gulf of Mexico (Cai et al., 2011; Laurent et al., 2017). That is, stratification weakens water mixing, resulting in the decoupling between the surface basification and subsurface acidification. Moreover, the PRE shows its characteristics in the elimination of eutrophication-induced acidification. Due to the shallow water depth (<15 m) and the strong influence of river discharge, vertical salinity gradient can dominate the stratification in the PRE. The decay of salinity stratification in autumn and winter benefits the CO\(_2\) mixing/evasion from the bottom water, which weakens the acidification of water column. In other marginal seas (Zhai, 2018), temperature stratification occurs in summer and autumn, which results in the CO\(_2\) generated by mineralization of organic matter accumulated in the bottom water, and the continuation of acidification in autumn. Therefore, the formation and evolution of seasonal stratification, as well as the effect of physical factors such as water residence time, may lead to significant differences in the intensity, range, and duration of ocean acidification in different coastal systems.

The existence of turbidity-enhanced type of eutrophication-induced acidification in the PRE indicates that processes inducing the decoupling of primary production and respiration in space and time will lead to the occurrence of acidification (Cai et al., 2011; Laurent et al., 2017). The high turbidity weakens the light availability and limits the primary production. In this case, the acidification cannot be balanced by local primary production. Moreover, eutrophication-induced acidification in the PRE is spatially varied. It exists in the Lingdingyang Bay almost all year round, while it is a seasonal phenomenon in the hypoxia zone. The year-round continuous positive \( \Delta \text{DIC} - \Delta \text{TA} \) supplementation induces eutrophication-induced acidification in the Lingdingyang Bay and leads to an important environmental risk. When eutrophication exacerbates in the plume area and coastal area, the eutrophication-induced acidification reported in summer (Laurent et al., 2017) may extend to other seasons and affect the coastal carbon cycle system (i.e., air-sea CO\(_2\) flux). The spatial variability of eutrophication-induced acidification in the PRE suggests that the combination of buffering capacity of the carbonate system from different water masses and the biochemical processes (e.g., primary productivity, Denit, precipitation/dissolution of CaCO\(_3\)) will result in diverse coastal acidification mechanisms (Carstensen & Duarte, 2019). For example, Laurent et al. (2017) found that the benthic DIC efflux and small detritus remineralization are the main factors driving local acidification in the north Gulf of Mexico, while the respiration and Nitr in water and sediment are the main factors in the PRE, and the oxidation of reduced chemicals (i.e., H\(_2\)S, \( \text{NH}_4^+ \), Mn\(^{4+}\), Fe\(^{3+}\)) is responsible for the pH minimum in the low O\(_2\) zone in the Chesapeake Bay (Cai et al., 2017).
4. Conclusions

In this study, we present the seasonal and spatial analysis of eutrophication-induced acidification in the PRE. The eutrophication-induced acidification in PRE is a dynamical evolution process throughout the year, which is connected with localized changes in primary production, remineralization of organic matters and physical processes. The different chemical characteristics of discharge water at the eight river outlets also affect the acidification and basification caused by local biochemical reactions in the PRE. The estuary receives continuous nutrient influxes from terrestrial and sediment throughout the year, resulting in the persistent risk of the eutrophication-induced acidification in the subtropical estuary such as the PRE. The mixing of runoff and open sea water in the estuary results in a sharp and variable seaward gradient of carbonate system in the estuary. Our results show that, stratification and turbidity are important local physical factors affecting the generation and elimination of eutrophication-induced acidification with significant spatial and temporal variabilities. In the hypoxia zone, eutrophication-induced acidification is primarily controlled by the remineralization occurs in the water bottom and sediment, and enhanced by stratifica-
tion in summer. It results in the coexistence of surface basification and bottom acidification in summer, which are absent in other seasons. In other regions, the evolution of eutrophication-induced acidification is dominantly regulated by local biochemical processes (Nitr and respiration) of the whole water column due to the existence of high turbidity.

Appendix A: Endmember Values of DIC, TA, Salinity, Potential Temperature and Temperature in Each Month of 2006

| Month | West four outlets | East four outlets |
|-------|------------------|------------------|
|       | DIC   | TA   | S   | θ   | T   | DIC   | TA   | S    | θ   | T    |
|       | mmol/L | mmol/L | %  | °C  | °C  | mmol/L | mmol/L | %  | °C  | °C  |
| Jan   | 2.09  | 2.07  | 3.12 | 17.65 | 17.67 | 2.11  | 2.12  | 4.79 | 17.51 | 17.52 |
| Feb   | 1.99  | 1.94  | 3.80 | 17.59 | 17.61 | 2.01  | 2.01  | 6.13 | 18.27 | 18.29 |
| Mar   | 1.89  | 1.80  | 1.10 | 18.53 | 18.56 | 1.89  | 1.82  | 1.92 | 19.28 | 19.29 |
| Apr   | 1.79  | 1.67  | 0.23 | 21.51 | 21.53 | 1.77  | 1.65  | 0.65 | 22.23 | 22.24 |
| May   | 1.70  | 1.58  | 0.11 | 25.77 | 25.80 | 1.57  | 1.45  | 0.18 | 25.46 | 25.47 |
| Jun   | 1.59  | 1.49  | 0.10 | 28.50 | 28.54 | 1.36  | 1.27  | 0.10 | 27.92 | 27.94 |
| Jul   | 1.48  | 1.40  | 0.10 | 29.50 | 29.54 | 1.14  | 1.10  | 0.10 | 29.43 | 29.45 |
| Aug   | 1.57  | 1.47  | 0.10 | 29.97 | 30.01 | 1.26  | 1.17  | 0.10 | 30.45 | 30.47 |
| Sep   | 1.66  | 1.56  | 0.13 | 29.84 | 29.88 | 1.37  | 1.27  | 0.19 | 30.66 | 30.68 |
| Oct   | 1.76  | 1.64  | 0.54 | 27.38 | 27.42 | 1.51  | 1.37  | 0.86 | 28.38 | 28.39 |
| Nov   | 1.83  | 1.72  | 1.08 | 22.66 | 22.69 | 1.54  | 1.46  | 1.00 | 23.27 | 23.28 |
| Dec   | 1.92  | 1.89  | 1.68 | 19.23 | 19.25 | 1.78  | 1.80  | 1.44 | 19.03 | 19.04 |

| Month   | Sea Surface | Sea Bottom |
|---------|-------------|------------|
| DIC     | TA          | S   | θ   | T   | DIC     | TA          | S   | θ   | T   |
| mmol/L  | mmol/L      | %  | °C  | °C  | mmol/L  | mmol/L      | %  | °C  | °C  |
| Jan     | 1.92        | 2.24 | 34.27 | 21.85 | 22.21 | 1.92        | 2.24 | 34.26 | 13.83 | 21.78 |
| Feb     | 1.93        | 2.21 | 34.44 | 21.58 | 21.93 | 1.93        | 2.21 | 34.44 | 13.60 | 21.43 |
| Mar     | 1.92        | 2.19 | 34.40 | 22.20 | 22.57 | 1.93        | 2.20 | 34.49 | 13.77 | 21.69 |
| Apr     | 1.91        | 2.16 | 33.47 | 24.64 | 25.05 | 1.95        | 2.19 | 34.48 | 13.71 | 21.60 |
| May     | 1.87        | 2.12 | 30.48 | 26.58 | 27.01 | 1.95        | 2.18 | 34.48 | 13.82 | 21.78 |
| Jun     | 1.82        | 2.08 | 28.44 | 28.30 | 28.76 | 1.96        | 2.17 | 34.49 | 13.94 | 21.97 |
| Jul     | 1.76        | 1.99 | 24.72 | 29.13 | 29.61 | 1.97        | 2.18 | 34.50 | 13.85 | 21.82 |
| Aug     | 1.80        | 2.07 | 26.34 | 29.10 | 29.58 | 1.95        | 2.19 | 34.46 | 14.25 | 22.45 |
| Sep     | 1.85        | 2.13 | 27.31 | 28.09 | 28.55 | 1.95        | 2.21 | 34.39 | 14.95 | 23.55 |
| Oct     | 1.93        | 2.25 | 32.83 | 26.94 | 27.38 | 1.97        | 2.24 | 34.16 | 15.80 | 24.90 |
| Nov     | 1.95        | 2.25 | 33.37 | 25.78 | 26.20 | 1.98        | 2.24 | 33.97 | 16.19 | 25.51 |
| Dec     | 1.96        | 2.23 | 33.57 | 24.13 | 24.52 | 1.97        | 2.20 | 33.81 | 15.26 | 24.04 |
Appendix B: Potential Energy Anomaly Calculation

As a convenient measure, the potential energy anomaly $\phi$ has been defined by Simpson and Bowers (1981) as the amount of mechanical energy (per m$^3$) required to instantaneously homogenize the water column with a given density stratification:

$$\phi = \frac{1}{D-h} \int gzd(\bar{\rho} - \rho)\,dz = \frac{1}{D-h} \int gzd\tilde{\rho}dz$$  \hspace{1cm} (B1)

with the depth-mean density

$$\bar{\rho} = \frac{1}{D-h} \int gzd\rho\,dz$$  \hspace{1cm} (B2)

the deviation from the depth-mean density, $\tilde{\rho} = \rho - \bar{\rho}$, the mean water depth $H$, the sea surface elevation $\eta$, the actual water depth $D = \eta + H$ and the gravitational acceleration $g$.

Appendix C: Biochemical Reactions in Water Column and Sediment Pore Water

Biochemical reactions in water column

Photosynthesis with ammonium:

$$106 CO_2 + 16NH_4^+ + H_2PO_4^- + 106H_2O \rightarrow Protoplasm + 106O_2 + 15H^+$$

Photosynthesis with nitrate:

$$106CO_2 + 16NO_3^- + H_2PO_4^- + 122H_2O + 17H^+ \rightarrow Protoplasm + 138O_2$$

Nitrification:

$$NH_4^+ + 1.89O_2 + 1.98HCNO \rightarrow 0.016C_9H_6O_2N + 0.984NO_3^- + 1.03H_2O + 1.90H_2CO_3$$

Denitrification:

$$5CH_4 + 4NO_3^- \rightarrow 3H_2O + 5CO_2 + 2N_2 + 4OH^-$$

Biochemical reactions in sediment pore water

Aerobic layer

Oxidation of hydrogen sulfide:

$$H_2S + 2O_2 \rightarrow SO_4^{2-} + 2H^+$$

Oxidation of methane:

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$$

Anaerobic layer

Sulphate reduction:

$$2H^+ + 2CH_4O + SO_4^{2-} \rightarrow 2CO_2 + H_2S + 2H_2O$$

Data Availability Statement

Data were not used, nor created for this research. The measurements at PRE and the model outputs in this study are available at http://doi.org/10.5281/zenodo.4300997.
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