We wish to thank the referee for the detailed and constructive comments which are very helpful to the revision of our manuscript. According to the comments, we have made revisions and improvements as below: 1) to include more results of validations and comparison of model skills between our model and other published studies; 2) to give clearer descriptions and explanations about 'physical modulation method' and its associated concepts; 3) to have an English editor edit our manuscript and correct grammatical mistakes throughout the text. The editing certificate and a marked-up manuscript version were provided at the end of this file.

7

8 Detailed responses to all comments are given below. (Responses are shown in *Italic Font*)

9

10 Referee #1

Comment: This paper reports on the use of a three-dimensional modeling system to explore the biogeochemical and 11 12 physical mechanisms regulating O2 dynamics and bottom water hypoxia in the Pearl River estuary. A novelty of the 13 study is the use of numerical O2 tracers to quantify the source and sink processes dictating O2 concentrations. The use 14 of these tracers benefitted a diagnostic O2 mass balance in this shallow and dynamic estuary. Further, the study 15 demonstrates the spatial connection between processes occurring in different locations in the system. From this 16 analysis, the conclusion is that air-sea mixing and sediment oxygen demand were the primary processes regulating 17 bottom-water O2 concentration and hypoxia. This is a different result than other well studied systems where hypoxia 18 occurs such as Chesapeake Bay and northern Gulf of Mexico. Overall, I think this is an interesting paper that for the 19 first time teases apart the biogeochemical and physical aspects of O2 dynamics in a shallow, river-dominated system. 20 Two major issues for the paper are the grammar and imprecise/incorrect use of language. I had to read many sentences 21 two or three times for the meaning to shine through. These issues should be resolved by having a fluent English 22 speaker edit the draft.

23 Response:

Thank the referee for the positive comments. As suggested, we have had an English editor edit the manuscript.

25 26 G

24

Comment: The use of 'ambient' here and throughout the paper is confusing to me. Do you mean to use 'adjacent'? It
 seems like you are inferring the advective and diffusive fluxes from adjacent grid cells. Please clarify.

28 Response:

Yes, the contributions of ambient biogeochemical processes (was changed into 'the contributions of adjacent source and sink processes (CAS)') represent the advective and diffusive fluxes of DO which is produced or consumed by the source and sink processes in the adjacent grid cells. According to Eq. 9, the contributions of ambient source and sink processes are described as $\Delta t \times [-ADV(DO_S) + DIFF(DO_S)]$.

We agree that the word 'ambient' could be misleading. Therefore, as suggested, we corrected the word 'ambient' to 'adjacent' throughout the revised manuscript. We also clarified this phrase in the revised manuscript (Page 8, line 4-7).

36 **Comment:** P1, line 25: As you haven't yet defined "modulation of physical processes" this phrase appears to be jargon

- 1 and is unclear to the reader.
- 2 Response:

We provided a clear definition of the 'physical modulation method' and its associated terms in Section 2.3 in the
revised manuscript.

With respect to the phrase 'modulation of physical processes', it should be the modulation of the effects of source 5 6 and sink processes on DO due to physical transport. In our study, we considered that DO concentrations could be 7 affected by the source and sink processes in two ways. Firstly, the source and sink processes can produce or consume 8 oxygen to change the local DO concentrations directly. Secondly, the source and sink processes can also change DO 9 concentrations in the adjacent grid cells and hence change the DO fluxes from these adjacent grid cell; as a result, the 10 DO concentrations will be affected by the source and sink processes occurred in the adjacent grid cells. We defined the latter mechanism as the modulation of the effects of source and sink processes on the DO due to physical transport. 11 To make it clear, we changed "modulation of physical processes" to "modulation of the effects of source and sink 12 13 processes on DO due to physical transport" accordingly throughout the revised manuscript.

14

15 Comment: P1, line 26: The values presented here and following seem like they should be process rates like 4.31 mg
16 l-1 d-1. Or if this value is an average over some seasonal or annual period, please state this.

17 Response:

This value (4.31 mg L^{-1}) represents the decrease in DO concentrations due to the sediment oxygen demand using the physical modulation method. It is averaged over July-August 2006. Specifically, the value of 4.31 mg L^{-1} indicates that the two-month averaged bottom DO concentrations will be higher by 4.31 mg L^{-1} if the effect of the sediment oxygen demand on DO is ignored. As suggested, we have clarified this in the revised manuscript (Page 1, line 16-17).

22

Comment: P1, line 32-33: This sentence doesn't make sense. On the one hand it is stated that photosynthesis increased the O2 concentration, but then it also increased the hypoxic area (decreased O2 concentration). Please clarify.

26 Response:

Yes, there is a mistake here. What it should be is that the hypoxic area is increased when turning off the
photosynthesis and water column respiration. This has been corrected in the revised manuscript (Page 1, line 27-29).

29

Comment: P2, lines 2-7: These sentences are not clear and appear unnecessary. I suggest deleting them and starting
 the Introduction with line 8,

32 Response:

- 33 As suggested, we deleted these sentences in the revised manuscript.
- 34
- **Comment:** P3 line4: "Pearl River Estuary", estuary should not be capitalized

36 Response:

37 As suggested, we have changed it to 'Pearl River estuary' throughout the revised manuscript.

1

2 Comment: P3, line 18: Describe here what you mean by "physical modulation of biogeochemical terms".

3 **Response**:

4 *As suggested, we provided a description to the physical modulation method here in the revised manuscript (Page* 5 *3, line 10-17).*

6

7 **Comment:** P3-8: Nice description of the modeling

8 Response:

Thank the referee for the positive comments.

9 10

11 **Comment:** P8, line 7: In the 'Model Validation' section you might also suggest some additional observations that 12 could be measured to assess the modulation model. Perhaps oxygen isotopes or additional rate measures would be 13 useful to validate the biogeochemical O2 terms.

14 Response:

As suggested, we provided more results for our model validation (e.g., water elevations, temperature and salinity profiles, chlorophyll-a, primary production, and particulate organic carbon; Page 8, line 28-29; Page 9, line 1-7; Page 9, line 28-30;) and also put forward some suggestions for further observations (e.g., oxygen isotopes, artificial tracers) that could be used to evaluate the physical modulation model performance in the revised manuscript (Page 10, line 29-31).

In addition, our model results show that the spatial distribution and duration of hypoxia in the Pearl River estuary were mainly controlled by the re-aeration process and the sediment oxygen demand. In order to make our conclusions more persuasive, we have compared our simulated results associated with these two important biogeochemical processes with historical observations (new Table 2). Such model-data comparison is of great importance but not enough at the current stage due to data insufficiency. Therefore, in the revised manuscript we will also suggest that the observations related to the important biogeochemical processes affecting DO should be strengthened in the near future (Page 9, line 31-32; Page 10, line 1-4).

27

28 **Comment:** P11, line 29: unclear what '905 l t' is

29 Response:

Here it means 9,051 tonnes. We have changed it to "9,051 tonnes" in the revised manuscript (Page 12, line 19).

30 31

Comment: P12, lines 4-6: I disagree with this statement. The O2 gradient driven by photosynthesis would only be
 uniform or small if the light were at levels saturating to photosynthesis throughout the water-column

34 Response:

35 Okay, this sentence should be better stated. In our study, the DO gradient driven by photosynthesis was 36 represented by the gradient of DO_{Phot} . We calculated the vertical diffusive fluxes of DO_{Phot} and DO_{Rea} and found that 37 the diffusive flux of DO_{Phot} (-0.04 mg L^{-1} day⁻¹) was much smaller than that of DO_{Rea} (-0.48 mg L^{-1} day⁻¹) (new Fig. 11c).

1	This result indicated that the gradient of DO_{Phot} was much smaller than that of DO_{Rea} since the diffusion coefficients
2	were the same. From new Fig. 11a it can be seen that at the surface layer of the PRE, the rates of re-aeration and
3	photosynthesis were estimated 0.55 and 0.28 mg L^{-1} day ⁻¹ , respectively; at the middle layer, these two rates were
4	estimated 0 and 0.14 mg L^{-1} day ⁻¹ , respectively. The difference of photosynthesis between the surface and middle layers
5	was much smaller than the difference of re-aeration, which means that the oxygen gradient driven by photosynthesis
6	was also much smaller.
7	We have modified this sentence and include the discussion above in the revised manuscript (Page 12, line 24-27;
8	Page 13, line 1).
9	
10	Comment: P15, line 27: Correct 'Fig.9921a and Fig.9921b
11	Response:
12	Okay, we corrected this to "Fig.15" in the revised manuscript.
13	
14	Comment: P16, line 11: '8 km3', use units consistent with what you present from the Gulf of Mexico and PRE (km2)
15	Response:
16	The Chesapeake Bay and the northern Gulf of Mexico are the two well-known and well-studied areas which suffer
17	from sever water hypoxia. We believe that it could be interesting and helpful to compare the hypoxia and its controlling
18	mechanism between the Pearl River estuary and these two areas. Generally, the hypoxic volume was frequently
19	estimated and reported for the Chesapeake Bay, while the hypoxic area was frequently estimated and reported for the
20	northern Gulf of Mexico. To facilitate the comparison, we calculated the hypoxic area (~237 km ²) and hypoxic volume
21	(0.1255 km ³) for the Pearl River estuary and compared them with the northern Gulf of Mexico and the Chesapeake
22	Bay accordingly in the revised manuscript (New equation (12); Page 12, line 3-5; Page 16, line 18-22).
23	
24	Comment: Table 2: In the heading do you mean 'WCR' instead of 'respiration by phytoplankton', which is hard to
25	measure in practice and which is usually small in comparison to WCR.
26	Response:
27	In fact, it is the respiration rate that was calculated by subtracting the nitrification oxygen consumption rate from
28	the WCR, neither WCR nor the respiration by phytoplankton (as the referee mentioned, it is difficult to measure). This
29	respiration rate was reported by He et al. (2014) and was used to validate our model. We have clarified and corrected
30	this in the revised manuscript (Page 9, line 24; Page 23, line 2).
31	Comment: Fig. 1b: Did you mean to show the cross-section (side-view) as noted in the figure
32	caption? Here it shows the map view of the river network.
33	Response:
34	We realize that it could be misleading using "cross-section" here, which in fact denotes the computational grids
35	for the 1-D river network model. To clarify this, we changed it to "computational cross-sections" in the revised
36	manuscript (Page 24, line 3; new Fig. 1b).
37	
	C4

1 **Comment:** Fig. 5: In the caption state the bias is between the two models, RCA and modulation

2 Response:

3 *As suggested, we explained the bias in the caption of Fig. 5 (new Fig. 8) in the revised manuscript (Page 30, line* 4 2-3).

5

6 **Comment:** Fig 6: Perhaps I missed it in the text, but why do the two models differ? Please discuss in text.

7 Response:

8 As suggested, we discussed the reason for the differences between the two models in the revised manuscript 9 (Page 10, line 6-7; Page 10, line 13-16). Theoretically, there should be no differences between the two models since the transport equation is a linear equation. However, in the numerical model, the partial differential equations are 10 approximately represented by difference equations. Some nonlinear numerical methods were applied to restrain the 11 errors caused by discretizing the partial differential equations. We found that the differences between the two models 12 13 are caused by these nonlinear numerical methods. We have conducted a test by turning off these nonlinear methods 14 and found that the differences between the two models are removed but the model results become inaccurate. We would 15 like to emphasize that the differences between the two models in our study are small and have little impact on the analysis of the hypoxia. 16

17

18 Comment: Fig 8e: define ABio and LBio in the caption Technical corrections: There are too many for me to 19 enumerate here. Please have an English editor assist with fixing plural noun/verb issues and other grammatical 20 mistakes.

21 Response:

As suggested, we had an English editor edit our manuscript and correct grammatical mistakes throughout the text. The
 editing certificate was provided at the end of this file.

24

25 Reference

He, B., Dai, M., Zhai, W., Guo, X., and Wang, L.: Hypoxia in the upper reaches of the Pearl River Estuary and its
maintenance mechanisms: A synthesis based on multiple year observations during 2000–2008, Mar. Chem., 167,
13-24, 2014.

- 29
- **30 Referee #2**
- Comment: This study by Wang et al. present a numerical investigation of the hypoxia condition in one of the largest
 river estuary along the Western Pacific the Pearl River Delta.

According to the author, the Pearl River has a similar nutrient load as that of the Mississippi and the Pearl river runs

through a highly populated region. The importance of this study is beyond question. And the coupling between 1D

river model and 3D coastal model as well as the author's efforts of improving the ECOM model is plausible. However,

36 I found this manuscript is not well written and the author failed to explain his/her points throughout the manuscript.

The so- called "physical modulation method" is merely to isolate lateral DO from in-situ biological source and sinks. In addition, throughout the manuscript the definition of ambient biogeochemical process is very vague and sometimes contradictive. The available observation data does not support the high frequency zone (HFZ) proposed by the author. I do agree with the other reviewer that this manuscript needs a throughout edits of scientific writing. I have a lot of problems to understand what the author wants to convey.

6 Response:

7 We would like to thank the referee for recognizing the importance of our study and the detailed comments. We 8 have carefully read these comments and summarized them into three main criticisms. We believe that most of these 9 criticisms were mainly due to the misunderstanding caused by improper use of words like 'ambient' (which should be 10 'adjacent') in the text and inadequate description on the 'physical modulation method'. We provided a further 11 description to the 'physical modulation method' and its associated terms in the revised manuscript and improved our 12 manuscript according to these comments. Responses to the three main comments are given below.

13 Firstly, for the comments on the 'physical modulation method', it actually means the modulation of the effects of 14 source and sink processes on DO due to physical transport. In our study, we applied this method to tease apart the 15 contributions of boundary conditions as well as the source and sink processes to DO transport flux by using numerical DO tracers and to further demonstrate the spatial connection between the source and sink processes occurring in 16 different locations in the system. Specifically, we considered that DO concentrations could be affected by the source 17 and sink processes in two ways: 1) the source and sink processes can produce or consume oxygen to change the local 18 19 DO concentrations directly; 2) the source and sink processes can also change DO concentrations in the adjacent grid 20 cells and hence change the DO fluxes from these adjacent grid cells; as a result, the DO concentrations will be 21 affected by the source and sink processes occurred in the adjacent grid cells. We defined the latter mechanism as the 22 modulation of the effects of the source and sink processes on the DO due to physical transport (Page 3, line 10-17; 23 *Page 7, line 3-4; Page 8, line 2-10, new equation (9)).*

Regarding the 'contributions of ambient biogeochemical processes' (has been changed into 'contributions of adjacent source and sink processes' in the revised manuscript), it means the advective and diffusive fluxes of oxygen which is produced or consumed by the source and sink processes in the adjacent grid cells. We have realized that the word 'ambient' is misleading and we changed it to 'adjacent' as suggested throughout the revised manuscript. We also clarified the 'contributions of adjacent source and sink processes' in the revised manuscript (Page 8, line 4-7).

29 Secondly, as to the comments on the observation data, we would like to emphasize that our model reasonably 30 reproduced the spatial distributions of physical variables (including water levels, salinity, and temperature) and DO as can be seen from the comparisons between our model results and the available observations (new Fig. 3-7). In 31 addition, we compared our simulated results associated with two important biogeochemical processes controlling 32 33 hypoxia (i.e. the re-aeration process and the sediment oxygen demand) with historical observations (new Table 3) in order to make our conclusions more persuasive. We realize that the available data for hypoxia is insufficient. In fact, 34 35 we have collected the observation data from 1976 to 2009 (Fig. r1) and found that there were very few observation 36 data available near the Modaomen sub-estuary (where the high frequency zone is located) on hand. However, hypoxia 37 near the Modaomen sub-estuary has been reported in previous observational studies (Lin et al., 2001; Cai et al., 2013)

and modeling studies (Zhang and Li, 2010). The spatial extent and characteristics of hypoxia in our study is consistent
 with these previous studies.

Nevertheless, we realize the necessity and importance to strengthen the relevant observations. Therefore, we put
forward some suggestions for further observations near the Modaomen sub-estuary in the revised manuscript (Page 9,
line 31-32; Page 10, line 1-4). We believe that our study will provide a scientific basis and guidance for conducting
these field observations. In addition, we also provided more results for our model validation (e.g., water elevations,
temperature and salinity profiles, chlorophyll-a, primary production, and particulate organic carbon, results can be
seen from new Fig. 3-7 and new Table 3) in the revised manuscript (Page 8, line 28-29; Page 9, line 1-7; Page 9, line
28-30).

Finally, for the comment on the language, we had an English editor edit our manuscript and correct grammatical
 mistakes throughout the text. We also provided the editing certificate at the end of this file.

12

13 **Comment:** First of all, the abstract contradicts with itself. The author first indicated DO is affected by both local 14 biological processes and DO fluxes from the ambient water (I would treat this as boundary condition). And the author 15 claims the later (ambient water) is unclear. Then in next paragraph, the author indicated that the re-aeration (air-sea, i.e. surface) and sediment oxygen demand (bottom) are most important. Again, the author indicates the importance of the 16 re-aeration, followed by a statement saying "turning off the re-aeration leads to hypoxia..... to the west lower estuary". 17 However, the author immediately states that hypoxia was observed in west lower estuary. So my question is re-aeration 18 19 good or bad? Important or not important at all? Then, in the last part of the abstract, the author states photosynthesis is 20 less important. Yet right following this, the author indicates that in HFZ, photosynthesis cause an increase of hypoxia area to 591 km2— it confusing me how photosynthesis would worsen hypoxia (should be respiration, right? But 21 22 respiration is not directly linked with photosynthesis).

23 Response:

Firstly, as mentioned above, the contributions of adjacent source and sink processes mean the advective and diffusive fluxes of DO which is produced or consumed by the source and sink processes in the adjacent grid cells, not the boundary conditions. We realize that the word 'ambient' is misleading and we have changed it to 'adjacent' as suggested throughout the revised manuscript.

28 Secondly, regarding the re-aeration, it is an important source for DO in the water column. In P1, line 28-30 of the 29 original manuscript (P1, line 25-27 in revised manuscript), we mentioned that turning off the re-aeration would lead to 30 a significant expansion of hypoxic area with the occurrence of persistent hypoxia in the west lower estuary (where no hypoxia occurred in the realistic simulation). This means that the re-aeration is good for alleviating the hypoxia in the 31 Pearl River estuary. Moreover, our DO budget analysis showed the re-aeration could affect the bottom layer through 32 33 the vertical diffusion (new Fig. 11c). As shown in the new Fig. 11a, the re-aeration provided a large amount of oxygen to the surface water, leading to a strong vertical DO gradient between the surface and middle layers. As a result, the 34 majority of oxygen entering into the surface layer by the re-aeration (represented by DO_{Rea}) was transported to the 35 36 middle layer and ~28% could reach the bottom layer eventually (new Fig. 11c).

37 Finally, regarding the photosynthesis, we realize that there is a mistake here. What it should be is that turning off

the photosynthesis and water column respiration would cause an increase in the hypoxic area. We corrected this in the
 revised manuscript (Page 1, line 27-29).

3

Comment: Page 2, line 29-34. The author first indicate DO from ambient water body, followed by "Take the re-aeration as an example". How would these two processes be connected (one is lateral boundary and the other is upper boundary)? The author then mentioned, "given the mechanism remains unclear", which one mechanism? Why it is not clear? Also, I do not think DO flux from ambient water bodies belong to the biogeochemical processes only, it indeed a combination of both bio and physical. Page 3, line 14-15, the author compared PRE with Northern Gulf of Mexico. I think one of the core mechanisms here is the tidal range difference (M2 in PRE vs S1 in NGOM).

10 Response:

Firstly, as mentioned above, the word 'ambient' is misleading and has been changed to 'adjacent' in the revised manuscript. Here we were referring to the DO fluxes from the adjacent water bodies affected by adjacent source and sink processes (not from lateral boundary). We took the re-aeration as an example to explain the contribution of adjacent source and sink processes on DO.

Secondly, regarding the statement "given the mechanism remains unclear", it is referring to the mechanism of how the adjacent source and sink processes affect DO concentrations. We claimed it unclear because traditional methods have not teased apart and quantified the contributions of boundary conditions as well as the source and sink processes to DO concentrations. In the revised manuscript, we modified the logic of the introduction to better state the purpose of our study.

Thirdly, we recognize that the contributions of adjacent source and sink process are indeed a combination of both biogeochemical and physical processes. As mentioned earlier, the 'contributions of adjacent source and sink processes mean the advective and diffusive fluxes of DO which is produced or consumed by the source and sink processes in the adjacent grid cells. We realize that this statement is misleading and we changed it to 'the contributions of adjacent source and sink processes due to physical transport' in the revised manuscript.

Finally, regarding the tidal range difference, we agree that it is an important factor affecting hypoxia. Currently,
we are actually working on another study addressing the impact of the tides as well as other physical factors (e.g. river
discharges, winds) on the hypoxia in the Pear River estuary.

28

29 Comment: Page 3, line 17. I do not agree that the mechanism remains unclear, since just two lines above the author 30 indicated that previous study suggest sediment oxygen demand and stratification are two main reasons. The author 31 should give a more persuasive justification for this study and I believe there are many indeed. *

32 Response:

Yes, we agree that the sediment oxygen demand and stratification are two important factors affecting the hypoxia in the Pearl River estuary. However, we note from our model results that the distributions of the sediment oxygen demand and hypoxia were inconsistent and there was a shift between the hypoxic zone and the high sediment oxygen demand areas. This inconsistency could also be found in previous studies (Zhang and Li, 2010) where however there was no further analysis or discussion on it. The shift between the hypoxic zone and the high sediment oxygen demand areas is caused by the modulation of the effects of source and sink processes on DO due to physical transport. In the
 revised manuscript, we have clarified this misinterpretation (Page 3, line 10-17).

- 3
- 4 **Comment:** Page 6. Line 3, what is RDOC, LDOC, ReDOC, ExDOC stands for?

5 Response:

6 RDOC, LDOC, ReDOC, and ExDOC are the abbreviations for four state variables in the RCA water quality 7 model. They represent refractory dissolved organic carbon (RDOC), labile dissolved organic carbon (LDOC), reactive 8 dissolved organic carbon (ReDOC), and algal exudate dissolved organic carbon (ExDOC). The explanations for these 9 abbreviations can be found in one sentence after these abbreviations (P6, line 3-4 in original manuscript). In the 10 revised manuscript, to make it easier to notice, we defined their meanings before using these abbreviations and showed 11 these abbreviations using a table along with other main state variables for the RCA and the physical modulation 12 method (Page 6, line 8-10; new Table 1).

13

- 14 Comment: Page 6. Line 15. The authors used a constant boundary condition to study the impact from ambient DO 15 transport which worries me a lot!
- 16 Response:

As mentioned earlier, we realize that the word 'ambient' could be misleading and we changed it to 'adjacent'.
What it means is the contributions of adjacent source and sink processes, not the contributions from the boundary conditions.

The river boundary conditions of water quality variables were specified using the monthly observations. The open
 boundary conditions were specified spatial constant according to limited observations.

22 Comment: Page 7 Line 7. Should not re-aeration of DO a physical process instead of a biological one?

23 Response:

Yes, the re-aeration should be a physical process and we modified this statement. In the revised manuscript, we changed 'biogeochemical source and sink processes into 'the source and sink processes' (Page 7, line 12-13). Other associated terms were also modified correspondingly in the revised manuscript.

- 27
- Comment: Page 7. I am confused why the author needs to give repeated information in equation (6)-(12). They simply
 divide DO in to DObc and DObio, and they can just use equation (13), that is enough.
- 30 Response:

Okay, we agree that there is repeated information in equations (9)-(12) and we deleted these equations in the revised manuscript. For equations (6)-(8) we argue that they should be kept in the text. Equations (6)-(7) are two important transport equations for DO_{BC} and DO_s , which explicitly demonstrate how to calculate these two variables. Equation (8) is also needed to illustrate DO_{Rea} , DO_{Phob} , DO_{WCR} , and DO_{SOD} as these variables were presented and discussed in the manuscript (section 2.3).

36

37 Comment: Page 8. Model validation, I think it is necessary to present more validation for both physics and water

quality, specifically some time series comparison. The Taylor diagram could represent the correlation yet we are not
 sure how the model could resolve temporal variability.

3 Response:

4 Firstly, as suggested, we provided more results for our model validation (e.g., water elevations, temperature and salinity profiles, chlorophyll-a, primary production, and particulate oxygen carbon) in the revised manuscript (Page 8. 5 6 line 28-29; Page 9, line 1-7; Page 9, line 28-30; new Fig 3-7; new Table 3). Regarding the time series comparison, 7 there were no time series observations (except water elevations) available for July-August 2006 (our study period). 8 However, our datasets used for model validation include salinity and temperature from 146 cruise sites and water 9 aualities from 53 cruise sites. These data were collected at different times of July and August 2006, with a time span of 10 39 days. The agreement between our simulations and observations shows that our model can reasonably reproduce the temporal and spatial distribution of hydrodynamic and water quality variables in the Pearl River estuary. 11

12

Comment: Page 9. Section 3.2. The author presents the difference between RCA and the Physical Modulation method.
 How about the difference between Physical modulation and the in-situ data? Is there any improvement compared with
 difference between RCA and in-situ data?

16 Response:

17 Please note that the physical modulation method is not an improvement of RCA. It is a new method that we applied to tease apart the contributions of boundary conditions as well as the source and sink processes to DO 18 dynamics by using RCA and the numerical DO tracers. Theoretically, there should be no differences between the two 19 20 models since the transport equation is a linear equation. However, in the numerical model, the partial differential 21 equations are approximately represented by difference equations. Some nonlinear numerical methods are introduced to 22 restrain the errors caused by discretizing the partial differential equations. We found that the differences between the 23 two models are caused by these nonlinear numerical methods. We have conducted a test by turning off these nonlinear methods and found that the differences between the two models are removed but the model results become inaccurate. 24 25 We would like to emphasize that the differences between the two models in our study are small and have little impact 26 on the analysis of the hypoxia. In the revised manuscript, we have included the discussion above to explain the differences between these two models (Page 10, line 6-7; Page 10, line 13-16). 27

28

29 **Comment:** Page 9. Line 30. "The agreement indicates : : :" which agreement?

30 Response:

It is the agreement between the DO fluxes calculated by RCA and those calculated using the physical modulation
 method. We have clarified this in the revised manuscript (Page 10, line 27-29).

33

Comment: Page 10. Line 16. The HFZ refers to high frequency zone of areas with DO < 3 mg/L. But why the author
 states "indicating HFZ is most possible to form hypoxia"?

- 36 Response:
- 37 We realize that this statement is repeated because by definition the HFZ (high frequency zone) refers to the area

1 2	where hypoxia is most likely to occur. We have deleted it in the revised version.
3	Comment: Page 11. Line 6. What does the author mean by "it is encompassed by the isoline of 10%"?
4	Response:
5	Here what it should be mean is that the HFZ is the area encompassed by the 10% isoline of hypoxic frequency. We
6	have clarified this in the revised manuscript (Page 11, line 12-13)
7	
8	Comment: Page 11. Line 7-16. Should not these abbreviation goes to the figure caption?
9	Response:
10	As suggested, these abbreviations and their explanations have been added in the figure caption in the revised
11	manuscript (Page 33, line 7-15)
12	
13	Comment: Page 13. Line 4. "Although: : :. However : : : "very awkward wording
14	Response:
15	As suggested, we have modified this in the revised manuscript and had an English editor edit our manuscript.
16	
17	Comment: Page 13, Line 10. "Both of which contribute 79% and 25% "I do not understand what the author wants
18	to convey here.
19	Response:
20	We realize that there is a grammatical mistake here. The sentence means that the sediment oxygen demand and
21	the re-aeration contribute 79% and 25% of vertical diffusive flux, respectively. We corrected it in the revised
22	manuscript (Page 13, line 25-27)
23	
24	Comment: Page 13. Line 19-20. From Figure 8e I could tell how horizontal and vertical advection balance each other.
25	Response:
26	Please note that the results related to the horizontal and vertical advective fluxes of DO are shown in Fig. 8a
27	(new Fig. 11a), not Fig. 8e. We have included a reference therein to new Fig. 11a in the revised manuscript (Page 13,
28	line 30-32). New Fig. 11a shows that the horizontal advection brings oxygen to the bottom layer in the PRE while the
29	vertical advection brings oxygen out of the bottom layer. The horizontal advective flux of DO is close to the vertical
30	advective flux of DO.
31	
32	Comment: Page 14. Line 10-11. The author mentioned "two distinct areas characterized by the high level of sediment
33	oxygen demands". However I could not find it on figure 10a referred here (I only see one area delineated by the white
34	line).
35	Response:
36	Please note that Fig. 10a (new Fig. 13a) shows the spatial distribution of the sediment oxygen demand in the PRE.
37	As shown in new Fig. 13a, the blue indicates high sediment oxygen demand and the red indicates low sediment oxygen

1 demand. There are two areas highlighted by the blue, one of which is located inside the Lingdingyang bay and the
2 other is located at the Modaomen sub-estuary. These two areas correspond to the 'two distinct areas characterized by
3 the high level of sediment oxygen demands'.

4 Regarding the area delineated by the white line, it represents the HFZ (please see the caption of new Fig. 13a). In
5 new Fig. 13a the HFZ was overlapped with the sediment oxygen demand in order to explicitly compare the spatial
6 distributions between the sediment oxygen demand and the hypoxia. It can be seen that there is a shift between the
7 hypoxic zone and the high sediment oxygen demand areas as mentioned earlier, which is caused by the modulation of
8 the effects of the source and sink processes on the DO due to physical transport.

9

10 Comment: Page 14. Line 21-22. I do not understand what does the author mean here "depth to water column 11 respiration and photosynthesis". Or the author means depth of water column respiration/photosynthesis. Also why this 12 estimation is underestimated?

13 Response:

Firstly, regarding this sentence "we therefore add sediment oxygen demand which is divided by the depth to water column respiration and photosynthesis to represent the gross depletion rate", it means that we used "SOD/depth+WCR+Phot" to represent the gross depletion of oxygen. Here, the SOD (sediment oxygen demand) and WCR (water column respiration) are negative to indicate that they are sinks for DO. In the revised manuscript, we have changed this sentence to make it clear (Page 14, line 29-30).

- 19 Secondly, in previous studies (Murrell and Lehrter, 2011; Shen et al., 2013) the sediment oxygen consumption rate $(mg L^{-1} day^{-1})$ was estimated using the sediment oxygen demand $(g m^{-2} day^{-1})$ divided by the depth below the 20 21 pycnocline, assuming that the water below the pycnocline is well-mixed. In the Pearl River estuary, the depth of 22 pycnocline significantly varies in time and space, which makes it difficult to determine. In additional, the shallow depth and large vertical velocities make it possible for SOD to affect the surface layer significantly. Therefore, we 23 alternatively estimated the sediment oxygen consumption rate (mg L^{-1} day⁻¹) by using the sediment oxygen demand (g 24 $m^{-2} dav^{-1}$) divided by the total depth of the water column. The result was underestimated compared to one calculated 25 26 using the depth below the pycnocline. It should be noted that this underestimated value in the Pearl River estuary is 27 larger than in other hypoxic areas (e.g. the Chesapeake Bay and northern Gulf of Mexico) so that the underestimation 28 has little impact on the qualitative comparisons between the Pearl River estuary and the other hypoxic areas.
- 29

30 **Comment:** Page 14. Line 27-28. Why such decrease cannot be explained only by biogeochemical processes?

31 Response:

Please note that in the original text we mentioned "This indicates that only the biogeochemical processes are not
sufficient to explain the hypoxia in the HFZ since the effects of physical processes are also important" (P14, Line
27-28 in original manuscript).

According to our model results, the distributions of the sediment oxygen demand and hypoxia are inconsistent.
There is a shift between the hypoxic zone and the high sediment oxygen demand areas as mentioned earlier, which is
caused by the modulation of the effects of the source and sink processes on DO due to physical transport. We rewrote

1 the discussion above in the revised manuscript for a better statement (Page 14, line 31; Page 15, line 1-3).

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Comment: Page 14. Line 34-36. I could not tell how "simulated DO distribution in the bottom is in reasonable agreement with DO distribution". If we look at the available DO observations in Fig.4. There are only 2 points in Figure 4(c) that shows low oxygen in the so-called HFZ zone.

6 Response:

Please note that in the original text we mentioned "Figure 10c shows the simulated DO_{Bio} distribution in the 7 bottom is in reasonable agreement with DO distribution"(P14, Line 34-36 in original manuscript). Here, the 8 9 distribution of DO_{Bio} (has been changed into DO_{S} in the revised manuscript; new Fig. 13c) was compared to hypoxia 10 (new Fig. 10b, d) in order to demonstrate that DO_s could resemble the occurrence of hypoxia in the PRE.

11 For the comments on the observation data, please see responses to the three main criticisms above (we would like 12 to emphasize that our model reasonably reproduced the spatial distributions of oxygen as can be seen from the 13 comparisons between our model results and the available observations. In addition, we compared our simulated 14 results associated with two important biogeochemical processes controlling hypoxia (i.e. the re-aeration process and 15 the sediment oxygen demand) with historical observations (new Table 3) in order to make our conclusions more persuasive. We realize that the available data for hypoxia is insufficient. In fact, we have collected the observation data 16 from 1976 to 2009 (Fig. r1) and found that there were very few observation data available near the Modaomen 17 sub-estuary (where the high frequency zone is located) on hand. However, hypoxia near the Modaomen sub-estuary 18 has been reported in previous observational studies (Lin et al., 2001; Cai et al., 2013) and modeling studies (Zhang 19 20 and Li, 2010). The spatial extent and characteristics of hypoxia in our study is consistent with these previous studies.

21

22 **Comment:** Page 15. Line 2-3. I could not tell that the lowest DOsod is observed in the HFZ zone from Fig 4. Although 23 the author mentioned Fig 11 here, but it is model result rather than in-situ observation.

24 **Response:**

25 Please note that Fig. 11 (new Fig. 14) shows the DO_{SOD} concentrations averaged over July-August 2006 and Fig. 4 (new Fig. 7) shows comparison of the simulated and observed DO concentrations during the cruise periods. These 26 27 two figures show results for different time periods.

29 **Comment:** Page 15. Line 25. Figure 9921a. I do not know what the author what to convey here.

30 **Response:**

- We have corrected this to "Fig.15" in the revised manuscript.
- 31 32 33

28

Comment: Page 16. Why "phosphorous limitation can not be convincing enough?" The author does not mention much

34 about phosphorous budget before this.

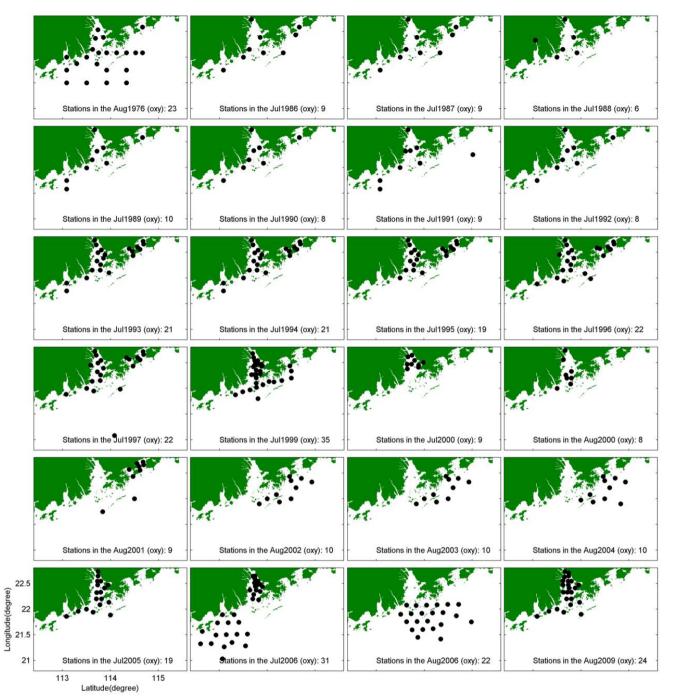
35 **Response:**

36 Yin et al. (2004) suggested that the occurrence of hypoxia in the Pearl River estuary was restricted due to 37 phosphorous limitation because phosphorous limitation inhibited the complete utilization of nutrients and eventually

1	limited oxygen consumption in the water column. In our study, we found that the sediment oxygen demand was the
2	dominant source of oxygen consumption at the bottom layer in the Pearl River estuary, which was consistent with
3	previous studies(Zhang and Li, 2010). In addition, the total oxygen consumption rate in the Pearl River estuary was
4	higher than those in the Chesapeake Bay and the northern Gulf of Mexico while the hypoxia in the Pearl River estuary
5	was less severe (see comparison in new Table 4). This indicates that there should be a different mechanism rather than
6	phosphorous limitation controlling the hypoxia in the Pearl River estuary. In the revised manuscript, we have rewritten
7	the above discussion for a better statement (Page 16, line 11-23).
8	
9	Comment: Page 16. Line 20-21. Again, I am not convinced that Fig.10c (model) shows the realistic condition (Fig. 4).
10	Response:
11	Please note that Fig. 10c (new Fig. 13) shows the DO_{Bio} (has been changed into DO_S in the revised manuscript)
12	averaged over July-August 2006 and Fig. 4 (new Fig. 7) shows comparison of the simulated and observed DO
13	concentrations during the cruise periods. These two figures show results for different time periods.
14	In the text, the distribution of DOs (new Fig. 13c) was compared to hypoxia (new Fig. 10b, d) in order to
15	demonstrate that DOs could resemble the occurrence of hypoxia in the PRE.
16	
17	Comment: Page 16. Line 28. "is comparable more important". Awkward wording.
18	Response:
19	As suggested, we have modified this in the revised manuscript and we had an English editor edit our manuscript.
20	
21	Comment: Page 17. Line 17. The author used a constant boundary condition, how can he/she justify that "DO
22	originating from the boundaries to the bottom of the PRE and HFZ"?
23	Response:
24	In our study, the physical modulation method was applied to tease apart the contributions of boundary conditions
25	as well as source and sink processes to the DO. The oxygen originating from the boundaries was represented by DO_{BC} .
26	Fig. 8d (new Fig. 11d) and Fig. 9d (new Fig. 12d) showed that at the bottom of the PRE and HFZ, the horizontal
27	advection fluxes of DO_{BC} were ~0.07 and 0.90 mg L^{-1} day ⁻¹ , respectively.
28	
29	Reference

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TITLE OF THE PAPER

A numerical analysis of biogeochemical controls with physical modulation on hypoxia during summer in the Pearl River estuary

AUTHORS

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A numerical analysis of biogeochemical controls with physical

2 modulation on hypoxia during summer in the Pearl River estuary

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9 Abstract. A three-dimensional (3-D) physical-biogeochemical coupled model was applied to explore the mechanisms 10 controlling the dissolved oxygen (DO) dynamics and bottom hypoxia during summer in the Pearl River estuary (PRE). By 11 using the numerical oxygen tracers, we proposed a new method (namely the physical modulation method) to quantify the 12 contributions of boundary conditions and each source and sink process occurring in local and adjacent waters to the DO 13 conditions. A mass balance analysis of DO based on the physical modulation method indicated that the DO conditions at the 14 bottom layer were mainly controlled by the source and sink processes, among which the sediment oxygen demand (SOD) at 15 the water-sediment interface and the re-aeration at the air-sea interface were the two primary processes determining the 16 spatial extent and duration of bottom hypoxia in the PRE. The SOD could cause a significant decrease in the bottom DO 17 concentrations (averaged over July-August 2006) by over 4 mg L^{-1} on the shelf off the Modaomen sub-estuary, leading to the 18 formation of a high frequency zone of hypoxia (HFZ). However, the hypoxia that occurred in the HFZ was intermittent and 19 distributed in a small area due to the combined effects of re-aeration and photosynthesis, which behaved as sources for DO 20 and offset a portion of the DO consumed by SOD. The bottom DO concentrations to the west of the lower Lingdingvang bay 21 (i.e. the western shoal near the Qi'ao Island) were also largely affected by high SOD, but there was no hypoxia occurring 22 there because of the influence of re-aeration. Specifically, re-aeration could lead to an increase in the bottom DO 23 concentrations by ~4.8 mg L^{-1} to the west of the lower Lingdingvang bay. The re-aeration led to a strong vertical DO 24 gradient between the surface and the lower layers. As a result, the majority (~89 %) of DO supplemented by re-aeration was 25 transported to the lower layers through vertical diffusion and ~28 % reached the bottom eventually. Additional numerical experiments showed that turning off re-aeration could lead to an expansion of the hypoxic area from 237 km² to 2.203 km² 26 27 and result in persistent hypoxia (hypoxic frequency >80 %) to the west of the lower Lingdingyang bay. Compared to 28 re-aeration and SOD, photosynthesis and water column respiration had relatively small impacts on the DO conditions; turning off these two processes increased the hypoxic area to 591 km^2 . In summary, our study explicitly elucidated the 29 30 interactive impacts of physical and biogeochemical processes on the DO dynamics in the PRE, which is critical to 31 understanding hypoxia in this shallow and river-dominated estuarine system.

1 1. Introduction

2 The formation and maintenance of hypoxia are related to physical and biogeochemical processes. Physical processes can 3 affect dissolved oxygen (DO) conditions by changing the horizontal and vertical DO transport fluxes. For example, hypoxia 4 in the Changjiang estuary is related to the inflow of the Taiwan Warm Current which brings low-oxygen waters to the estuary 5 and facilitates stratification, inhibiting vertical diffusion, and thus isolating the bottom waters from the oxygenated surface 6 waters (Wang, 2009; Wang et al., 2012). Other studies have also suggested that stratification was the major cause of hypoxia 7 in many areas (Ni et al., 2014:Du and Shen, 2015;Yu et al., 2015a). Biogeochemical processes can have a significant impact 8 on DO as well by affecting its internal production and consumption. For example, phytoplankton growth can be stimulated 9 by excessive nutrient loading producing abundant DO by photosynthesis in the water column. In addition, phytoplankton 10 utilize DO for respiration during their growth and generate detrital organic matter after death that can deposit on the 11 sediment resulting in sediment oxygen demand (SOD). The statistical linkage between nutrient loadings and the spatial 12 extent of hypoxia was well documented for the Chesapeake bay (Hagy et al., 2004) and the northern Gulf of Mexico (Justic 13 et al., 2003). In some coastal areas, the terrestrial inputs of particulate organic matter are important to the formation of 14 hypoxia. Zhang and Li (2010) suggested that terrestrial particulate organic carbon played a significant role in generating high 15 SOD, which is the main cause of hypoxia in the Pearl River estuary. Furthermore, physical and biogeochemical processes are 16 closely coupled and highly interacted with each other in regulating the DO dynamics. Physical processes can affect the DO 17 concentrations by altering the distribution of nutrients and phytoplankton and their relevant biogeochemical processes that 18 can affect the DO fluxes by producing or consuming DO along with the physical transport. One important question on 19 hypoxia is to elucidate the relative contributions of physical and biogeochemical processes. A mass balance analysis on DO 20 is a commonly used method, widely applied to many hypoxic areas including the Chesapeake bay and the northern Gulf of 21 Mexico to address this question (Scully, 2010; Montes et al., 2014; Li et al., 2015; Yu et al., 2015b). Shen et al. (2013) 22 introduced a conceptual model by using two different time scales for physical and biogeochemical processes to quantify their 23 contributions to the DO dynamics.

The Pearl River is the second largest river in China with an annual discharge rate of 10,524 m³ s⁻¹, 80 % of which is 24 25 transported during the wet season (Ou et al., 2009:Zhang and Li, 2010). The Pearl River network (Fig. 1) includes Beijiang (North River), Xijiang (West River), Dongjiang (East River), Liuxi River, and Tan River, covering a drainage area of 4.5×10^5 26 27 km². Freshwater from the river network is emptied into the Northern South China Sea (NSCS) through eight outlets, Humen, 28 Jiaomen, Honggili, Hengmen, Modaomen, Jitimen, Hutiaomen, and Yamen. The Pearl River estuary (PRE; Fig. 1) is located 29 on NSCS and adjacent to the river network. The PRE consists of four sub-estuaries, including the Lingdingvang bay, 30 Modaomen, Jitimen, and Huangmaohai sub-estuaries, among which the Lingdingyang bay is the largest one with an area of almost 2,000 km². The PRE is a complex estuarine system characterized by a shallow bank to the west of the estuary with a 31 32 depth of less than 5 m and two deep channels with depths larger than 10 m and widths of 1 km. In summer, physical

processes in the PRE are influenced by abundant river discharge and southwesterly prevailing winds. Complicated 1 2 hydrodynamics and topography significantly affect the spatial and temporal distributions of nutrients, phytoplankton, and DO. Seasonal hypoxia has been reported in the PRE from several large-scale field observations since the 1970s (Yin et al., 3 4 2004). Several modelling studies have also been conducted to investigate hypoxia in the PRE (Weibing et al., 2001b, a:Luo 5 et al., 2008). Unlike the northern Gulf of Mexico, hypoxia in the PRE is intermittent and confined to a small scale (Rabouille 6 et al., 2008), although nitrogen loadings in the PRE are close to those in the Mississippi River (Hu and Li, 2009). Previous 7 studies suggested that high SOD dominated the DO depletion at the bottom waters and was responsible for the occurrence of 8 bottom hypoxia in the PRE (Yin et al., 2004; Zhang and Li, 2010). However, spatial distributions of SOD and hypoxia were 9 inconsistent and there was a location shift between the hypoxic zone and high SOD areas (Zhang and Li, 2010). No further 10 discussion has been provided for this problem in those studies. According to our study (see details in the following sections), 11 this location shift is ascribed to the modulation of the effects of the source and sink processes on DO due to physical 12 transport. Specifically, in addition to the local source and sink processes, DO concentrations in local waters can also be 13 influenced by the source and sink processes occurring in adjacent waters, which produce or consume DO in adjacent waters 14 and then affect the DO fluxes transported from adjacent to local waters. This process demonstrates the spatial connection of 15 each source and sink process occurring in different locations and is of great importance to the DO dynamics in a shallow 16 river-dominated system, as in the PRE. In the traditional mass balance analysis of DO, the contribution of the adjacent 17 source and sink processes is included in the DO transport fluxes but its impact on hypoxia is not explicitly revealed.

The main objectives of this study are 1) to investigate the characteristics of hypoxia in the PRE, including the spatial distribution, intensity, and duration, and 2) to propose a new method (physical modulation method) to depict the modulation of the effects of the source and sink processes on DO due to physical transport and explore the mechanisms controlling the DO balance as well as the hypoxia in the PRE. The manuscript is organized as follows. In section 2, we describe the physical and water quality models used in this study as well as the theory and methodology of the proposed physical modulation method. In section 3, we present the validation of our models and the physical modulation method. Section 4 provides the results and discussion. Section 5 presents the main conclusions.

25 2. Methods

26 2.1 Physical model

In order to properly account for the interactive impacts of riverine, estuarine, and shelf-sea processes on hydrodynamics, we use a one-dimensional (1-D) and a three-dimensional (3-D) coupled physical model (Hu and Li, 2009;Hu et al., 2011) that integrate the Pearl River network, the Pearl River estuary (PRE), and adjacent coastal waters into an overall modelling system. Specifically, the 1-D river network model is dynamically coupled with the 3-D coastal model for the PRE using an explicit coupling approach. The eight river outlets (Fig. 1a) serve as the coupling interface between the 1-D and the 3-D model domains. These two models run in parallel and their model quantities are exchanged across the coupling interface during runtime. At each time step, the 3-D model utilizes the simulated discharge obtained from the 1-D model as the river boundary forcing and the 3-D model sends simulated water levels to the 1-D model as the downstream boundary forcing for the next time step. A detailed description of the methodology and implementation of the coupled model can be found in Hu and Li (2009).

6 The 1-D model uses a Preissmann implicit scheme and an iterative approach to solve the Saint Venant equations of mass 7 and momentum conservation. A salinity transport module is also incorporated in the model. For details on the 1-D model and 8 its governing equations, see Hu and Li (2009). The 1-D model simulates 299 major branches of the river network with 1,726 9 computational cross-sections and 189 nodes (Fig. 1b). For the upstream boundaries, the real-time river discharge or water 10 levels with zero salinity are specified at Shizui, Gaoyao, Shijiao, Laoyagang, and Boluo (see Fig. 1a for their locations). The 11 initial conditions of water level and salinity are set to zero. The time step is 5 s for the 1-D hydrodynamic model.

12 The 3-D model used in this study is the Estuaries and Coastal Ocean Model with Sediment Module (ECOMSED; 13 HydroQual (2002), extensively used in estuaries. The model solves the Navier-Stokes equations with hydrostatic and 14 Boussinesq approximations. A Smagorinsky-type formula is applied to parameterize horizontal mixing and the 15 Mellor-Yamada turbulent closure model is applied to calculate vertical viscosity and diffusivity (Mellor and Yamada, 1982). 16 Details on the ECOMSED and its governing equations can be found in HydroQual (2002). The 3-D model has 183×186 17 horizontal grids with resolutions ranging from 400-500 m inside the estuary to 3-4 km near the open boundary (Fig. 1b). 18 Vertically, there are 16 sigma levels with refined resolutions at the surface and bottom layers. At the open boundaries, tide 19 forcing is prescribed using water levels derived from the Oregon State University Tidal Data Inversion Software (OTIS), 20 with the uniform salinity and temperature boundary conditions based on the observed data from Wanshan Island (Hu and Li, 21 2009). Atmospheric forcing is interpolated into our model grid using wind, air pressure, and net solar radiation obtained from 22 the ERA-interim (the Interim ECMWF Re-Analysis, http://www.ecmwf.int/en/research/climate-reanalysis/era-interim). The spatial resolution of the ERA-interim data is $0.125^{\circ} \times 0.125^{\circ}$ and the temporal resolution is 6 h. The initial conditions of the 23 24 water level and salinity are set to zero. The time steps are 5 s and 30 s for the external mode and internal mode in the 25 ECOMSED, respectively.

The 1-D and 3-D coupled physical model was first implemented in November and December 2005 to reach steady state and then continuously run from January 1, 2006 to December 31, 2006. The results of the runs for July and August 2006 were used for the analysis of summer hypoxia in the PRE.

29 2.2 Water quality model

The water quality model used in this study is the Row-Column Aesop (RCA) developed by HydroQual (2004). In the water column, RCA simulates five interactive systems including the carbon cycle, nitrogen cycle, phosphorus cycle, silicon cycle, and DO balance (Fig. 2a). In addition, a sediment flux module is incorporated into RCA to simulate the depositional flux of particulate organic matter (including particulate organic nitrogen, particulate organic phosphorus, and particulate organic carbon), diagenesis processes in the sediment converting particulate organic matter to dissolved matters, and the transportation of dissolved matters from the sediment to the overlying water (Fig. 2b). Interactions between the water column and the sediment can be simulated internally by RCA. At each time step, the water quality module passes the calculated depositional fluxes of particulate organic matters to the sediment flux module, which in return sends the simulated SOD and nutrient fluxes to the water quality module as its bottom boundary conditions.

8 In the summer, the sediment concentrations are high in the PRE, significantly limit the growth of phytoplankton by 9 reducing the light penetration through the water column. The shading effects of suspended sediments are considered in RCA 10 as follows (Di Toro, 1978):

11

12

 $K_{\rm e} = 0.052N + 0.174D + 0.031P \tag{1}$

where K_e represents the light extinction coefficient (1 m⁻¹; Table 1); *N* represents the sediment concentrations (mg L⁻¹); *D* represents the concentrations of particulate organic matters (mg L⁻¹); *P* represents the concentrations of Chlorophyll- α (µg L⁻¹). The sediment concentrations are simulated by a sediment transport module incorporated into ECOMSED (HydroQual, 2002;Hu and Li, 2009).

17 The equation for each water quality variable is given as:

18

$$\frac{\partial C}{\partial t} = \frac{\partial}{\partial x} \left(E_x \frac{\partial C}{\partial x} \right) + \frac{\partial}{\partial y} \left(E_y \frac{\partial C}{\partial y} \right) + \frac{\partial}{\partial z} \left(E_z \frac{\partial C}{\partial z} \right) - u \frac{\partial C}{\partial x} - v \frac{\partial C}{\partial y} - w \frac{\partial C}{\partial z} + S - W$$
(2)

19

where *C* represents the concentrations of each water quality variable; *x*, *y*, and *z* represent the two horizontal coordinates and the vertical coordinate; *u*, *v*, and *w* represent the corresponding velocity components in the *x*, *y*, and *z* coordinates, respectively; E_x , E_y , and E_z represent the dispersion coefficients; *S* represents the sources and sinks for water quality variables; *W* represents the external inputs of nutrients and oxygen-demanding materials which originate from municipal and industrial discharges, river discharges, and atmospheric deposition.

The source processes for DO include re-aeration at the air-sea interface and photosynthesis, while the sink processes for DO include nitrification of ammonia, oxidation of dissolved organic matter and dissolved sulfide, respiration by phytoplankton, and SOD at the water-sediment interface. Here, we combine nitrification, oxidation, and respiration into a single process called the water column respiration (WCR) to represent the total DO depletion in the water column. The equation describing the kinetic processes of DO is given as:

$$S_{DO} = k_{a}\theta_{a}^{T-20}(DO_{sat} - DO) + \alpha_{OC} \cdot \alpha_{NH_{4}} \cdot G_{P} \cdot P_{c} + (\alpha_{NO_{23}c}) \cdot (1 - \alpha_{NH_{4}}) \cdot G_{P} \cdot P_{c}$$

- $2 \cdot \alpha_{ON} \cdot k_{14,15}\theta_{14,15}^{T-20} \cdot NH_{4} \cdot \frac{DO}{K_{nitri} + DO}$
- $\alpha_{OC} \cdot \left[k_{20,0}\theta_{20,0}^{T-20} \cdot RDOC + k_{21,0}\theta_{21,0}^{T-20} \cdot LDOC \cdot \frac{LDOC}{K_{LDOC} + LDOC} + k_{22,0}\theta_{22,0}^{T-20} \cdot ReDOC \cdot \frac{ReDOC}{K_{LDOC} + ReDOC} + k_{23,0}\theta_{23,0}^{T-20} \cdot ExDOC \cdot \frac{ExDOC}{K_{LDOC} + ExDOC}\right] \cdot \frac{P_{c}}{K_{Pc} + P_{c}} \cdot \frac{DO}{K_{DO} + DO}$

2
$$-\alpha_{\rm OC} \cdot k_{\rm PR}(T) \cdot P_{\rm c}$$

 $-k(DO_{\rm sed} - DO)$

$$-k_{0_{2}^{*}}\theta_{0_{2}^{*}}^{T-20} \cdot O_{2}^{*} \cdot \frac{P_{c}}{K_{Pc} + P_{c}} \cdot \frac{DO}{K_{D0_{0_{2}^{*}}} + DO}$$
(3)

where k_a represents the surface mass transfer coefficient (m day⁻¹) for re-aeration; θ_a , $\theta_{14,15}$, $\theta_{20,0}$, $\theta_{21,0}$, $\theta_{22,0}$, $\theta_{23,0}$, $\theta_{0_2^*}$ represent the temperature coefficients; DO_{sat} represents the saturation concentration of DO (mg O L⁻¹); α_{OC} represents the soxygen to carbon ratio; α_{NH_4} represents the preference for ammonium uptake by phytoplankton; G_P represents the specific phytoplankton growth rate (day⁻¹); P_c represents the phytoplankton biomass (mg C L⁻¹); $\alpha_{NO_{23}c}$ represents the oxygen to carbon ratio for nitrate uptake; α_{ON} represents the oxygen to nitrogen ratio; $k_{14,15}$ represents the nitrification rate at 20 °C (day⁻¹); K_{nitri} , K_{DO} , and $K_{DO_{02}}$ represent the half saturation constants for oxygen limitation (mg O L⁻¹); $k_{20,0}$, $k_{21,0}$, $k_{22,0}$,

9 and $k_{23,0}$ represent the oxidation rates for refractory dissolved organic carbon (RDOC), labile dissolved organic carbon 10 (LDOC), reactive dissolved organic carbon (ReDOC), and algal exudate dissolved organic carbon (ExDOC) at 20 °C (day⁻¹); 11 K_{LDOC} represents the Michaelis constant for LDOC (mg C L⁻¹); K_{Pc} represents the half saturation constant for 12 phytoplankton limitation (mg C L⁻¹); $k_{\text{PR}}(T)$ represents the temperature corrected algal respiration rate (day⁻¹); k13 represents the transfer coefficient between the sediment and the overlying water; DO_{sed} represents the concentration of DO 14 in the sediment (mg O L⁻¹); $k_{O_2^*}$ represents the oxidation rate of dissolved sulfide.

15 The simulation period for the water quality model is identical to those for the physical model with a time step of 30 s. The initial conditions for water quality variables were derived from a 61 d spin up simulation, which was repeated three 16 17 times in order to reach steady state. The river boundaries are prescribed based on the monthly observations (including DO, 18 NH₄, NO₂+NO₃, and PO₄) in 2006 collected by the State Oceanic Administration and reported in Liu et al. (2015). The open 19 boundaries are specified using historical monthly observations obtained from the State Oceanic Administration and reported 20 in Zhang and Li (2010). The nutrient loadings were provided by the Shenzhen Environmental Protection Monitoring Centre, 21 the Environment Council of Macau Special Administrative Region, and the Environment Protection Department of the Hong 22 Kong Special Administrative Region. The primary parameters in the water quality model are set based on HydroQual (2004) 1 and previous modelling studies conducted in the PRE (Table 2).

2 2.3 The physical modulation method

A new method (physical modulation method) was introduced in this study to explicitly depict the modulation of the effects of source and sink processes on DO due to physical transport. This method assumes that DO concentrations can be divided into two separate parts (Eq. (4)), including the simulated DO concentrations merely driven by boundary conditions (DO_{BC}) and the ones merely driven by internal source and sink processes (DO_S).

7

$$DO = DO_{\rm BC} + DO_{\rm S} \tag{4}$$

8

9 where DO_{BC} and DO_{S} represent the changes in DO concentrations due to the effects of boundary conditions and the source 10 and sink processes, respectively. Governing equations for DO, DO_{BC} , and DO_{S} are given as:

$$\frac{\partial DO}{\partial t} + ADV(DO) - DIFF(DO) = S$$
(5)

$$\frac{\partial DO_{\rm BC}}{\partial t} + ADV(DO_{\rm BC}) - DIFF(DO_{\rm BC}) = 0$$
(6)

$$\frac{\partial DO_{\rm S}}{\partial t} + ADV(DO_{\rm S}) - DIFF(DO_{\rm S}) = S$$
⁽⁷⁾

11 where *ADV* represents the process of advection $(u\frac{\partial}{\partial x} + v\frac{\partial}{\partial y} + w\frac{\partial}{\partial z})$; *DIFF* represents the process of diffusion $(\frac{\partial}{\partial x}(E_x\frac{\partial}{\partial x}) + w\frac{\partial}{\partial z})$

- 12 $\frac{\partial}{\partial y} \left(E_y \frac{\partial}{\partial y} \right) + \frac{\partial}{\partial z} \left(E_z \frac{\partial}{\partial z} \right)$; *S* represents the source and sink terms including the re-aeration, photosynthesis, WCR, and SOD 13 (Eq. (3)). The *DO_S* can be further divided into four different terms:
- 14

$$DO_{\rm S} = DO_{\rm Rea} + DO_{\rm Phot} + DO_{\rm WCR} + DO_{\rm SOD}$$

$$\tag{8}$$

15

where DO_{Rea} , DO_{Phot} , DO_{WCR} , and DO_{SOD} represent the changes in DO concentrations due to the effects of re-aeration, photosynthesis, WCR, and SOD, respectively (Table 1). These four variables can be simulated using Eq. (7) except that *S* refers to their corresponding source and sink terms. The positive values of DO_{Rea} and DO_{Phot} indicate that re-aeration and photosynthesis are the sources of DO and thus lead to an increase in DO concentrations; on the other hand, negative values of DO_{WCR} and DO_{SOD} indicate that the WCR and SOD are the sinks of DO and thus cause a decrease in DO concentrations. By combining Eqs. (4)-(7), the changes in DO can be divided into three parts:

22

$$\Delta DO = \Delta DO_{\rm BC} + \Delta DO_{\rm S}$$

$$= \underbrace{\Delta t \times \left[-ADV(DO_{BC}) + DIFF(DO_{BC})\right]}_{CBC} + \underbrace{\Delta t \times \left[-ADV(DO_{S}) + DIFF(DO_{S})\right]}_{CAS} + \underbrace{\Delta t \times S}_{CLS}$$
(9)

1

where $\Delta t \times [-ADV(DO_{BC}) + DIFF(DO_{BC})]$ represents the contributions of boundary conditions (CBC); $\Delta t \times S$ 2 3 represents the contributions of local source and sink processes (CLS), which directly affect the DO concentrations in local 4 waters; $\Delta t \times [-ADV(DO_s) + DIFF(DO_s)]$ represents the contributions of adjacent source and sink processes (CAS). 5 which affect the advective and diffusive DO fluxes by altering the DO concentrations in adjacent waters. The last term 6 presents the modulation of the effects of the source and sink processes on DO due to physical transport and denotes the 7 interactive impacts of physical and biogeochemical processes occurring in different locations. The traditional mass balance 8 analysis of DO is not able to distinguish CBC and CAS as they are combined into the overall DO transport flux. However, 9 with the application of the physical modulation method proposed here, these two terms can be separated from one another so 10 that their respective contributions on the DO dynamics can be accurately quantified.

Additional numerical oxygen tracers were implemented in RCA to simulate five new variables associated with the physical modulation method, namely DO_{BC} , DO_{Rea} , DO_{Phot} , DO_{WCR} , and DO_{SOD} . The simulation of DO_{BC} is forced by the same initial and boundary conditions with the DO simulation. For the simulations of DO_{Rea} , DO_{Phot} , DO_{WCR} , and DO_{SOD} , the initial and boundary conditions are all set to zero. Each source and sink term associated with DO is calculated at each time step using Eq. (3). The validation of the physical modulation method is presented in Section 3.

16 **3.** Model validation

17 3.1 Validations of physical and water quality models

18 Datasets used for model validation include hourly water levels at eight tidal stations and cruise observations conducted 19 during July and August 2006 (see Fig. 3a for the locations of the survey stations). The tidal stations are located at Jiaomen, 20 Hengmen, Modaomen, Jitimen, Hutiaomen, Yamen, Zhuhai, and Wanshan Islands. Cruise observations include the profiles 21 of salinity, temperature, and DO. The Taylor diagram in Fig. 3b gives a general statistical evaluation of our physical and 22 water quality models. Green isolines provide a measure of model performance, denoted by the centred root-mean-square 23 difference (RMSD) normalized by observed values. The distances between the reference point of observations (red 24 pentagram) and the points for simulated variables are proportional to the normalized RMSD. The angular coordinate shows 25 the magnitude of the correlation with the observations and the radial coordinate represents the standard deviations of the 26 simulated values normalized by the observed values. A perfect match between the model and the observations would have a 27 correlation coefficient of 1, a normalized RMSD of 0, and a normalized standard deviation of 1.

There is a good agreement between the simulated and observed water levels at the eight tidal stations (Fig. 4), with the normalized RMSD <0.30 of the standard deviation of observations, correlation coefficients >0.95, and the normalized standard deviations close to 1 at all stations (Fig. 3b). In general, our model successfully reproduced the realistic variations of tidal ranges and the spring-neap tidal cycles. Comparisons of the simulated salinity and temperature with the observations are shown in Figs. 5 and 6, respectively. The simulated results follow the observed spatial distributions closely. Both the model results and the observations indicate that during the summer, the PRE is mainly occupied by freshwater originated from the Pearl River network, with a significant westward spreading of the river plume along the coast, while the shelf is mostly filled with saline water. The normalized RMSDs for salinity and temperature were relatively small (<0.60 of the standard deviation of observations) and the correlation coefficients were high (>0.90) (Fig. 3b).

8 The comparison between the simulated and observed DO concentrations at the bottom layer is shown in Fig. 7. The 9 observations were collected in four different monitoring cruises, each of which lasted for 3-4 d. The simulated DO 10 concentrations averaged over the same period were adopted for comparison purposes. Our model generally reproduced the 11 observed DO distributions and captured the observed hypoxia on the shelf off the Modaomen sub-estuary (Fig. 7c). This 12 hypoxic zone has also been reported by previous observational (Cai et al., 2013) and modelling studies (Zhang and Li, 2010). 13 The DO concentrations are relatively low in the upper Lingdingyang bay due to the inflow of low-oxygen water from the river outlets but they increase gradually along the estuary to 5 mg L^{-1} in the lower Lingdingvang bay. The simulated results 14 15 generally follow the observed patterns. However, the model underestimates the variations in DO concentrations, with a 16 normalized standard deviation of ~0.63 because the model fails to reproduce the super saturation of DO observed at the 17 surface. The correlation coefficient for DO is relatively high (>0.60) and the normalized RMSD is less than 0.80 of the 18 standard deviation of observations (Fig. 3b). To further gain an insight into the differences between the simulation results and 19 the observations, we analyse the frequency distribution of their biases normalized by the standard deviation of observations 20 (Figs. 3c and d). Overall, 85 % of the normalized biases are within ± 1 and the model underestimates the DO concentrations 21 by 0.34 of the standard deviation of observations.

22 In order to further evaluate the model performance in terms of depicting the important kinetic processes controlling the 23 DO dynamics, we compared the simulated re-aeration, SOD, and respiration rates with historical estimated values obtained 24 from previous studies (Table 3). The respiration rate was estimated by subtracting the nitrification rate from WCR (He et al., 25 2014). The simulated values were comparable to the historical estimations (Table 3). The observed re-aeration rates exhibit 26 strong spatial variability with the maximum values occurring near river outlets and decreasing sharply to negative values in 27 the mouth of the estuary, while the maximum values of SOD occur in the middle of the estuary. Our model reasonably 28 reproduced the observed patterns of the re-aeration and SOD. We also conducted the model-data comparisons for 29 chlorophyll-a, particulate organic carbon (POC), and primary productivity as they are important variables associated with the 30 respiration rate and SOD; as shown in Table 3, the simulated values were in agreement with the observations.

The comparisons show that our models are robust to the spatial and temporal variability of hydrodynamic parameters and DO as well as relevant important biogeochemical parameters. The spatial extent of hypoxia near the Modaomen sub-estuary from our simulation is consistent with the previous studies as mentioned above. Nevertheless, the model-data
comparison for hypoxia presented here is limited due to data insufficiency at the current stage. We suggest strengthening the
direct observations on hypoxia and those related to the important kinetic processes affecting DO in future studies to provide
a more comprehensive evaluation of the model performance.

5 **3.2** Validation of the physical modulation method

6 Theoretically, there should be no differences in terms associated with DO dynamics between the physical modulation method 7 and RCA if the methodology and implementation of the physical modulation method are right. Therefore, the comparisons of 8 the July-August-averaged DO distributions simulated by these two methods are shown in Fig. 8 to assess the accuracy of the 9 physical modulation method. Overall, DO distributions simulated by the physical modulation method were in good 10 agreement with those simulated by RCA. At the surface layer, the physical modulation method slightly overestimated RCA 11 simulations in the Lingdingyang bay and its adjacent areas, yet underestimated RCA simulations on the shelf (Fig. 8a). This 12 is also true for the middle layer (Fig. 8b). At the bottom layer, the physical modulation method simulated DO concentrations 13 slightly higher within the model domain (Fig. 8c). Additional numerical tests suggested that the differences in DO 14 concentrations between the two methods were caused by the nonlinear numerical methods used in the water quality model. 15 These nonlinear numerical methods are applied to restrain the errors brought by discretizing the linear partial differential 16 equations.

17 Frequency distributions of the biases between the physical modulation method and RCA are computed over the whole model domain and for different bias bins between -1.0 and 1.0 mg L^{-1} (Fig. 9a). The layers where the bias varies between 18 -0.1 and 0.3 mg L⁻¹ occupy about 97 % of the total volume in our model domain. Therefore, the DO concentration simulated 19 20 by the physical modulation method is close to the DO concentration derived from RCA, whereas it is slightly overestimated 21 by the physical modulation method. A linear regression of the spatially-averaged DO concentration (averaged over the area represented by the red box in Fig. 8) further suggested that the physical modulation method reproduced the comparable 22 23 temporal patterns of DO concentrations, which agreed well with the temporal pattern obtained from RCA with the regression 24 coefficient of R^2 >0.99 and the regression slope of ~1:1 (Fig. 9b). Therefore, the acceptable differences in DO concentrations 25 between these two methods indicated the feasibility of the physical modulation method.

Comparisons of the horizontal advective DO fluxes, vertical advective DO fluxes, and vertical diffusive DO fluxes were also conducted (Fig. 9 c-e). Horizontal diffusive DO fluxes were much smaller than the other terms and hence omitted. The agreement between the DO fluxes calculated by the physical modulation method and RCA indicates that the physical modulation method is also practical for use in the diagnostic analysis of the DO balance (Figs. 9c-e). For a better assessment of the physical modulation method, some additional techniques (e.g. oxygen isotopes and artificial tracers) can be applied so that the distributions of each DO part (e.g. DO_{Rea}, DO_{Phot}, DO_{WCR}, and DO_{SOD}) can be validated directly.

1 4. Results and discussion

2 4.1 Characteristics of DO distribution during summer in the PRE

3 The simulated distributions for July-August-averaged DO concentration at the surface and bottom layers are shown in Figs. 4 10a,b. Compared with the bottom layer, DO concentrations at the surface layer were higher in most of areas except in the 5 upper estuary (Fig. 10a) that receives a large number of low-oxygen water discharged from the river outlets. At the bottom layer, the lowest DO concentration was approximately 2 mg L^{-1} between the Jitimen and Modaomen sub-estuaries (Fig. 10b). 6 7 There is a slender zone with relatively lower DO concentrations located on the shelf off the Modaomen sub-estuary, 8 extending from the Gaolan Island to the Henggin Island. The simulated July-August-averaged DO concentration remained above 3 mg L^{-1} defined as the threshold of hypoxia (Luo et al., 2008). In order to identify whether the hypoxia has occurred, 9 we estimated the hypoxic frequency in each model grid as follows: 10

$$P_h = \frac{N_h}{N_T} * 100 \%$$
 (10)

where $N_{\rm h}$ is the number of hours when hypoxia occurs; and $N_{\rm T}$ is the total number of hours in July and August (i.e., 1,488). The hypoxic frequency in Fig. 10d shows that there is a high frequency zone (HFZ) near the Modaomen sub-estuary. This HFZ zone is encompassed by 10 % isoline of hypoxic frequency and resembles the low DO-concentration zone. In the HFZ, the hypoxic frequency varies from 10 % to over 50 % with the spatial average of 35 %, which means that there are, on average, 22 days during July and August with hypoxia. Furthermore, when the severe hypoxia was defined as DO<2 mg L⁻¹ (Rabalais et al., 2010), the highest hypoxic frequency in the HFZ decreased to approximately 40 % and the average hypoxic frequency was 16 % (Fig. 10c).

18 The vertical patterns of the DO concentrations along the two transects are shown in Figs. 10e,f. These two transects 19 represent the central areas of the HFZ and their locations are shown in Figs. 10a-d. Transect A starts from the inner 20 Modaomen sub-estuary and extends southward, while transect B starts from the Gaolan Island and ends near the Henggin Island. The parallel distribution of DO concentrations to the bottom topography can be observed in both transects during July 21 and August (Figs. 10e,f). In transect A, surface DO concentrations range from 6 to 7 mg L⁻¹ and the lowest bottom DO 22 concentration is almost 4 mg L^{-1} (Fig. 10e). The relatively low-DO water is confined to a thin layer above the sediment. In 23 the south end of transect A, where the depth is as much as 25 m, 7 mg L^{-1} isoline of DO concentration can penetrate into 24 depths greater than 15 m. The same is true for transect B (Fig. 10f), where the surface DO concentration is above 6 mg L^{-1} 25 and the bottom DO concentration is almost 4 mg L^{-1} . 26

Compared with the Chesapeake Bay (Hagy et al., 2004) and the northern Gulf of Mexico (Scavia et al., 2003;Rabouille
et al., 2008), hypoxia in the PRE was much less severe with higher DO concentrations, a lower hypoxic frequency, and a
smaller hypoxic extent. Here, we estimate the hypoxic area and hypoxic volume as follows:

hypoxic area =
$$\sum P_{\rm h} * \Delta s$$
 (11)

hypoxic volumn =
$$\sum P_{\rm h} * \Delta v$$
 (12)

1 where $P_{\rm h}$ is the hypoxic frequency calculated using Eq. (10); Δs and Δv are the area and volume of each model grid cell, 2 respectively. Hypoxic area and hypoxic volume are the expected values which consider the temporal variability of hypoxia. 3 If hypoxia is defined as DO<3 mg L⁻¹, the expected hypoxic area and volume are 237 km² and 0.13 km³, respectively, much 4 smaller than those in the northern Gulf of Mexico (13,500 km²; Rabalais et al. (2007)) and the Chesapeake Bay (8 km³; 5 Rabalais et al. (2010)).

6 **4.2 DO balance**

7 In order to investigate the processes that control the DO conditions, a diagnostic analysis of DO balance was conducted for 8 the PRE (Fig. 11) and the HFZ (Fig. 12). All of the diagnostic terms are combined at each desired grid cell and given for the 9 upper layer, middle layer, and bottom layer. According to the survey data of the Pearl River Estuary Pollution Project (Chen 10 et al., 2004), the pycnocline in the PRE is located at depths ranging from 1.5 to 3 m. We, therefore, define the upper layer as 11 the top 20 % of the 10-m average depth in the PRE. The bottom layer is limited to 20 % of the depth above the sediment 12 where the DO concentration is relatively lower as demonstrated in Figs. 10e,f. We also estimated the contribution of each 13 source and sink process as well as the boundary conditions to vertical advective DO fluxes (Fig. 11b and Fig. 12b), vertical 14 diffusive DO fluxes (Fig. 11c and Fig. 12c), and horizontal advective DO fluxes (Fig. 11d and Fig. 12d). Horizontal diffusive 15 DO fluxes are much smaller than the other terms and hence are omitted. The contributions of the boundary conditions (CBC 16 in Eq. (9)), adjacent source and sink processes (CAS in Eq. (9)), and local source and sink processes (CLS in Eq. (9)) to the 17 DO balance for the PRE and the HFZ are shown in Fig. 11e and Fig. 12e, respectively.

18 4.2.1 PRE

At the upper layer of the PRE, there is a DO influx of 9,051 tonnes day⁻¹ induced by re-aeration, which causes an increase in 19 July-August averaged DO concentrations by 0.55 mg L^{-1} day⁻¹ (Fig. 11a). This reoxygenation will enhance the DO vertical 20 gradient and supplement the DO at the middle and bottom layers by vertical diffusion. According to Fig. 11c, 89 % (0.48 mg 21 22 L^{-1} day⁻¹) of oxygen entering the upper layer via re-aeration will be transported to the middle layer by vertical diffusion and eventually 28 % (0.15 mg L⁻¹ day⁻¹) will reach the bottom layer (Fig. 11c). Figure 11c also shows that re-aeration is a major 23 contributor (accounts for 99 %) to vertical diffusive DO fluxes. Another important source of DO is photosynthesis. As shown 24 25 in Fig. 11c, the vertical diffusive flux of DO_{Phot} (changes in DO concentrations due to the effects of photosynthesis; Table 1) is much smaller than that of DO_{Rea} (changes in DO concentrations due to the effects of re-aeration). This indicates that the 26 27 DO gradient driven by photosynthesis is much smaller than that driven by re-aeration since the diffusion coefficients are the

same. The surface DO_{Phot} rarely reaches the middle and bottom layers through vertical diffusion (Fig. 11c), but can be 1 transported by horizontal and vertical advection (Figs. 11b,d). Approximately 0.56 mg L⁻¹ day⁻¹ of DO_{Phot} is transported off 2 the upper layer of the PRE while at the same time vertical advection brings about 0.35 mg L^{-1} day⁻¹ of DO_{Phot} from the 3 4 middle layer, 2 and 1.2 times the photosynthesis rate at the upper layer, respectively. The DO_{BC} (changes in DO 5 concentrations due to the effects of the boundary conditions) and DO_{WCR} (changes in DO concentrations due to the effects of 6 WCR) are also transported mainly by horizontal and vertical advection (Figs. 11b,d). Moreover, SOD can exert significant 7 negative effects on DO concentrations in the upper layer (Fig. 11b) by decreasing DO concentrations and thereby preventing 8 the upward vertical advective DO fluxes from reaching the upper layer. In general, CAS and CLS are the most important 9 factors controlling the DO balance (Fig. 11e). Although the boundary conditions can affect DO concentrations at the upper 10 layer, the negative horizontal advective DO_{BC} fluxes are close to positive vertical advective DO_{BC} fluxes; therefore, these 11 two processes compensate each other (Fig. 11e).

At the middle layer, horizontal and vertical advections are the main processes controlling the DO dynamics (Fig. 11a). As the DO content transported from the middle layer to the upper layer exceeds the content transported to the middle layer from the bottom layer, the overall performance of vertical advection leads to a decrease in DO concentrations. In addition, both the horizontal and vertical advection are dominated by the contribution of boundary conditions (Figs. 11b,d), indicating that the DO balance at the middle layer is mainly controlled by *CBC* (Fig. 11e).

17 As light becomes weak at the bottom layer, the growth of phytoplankton is limited along the shallow coastal areas. As a 18 result, photosynthesis and WCR play trivial roles in affecting the DO balance; thus, SOD becomes a major sink for DO at the 19 bottom layer. This is in contrast to the situation in the Chesapeake Bay (Li et al., 2015). The discrepancies in the dominant 20 role of SOD responsible for the total DO depletion at the bottom layer result from the differences in geometry. The 21 Chesapeake Bay has a relatively deep channel where SOD ranges from 0.86 to 3.2 g m⁻² day⁻¹ and accounts for 16 % of total 22 DO depletion at the bottom layer (Boynton and Kemp, 1985). However, the PRE is characterized by the shallow banks with depths <5 m where SOD ranges from 0.49 to 3.5 g m⁻² day⁻¹. Therefore, SOD dominates the total DO depletion at the bottom 23 layer with a consumption rate of 0.53 mg L^{-1} day⁻¹ (Fig. 11a). Furthermore, this deoxygenation results in a strong vertical DO 24 25 gradient between the middle and bottom layers and thereby facilitates the downward vertical diffusion. Figure 11c shows that 26 SOD is a major cause of vertical diffusion between the middle and bottom layers followed by re-aeration, which contribute 27 79 % and 25 % of vertical diffusive DO fluxes, respectively. Therefore, re-aeration can also have significant effects on DO 28 concentrations at the bottom layer. Vertical advection is a major mechanism by which SOD can affect the middle layer and 29 especially the upper layer, while vertical diffusion is a mechanism by which SOD can only affect a thin layer above the 30 sediment (Figs. 11b, c). Figure 11a shows that the horizontal advective DO_{BC} fluxes are close to vertical advective DO_{BC} 31 fluxes and these two processes compensate each other. As a result, the DO balance at the bottom layer is mainly controlled 32 by CAS and CLS (Fig. 11e).

1 4.2.2 HFZ

Compared with the upper layer in the PRE, the vertical advective DO fluxes in the HFZ are almost 5.5-fold larger because of its shallower depth and larger vertical velocity. As a result, vertical advection becomes the most important process controlling the DO balance at the upper layer (Fig. 12a). Besides vertical advection, re-aeration is another important source for DO. In the HFZ, re-aeration brings about 1.24 mg L⁻¹ day⁻¹ oxygen to the upper layer (Fig. 12a), 64 % of which is transported to the middle layer via vertical diffusion (Fig. 12c).

7 At the middle layer, the DO is mainly balanced by horizontal and vertical advection (Fig. 12a), both of which are
8 mainly contributed by boundary conditions (Fig. 12b, d).

9 At the bottom layer, SOD dominates the DO depletion rate (Fig. 12a) and leads to a significant vertical DO gradient 10 between the middle and bottom layers, which results in 88 % of vertical diffusive DO fluxes (Fig. 12c). In addition, SOD can 11 affect DO concentrations at the upper layer through vertical advection (Fig. 12b). Unlike the bottom layer of the PRE, 12 boundary conditions play a more important role in the DO balance at the bottom layer of the HFZ through horizontal and 13 vertical advection. According to Figs. 12b,d, horizontal advection brings DO_{BC} to the bottom layer of the HFZ, while vertical 14 advection transports DO_{BC} upward to the middle layer. However, these two processes compensate each other and the DO 15 balance at the bottom layer is mainly controlled by CAS and CLS (Fig. 12e). Therefore, the processes controlling the DO 16 balance at the bottom layer of the HFZ and the PRE are basically similar, suggesting the need for further discussion on the 17 mechanisms of hypoxia in the PRE.

18 4.3 Why hypoxia occurs in the HFZ?

In Zhang and Li (2010) showed that the distribution of hypoxia in the PRE was related to SOD because of the dominant roles of SOD in the bottom DO depletion rates. However, as shown in Fig. 13a, the HFZ is not located where high SOD is and there is a location shift between the hypoxic zone and the high SOD areas (Zhang and Li, 2010). One possible reason for this shift is the lack of the full consideration of all source and sink processes. Therefore, we will primarily examine the distribution of the gross DO depletion rate at the bottom layer (Fig. 13b).

24 In fact, it is hard to estimate the gross DO depletion rate since we cannot confirm the thickness affected by SOD. In the 25 Chesapeake Bay (Hong and Shen, 2013; Shen et al., 2013) and northern Gulf of Mexico (Yu et al., 2015b), SOD is 26 characterized by the thickness of the bottom layer to evaluate the contributions to the DO depletion rate, assuming that the 27 bottom water mixes evenly below the pycnocline. In the PRE, the depth of pycnocline significantly varies in time and space, 28 which makes it hard to estimate. As mentioned above, the shallow depth and large vertical velocities make it possible for 29 SOD to affect the surface layer significantly. Therefore, the gross DO depletion rate was alternatively estimated by summing 30 the WCR, photosynthesis, and SOD which was divided by depth. The negative values represent DO consumption while the 31 positive values represent DO production. As shown in Fig. 13b, the distribution of hypoxia and the gross DO depletion rate are also inconsistent. Specifically, the gross DO depletion rate ranges from 0.6 to more than 1.0 mg L⁻¹ day⁻¹ in the middle of
the Lingdingyang bay but no hypoxia occurs. In contrast, the gross DO depletion rates are much lower at the bottom layer of
the HFZ because the effects of adjacent source and sink processes should be included in the discussion on hypoxia.

Figure 13c shows the agreement in the distribution between DO_s (changes in DO concentrations due to the effects of the source and sink processes; Table 1) and hypoxia with the lowest DO_s areas resembling the HFZ. According to the physical modulation method, DO_s is only controlled by the combination of *CAS* and *CLS*. Therefore, hypoxia in the HFZ is caused by the largest negative effect of all source and sink processes occurring not only in local waters but also in adjacent waters, consistent with the diagnostic analysis that the DO balance at the bottom layer is mainly controlled by *CAS* and *CLS*. Based on this result, we will continue to investigate why the source and sink processes exert the largest negative effect on the HFZ.

10 The spatial distribution of DO_{SOD} (changes in DO concentrations due to the effects of SOD), DO_{WCR} , DO_{Rea} , and DO_{Phot} are shown in Fig. 14. Because of the similar distributions and magnitudes of DO_{WCR} and DO_{Phot}, the distribution of 11 12 hypoxia is mainly controlled by re-aeration and SOD. At the bottom layer, a low DO_{SOD} zone is observed along the west 13 coast extending from the west of the lower Lingdingvang bay to the HFZ where the July-August averaged DO_{SOD} concentration ranges from -4 to -5 mg L⁻¹ (Fig. 14a). Therefore, the July-August averaged DO concentration can be 14 15 decreased by 4 to 5 mg L^{-1} due to the effects of SOD, causing the west of lower Lingdingyang bay and HFZ potentially 16 hypoxic. The reasons of no hypoxia occuring to the west of the lower Lingdingyang bay is related to re-aeration. Figure 14c 17 shows that at the bottom layer, re-aeration has distinct positive effects to the west of the lower Lingdingvang bay, which 18 offsets the high negative effects of SOD there. As a result, only the HFZ is conductive to hypoxia. Additional numerical 19 experiments suggest that turning off re-aeration will lead to a significant expansion of the hypoxic area by more than 9 times 20 to 2,203 km² and result in a shift of the hypoxic centre to the west of the lower Lingdingyang Bay (Fig. 15b, d). Compared to 21 re-aeration and SOD, photosynthesis and WCR had relatively small impacts on DO conditions; turning off these two processes increased the hypoxic area to 591 km^2 (Fig. 15a, c). One interesting question remains unclear: Why does 22 23 re-aeration have the largest positive effects to the west of the lower Lingdingvang Bay. In order to investigate this question, 24 the DO_{Rea} balance analysis is conducted for this area (the western shoal near Qi'ao Island and encompassed by a DO_{Rea} 25 isoline of 4 mg L^{-1} ; as shown in Fig. 14c) (Fig. 14 e-g). As shown in Fig. 14e, there is a high oxygen influx driven by 26 re-aeration in the upper layer (blue arrow in Fig. 14e), among which the vast majority (76 %) is transported to the middle 27 layer (red arrow in Fig. 14e) and eventually 21 % reach the bottom layer (red arrow in Fig. 14g) through vertical diffusion. In 28 addition, due to the high re-aeration rate on the surface of the upper Lingdingyang Bay, the horizontal advection brings about 0.31 mg L⁻¹ day⁻¹ DO originating from the upstream re-aeration (green arrow in Fig. 14g). Since the supplement brought by 29 30 vertical diffusion and horizontal advection exceed the loss caused by vertical advection, there remains a considerable amount 31 of oxygen originating from surface re-aeration. In the HFZ, the re-aeration rate is 0.39 times lower; therefore, the vertical 32 diffusive DO_{Rea} flux to the bottom layer is only one-fourth with the value to the west of Lingdingyang Bay estuary. Finally,

no hypoxia occurs in the upper Lingdingyang Bay because it is adjacent to the river network and influenced by river
discharges largely. As a result, the quick water exchange here brings low-DO fresh water out of the upper Lingdingyang Bay
quickly, making it difficult for hypoxia to occur. This can be demonstrated by the high gross DO depletion rates and low *DO*_s
concentration levels at the bottom layer of the upper Lingdingyang Bay (Fig. 13b, c).

5 4.4 Why the hypoxia in the PRE is not severe?

6 Unlike persistent and extensive hypoxia in the Chesapeake Bay (Hagy et al., 2004) and northern Gulf of Mexico (Rabouille
7 et al., 2008), hypoxia in the PRE is intermittent and confined to small areas. Previous studies suggested that it is because the
8 short residence time (3-5 d) in the PRE prevents the organic matter from completing their biogeochemical cycle (Yin et al.,
9 2004;Rabouille et al., 2008). Moreover, the phosphorus limitation and high turbidity also inhibit the complete utilization of
10 nutrients and growth of phytoplankton in the PRE (Yin et al., 2004).

11 However, according to Zhang and Li (2010), hypoxia in the PRE is mainly controlled by SOD which is mainly 12 determined by terrestrial particulate organic matter. In addition, we also compared the gross depletion rate in the PRE with 13 that in the northern Gulf of Mexico and Chesapeake Bay (Table 4). In the northern Gulf of Mexico, SOD ranges from 0.06 to 0.70 g m^{-2} day⁻¹ during the summer of 2003-2006 and the net water column respiration (estimated by multiplying the WCR 14 and photosynthesis by the depth below the pycnocline) ranges from 0.57 to 3.60 g m⁻² day⁻¹ below the pycnocline. Given the 15 depth below the pycnocline is 8.8 to 22.8 m, the gross depletion rate ranges from 0.11 to 0.55 mg L^{-1} day⁻¹, with the areal 16 extent of hypoxia averaged 13,500 km². In the summer in the Chesapeake Bay, the gross depletion rate ranges from 0.16 to 17 0.96 mg L^{-1} day⁻¹ in the main stem of the bay and the persistent hypoxia extends for 8 km³. In the HFZ, the model results 18 (Fig. 13b) show that the gross depletion ranges from less than 0.2 to more than 1.0 mg L^{-1} day⁻¹ with the hypoxic area and 19 20 hypoxic volume of 237 km² and 0.13 km³, respectively. These comparisons show that the gross DO depletion rates are 21 comparable to or even higher while hypoxia is less severe in the PRE compared to the Chesapeake Bay and the northern 22 Gulf of Mexico. Therefore, there should be a different mechanism rather than phosphorous limitation or high concentrations 23 of sediments controlling the hypoxia in the Pearl River estuary.

Hypoxia in the PRE is not severe because of limited hypoxic area, relatively high DO concentrations, and the intermittency of hypoxia. As mentioned earlier, hypoxia is confined within the HFZ due to the effects of SOD and re-aeration. When we focus on hypoxia in the HFZ, relatively high DO concentrations are caused by the mild effects of source and sink processes on DO. According to Fig. 14c, the July-August averaged DO_S concentration ranges from -2 to -3 mg L⁻¹ at the bottom layer of HFZ, which indicates that July-August averaged DO concentration varies from 3 to 4 mg L⁻¹ given the July-August averaged DO_{BC} concentration is approximately 6 mg L⁻¹. Based on this result, we will continue to study the reasons for such low DO_S concentrations at the bottom layer of the HFZ.

Figure 17 reveals that DO_{SOD} ranges from -4 to -5 mg L⁻¹ at the bottom layer of the HFZ, with the spatially averaged

1 value of -4.31 mg L^{-1} . This result indicates that the average DO concentrations at the bottom layer of HFZ will be as low as 1.76 mg L^{-1} , assuming that other source and sink processes are neglected. This result implies that SOD alone is large enough 2 3 to form severe hypoxia in HFZ. However, photosynthesis production rates exceed the WCR consumption rate and eventually increase the average DO concentrations significantly by 0.94 mg L^{-1} at the bottom layer of HFZ (Fig. 16). Numerical 4 experiments showed that turning off photosynthesis and WCR decreased DO concentrations to below 3 mg L⁻¹ and increased 5 the hypoxic frequency to more than 60 % in HFZ (Figs. 15c,d). In addition to photosynthesis, re-aeration is another 6 important source of DO, which can cause an increase in average DO concentrations by 0.88 mg L⁻¹ at the bottom laver of the 7 8 HFZ (Fig. 16). As shown in Fig. 15, turning off re-aeration can also decrease the DO concentrations and increase the hypoxic 9 frequency at the bottom layer of the HFZ. Moreover, the hypoxic frequency averaged over the bottom layer of the HFZ was 10 increased to about 59 %; thus, hypoxia would occur for over a month during July and August in the HFZ. Therefore, there 11 are two reasons for hypoxia not being severe in the PRE. First, the hypoxic area is limited due to the effects of SOD and 12 re-aeration. Second, the intermittent hypoxia in the HFZ is caused by re-aeration and photosynthesis which offset a portion 13 of DO consumed by SOD.

14 5. Summary and conclusions

We used a physical-biogeochemical coupled model incorporated with the physical modulation method to investigate the DO dynamics and hypoxia during summer in the PRE. Model validations using the available *in situ* data and historical observations showed that our model could reasonably reproduce the observed patterns of hydrodynamic parameters and DO concentrations as well as the key processes controlling hypoxia (i.e. re-aeration and SOD). In addition, the physical modulation method was able to predict the simulated concentrations and mass budgets of DO from the RCA model and therefore, could be used to quantify the relative impacts of boundary conditions and source and sink processes occurring in local and adjacent waters on the DO conditions.

22 The model results showed a high frequency zone (HFZ) of hypoxia on the shelf off the Modaomen sub-estuary, 23 consistent with the previous studies. Hypoxia in the HFZ was confined to a thin layer above the sediment and was not severe 24 because of its intermittency in time and limited spatial extent ascribed to the contributions of re-aeration and photosynthesis. 25 Based on the diagnostic analysis using the physical modulation method, the DO balance at the bottom layer was largely 26 affected by local and adjacent source and sink processes. Re-aeration and SOD were the two principle kinetic processes 27 controlling the spatial distribution and duration of bottom hypoxia in the PRE. SOD could exert significant negative effects 28 on the bottom DO concentrations in the HFZ and to the west of the lower Lingdingyang Bay, making these two areas prone 29 to hypoxia. On the other hand, re-aeration along with physical transport could supply a considerable amount of DO to the 30 bottom layer and largely offset the oxygen consumed by SOD. Consequently, no hypoxia occurred to the west of the lower 31 Lingdingyang Bay, while hypoxia in the HFZ was intermittent and confined to a smaller area compared to those in the Chesapeake Bay and the northern Gulf of Mexico. Furthermore, our numerical experiments suggested that turning off
 re-aeration could produce a larger, more persistent hypoxic area in the PRE.

Finally, the physical modulation method proposed in this study could be useful for further investigation of other water
quality issues in the PRE and could also be applied to other shallow and river-dominated estuaries.

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23

1 Table 1. List of state variables in the water quality model (RCA) and the physical modulation method

Kelight extinction coefficient (m ⁻¹)Nsediment concentration (mg L ⁻¹)Dconcentration of POM (mg L ⁻¹)Pconcentration of Chlorophyll- α (µg L ⁻¹)DOdissolved oxygen (mg O L ⁻¹)DOsaturation concentration of dissolved oxygen (mg O L ⁻¹)DOsaturation concentration of dissolved oxygen (mg O L ⁻¹)DOsaturation concentration of dissolved oxygen (mg O L ⁻¹)DOsediment (mg C L ⁻¹)Pcphytoplankton biomass (mg C L ⁻¹)LDOClabile dissolved organic carbon (mg C L ⁻¹)REDOCrefractory dissolved organic carbon (mg C L ⁻¹)REDOCreactive dissolved organic carbon (mg C L ⁻¹)ExDOCalgal exudate dissolved organic carbon (mg C L ⁻¹)DOsediment (mg O L ⁻¹)DOsediment (mg O L ⁻¹)	Variables	Descriptions (unit)
Dconcentration of POM (mg L ⁻¹)Pconcentration of Chlorophyll- α (µg L ⁻¹)DOdissolved oxygen (mg O L ⁻¹)DOsaturation concentration of dissolved oxygen (mg O L ⁻¹)DOsaturation concentration of dissolved oxygen (mg O L ⁻¹)DOsed DO_{sed} concentration of dissolved oxygen in the sediment (mg O L ⁻¹) O_2^* dissolved oxygen equivalents (mg O L ⁻¹) P_c phytoplankton biomass (mg C L ⁻¹)LDOClabile dissolved organic carbon (mg C L ⁻¹)RDOCrefractory dissolved organic carbon (mg C L ⁻¹)ReDOCreactive dissolved organic carbon (mg C L ⁻¹)ExDOCalgal exudate dissolved organic carbon (mg C L ⁻¹)DO _{BC} changes in DO concentrations due to the effects of boundary conditions (mg O L ⁻¹)	Ke	light extinction coefficient (m ⁻¹)
Pconcentration of Chlorophyll- α (µg L ⁻¹)DOdissolved oxygen (mg O L ⁻¹)DO_{satsaturation concentration of dissolved oxygen (mg O L ⁻¹)DO_{sedconcentration of dissolved oxygen in the sediment (mg O L ⁻¹) O_2^* dissolved oxygen equivalents (mg O L ⁻¹) P_c phytoplankton biomass (mg C L ⁻¹)LDOClabile dissolved organic carbon (mg C L ⁻¹)RDOCrefractory dissolved organic carbon (mg C L ⁻¹)REDOCreactive dissolved organic carbon (mg C L ⁻¹)ExDOCalgal exudate dissolved organic carbon (mg C L ⁻¹)DO_{BC}changes in DO concentrations due to the effects of boundary conditions (mg O L ⁻¹)	Ν	sediment concentration (mg L ⁻¹)
DO dissolved oxygen (mg O L ⁻¹) DO_{sat} saturation concentration of dissolved oxygen (mg O L ⁻¹) DO_{sed} concentration of dissolved oxygen in the sediment (mg O L ⁻¹) O_2^* dissolved oxygen equivalents (mg O L ⁻¹) O_2^* phytoplankton biomass (mg C L ⁻¹) P_c phytoplankton biomass (mg C L ⁻¹)LDOClabile dissolved organic carbon (mg C L ⁻¹)RDOCrefractory dissolved organic carbon (mg C L ⁻¹)REDOCreactive dissolved organic carbon (mg C L ⁻¹)ExDOCalgal exudate dissolved organic carbon (mg C L ⁻¹) DO_{BC} changes in DO concentrations due to the effects of boundary conditions (mg O L ⁻¹)	D	concentration of POM (mg L^{-1})
DO_{sat} saturation concentration of dissolved oxygen (mg O L ⁻¹) DO_{sed} concentration of dissolved oxygen in the sediment (mg O L ⁻¹) O_2^* dissolved oxygen equivalents (mg O L ⁻¹) P_c phytoplankton biomass (mg C L ⁻¹)LDOClabile dissolved organic carbon (mg C L ⁻¹)RDOCrefractory dissolved organic carbon (mg C L ⁻¹)ReDOCreactive dissolved organic carbon (mg C L ⁻¹)ExDOCalgal exudate dissolved organic carbon (mg C L ⁻¹) DO_{BC} changes in DO concentrations due to the effects of boundary conditions (mg O L ⁻¹)	Р	concentration of Chlorophyll- α (µg L ⁻¹)
DO_{sed} concentration of dissolved oxygen in the sediment (mg O L ⁻¹) O_2^* dissolved oxygen equivalents (mg O L ⁻¹) P_c phytoplankton biomass (mg C L ⁻¹)LDOClabile dissolved organic carbon (mg C L ⁻¹)RDOCrefractory dissolved organic carbon (mg C L ⁻¹)ReDOCreactive dissolved organic carbon (mg C L ⁻¹)ExDOCalgal exudate dissolved organic carbon (mg C L ⁻¹) DO_{BC} changes in DO concentrations due to the effects of boundary conditions (mg O L ⁻¹)	DO	dissolved oxygen (mg O L ⁻¹)
O_2^* dissolved oxygen equivalents (mg O L ⁻¹) P_c phytoplankton biomass (mg C L ⁻¹)LDOClabile dissolved organic carbon (mg C L ⁻¹)RDOCrefractory dissolved organic carbon (mg C L ⁻¹)ReDOCreactive dissolved organic carbon (mg C L ⁻¹)ExDOCalgal exudate dissolved organic carbon (mg C L ⁻¹) DO_{BC} changes in DO concentrations due to the effects of boundary conditions (mg O L ⁻¹)	DO _{sat}	saturation concentration of dissolved oxygen (mg O L ⁻¹)
P_c phytoplankton biomass (mg C L ⁻¹)LDOClabile dissolved organic carbon (mg C L ⁻¹)RDOCrefractory dissolved organic carbon (mg C L ⁻¹)ReDOCreactive dissolved organic carbon (mg C L ⁻¹)ExDOCalgal exudate dissolved organic carbon (mg C L ⁻¹) DO_{BC} changes in DO concentrations due to the effects of boundary conditions (mg O L ⁻¹)	DO _{sed}	concentration of dissolved oxygen in the sediment (mg O L^{-1})
LDOClabile dissolved organic carbon (mg C L ⁻¹)RDOCrefractory dissolved organic carbon (mg C L ⁻¹)ReDOCreactive dissolved organic carbon (mg C L ⁻¹)ExDOCalgal exudate dissolved organic carbon (mg C L ⁻¹)DO _{BC} changes in DO concentrations due to the effects of boundary conditions (mg O L ⁻¹)	<i>0</i> [*] ₂	dissolved oxygen equivalents (mg O L^{-1})
RDOCrefractory dissolved organic carbon (mg C L ⁻¹)ReDOCreactive dissolved organic carbon (mg C L ⁻¹)ExDOCalgal exudate dissolved organic carbon (mg C L ⁻¹) DO_{BC} changes in DO concentrations due to the effects of boundary conditions (mg O L ⁻¹)	Pc	phytoplankton biomass (mg C L ⁻¹)
ReDOCreactive dissolved organic carbon (mg C L ⁻¹)ExDOCalgal exudate dissolved organic carbon (mg C L ⁻¹) DO_{BC} changes in DO concentrations due to the effects of boundary conditions (mg O L ⁻¹)	LDOC	labile dissolved organic carbon (mg C L ⁻¹)
ExDOCalgal exudate dissolved organic carbon (mg C L^{-1}) DO_{BC} changes in DO concentrations due to the effects of boundary conditions (mg O L^{-1})	RDOC	refractory dissolved organic carbon (mg C L ⁻¹)
DO_{BC} changes in DO concentrations due to the effects of boundary conditions (mg O L ⁻¹)	ReDOC	reactive dissolved organic carbon (mg C L ⁻¹)
	ExDOC	algal exudate dissolved organic carbon (mg C L ⁻¹)
	DO _{BC}	changes in DO concentrations due to the effects of boundary conditions (mg O L^{-1})
$DO_{\rm S}$ changes in DO concentrations due to the effects of source and sink terms (mg O L ⁺)	DOS	changes in DO concentrations due to the effects of source and sink terms (mg O L^{-1})
DO_{Rea} changes in DO concentrations due to the effects of air-sea re-aeration (mg O L ⁻¹)	DO _{Rea}	changes in DO concentrations due to the effects of air-sea re-aeration (mg O L^{-1})
DO_{Phot} changes in DO concentrations due to the effects of photosynthesis (mg O L ⁻¹)	$DO_{\rm Phot}$	changes in DO concentrations due to the effects of photosynthesis (mg O L^{-1})
DO_{WCR} changes in DO concentrations due to the effects of WCR (mg O L ⁻¹)	DO _{WCR}	changes in DO concentrations due to the effects of WCR (mg O L^{-1})
DO_{SOD} changes in DO concentrations due to the effects of SOD (mg O L ⁻¹)	DO _{SOD}	changes in DO concentrations due to the effects of SOD (mg O L ⁻¹)

1 Table 2. Parameters for the water quality model (RCA)

Parameters	Range	Value	Units
Maximum specific growth rate of phytoplankton	1.7-3.0 ^a	2.0 ^c	day ⁻¹
Respiration rate	0.1-0.3 ^a	0.1 ^c	day ⁻¹
RDON mineralization rate	0.008-0.01 ^a	0.009 °	day ⁻¹
LDON mineralization rate	0.085-0.1 ^a	0.09 ^c	day ⁻¹
RPON hydrolysis rate	0.007-0.01 ^a	0.008 ^c	day ⁻¹
LPON hydrolysis rate	0.05-0.07 ^a	0.06 °	day ⁻¹
RDOP mineralization rate	0.01-0.02 ^a	0.01 ^c	day ⁻¹
LDOP mineralization rate	0.1-0.2 ^a	0.1 ^c	day ⁻¹
RPOP hydrolysis rate	0.007-0.1 ^a	0.008 ^c	day ⁻¹
LPOP hydrolysis rate	0.085-0.1 ^a	0.09 ^c	day ⁻¹
RDOC mineralization rate	0.007-0.01 ^a	0.009 °	day ⁻¹
LDOC mineralization rate	0.1-0.15 ^a	0.1 ^c	day ⁻¹
RPOC hydrolysis rate	0.007-0.01 ^a	0.01 ^c	day ⁻¹
LPOC hydrolysis rate	0.07-0.1 ^a	0.08 ^c	day ⁻¹
RPON, LPON, RPOP, LPOP, RPOC, LPOC settling rates	0.5-1.0 ^a	0.5 °	m dag
Nitrification rate	0.05-0.1 ^a	0.08 ^c	day ⁻¹
Denitrification rate	0.05-0.4 ^a	0.09 ^c	day ⁻¹
G1 POM diagenesis rate	0.035 ^b	0.035 ^b	day ⁻¹
G2 POM diagenesis rate	0.0018 ^b	0.0018^{b}	day ⁻¹
G3 POM diagenesis rate	0-1.0E-6 ^b	1.0E-7 ^c	day ⁻¹
Nitrification rate in the sediment	0.1313 ^b	0.1313 ^b	m dag
Denitrification rate in the aerobic layer	0.2-1.25 ^b	1.25 °	m day
Denitrification rate in the anaerobic layer	0.25 ^b	0.25 ^b	m day

2 ^a HydroQual (2004)

^b Di Toro (2001)

4 ^c Zhang and Li (2010)

1 Table 3 Comparisons between the simulated and historically estimated values during summer at the Lingdingyang bay:

2 re-aeration rate (Rea); sediment oxygen demand (SOD); respiration rate (Resp); chlorophyll-*a* (Chl-*a*) concentrations;

3 primary productivity (PP); particulate organic carbon (POC) concentrations. Note that positive values represent DO

4 production rates, while negative values represent DO consumption rates.

	Simulated	Historically estimated	Time period
Rea (g m ⁻² day ⁻¹)	-0.09 ~ 9.59	$-0.68 \sim 6.8^{a}$	Aug. 2005; Aug. 2008
SOD (g m ⁻² day ⁻¹)	-1.01 ~ -3.53	$-0.72 \sim -3.89^{b}$	Jul. 1999
$\operatorname{Resp}\left(\operatorname{mg}\operatorname{L}^{-1}\operatorname{day}^{-1}\right)$	0.00 ~ -0.27	-0.11 ~ -0.37 ^a	Aug. 2008
Chl- a (µg L ⁻¹)	1.92±1.96	1.64 ^c	Jun. 2012
$PP (mg m^{-2} day^{-1})$	310.8±427.5	302.9 ^c	Jun. 2012
POC (mg L^{-1})	<0.5-3.01	$0.40 \sim > 2.50^{d}$	Nov. 2013, Feb. 2014, May 2014, and Aug. 2014

^a He et al. (2014)

6 ^b Chen et al. (2004)

^c Ye et al. (2015)

8 ^d Guo et al. (2015)

9

Table 4 A summary of the sediment oxygen demand (SOD), net water column respiration rate (NWCR, estimated by multiplying WCR and photosynthesis by the depth below the pycnocline), and gross depletion rate (GD) below the pycnocline reported for the northern Gulf of Mexico and the Chesapeake Bay. Note that negative values represent DO consumption rates. The thickness of the bottom layer below the pycnocline and the hypoxic estimations for these two regions are also included.

	Time nonied	SOD	NWCR	GD	Depth of the	Hypoxic area
	Time period	(g m-2 day-1)	(g m-2 day-1)	(mg L-1 day-1)	bottom layer (m)	or volume
Northern Culf of	Jun. 2003a	-0.06 ~ -0.70	-0.57 ~ -2.39	-0.11 ~ -0.24	15.0 ~ 22.5	
Northern Gulf of	Jun. 2006 a	-0.06 ~ -0.58	-2.69 ~ -3.50	-0.24 ~ -0.33	18.8 ~ 21.4	13,500 km2 b
Mexico	Aug. 2007 a	-0.06 ~ -0.53	-1.06 ~ -2.23	-0.23 ~ -0.55	8.8 ~ 22.8	
Chesapeake Bay	Aug. c	-1.5 ~ -3.2	-1.7 ~ -16.0	-0.16 ~ -0.96	20	8 km3 d

15 ^a Murrell et al. (2011)

16 ^b Rabalais et al. (2007)

17 ^c Hong and Shen (2013)

18 ^dRabalais et al. (2010)

19

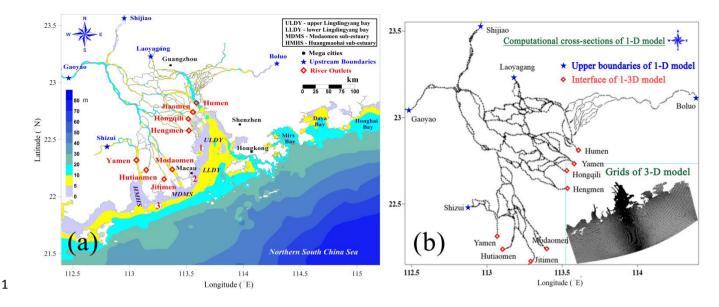


Fig. 1 Maps showing (a) the Pearl River Delta with the Pearl River network and the Pearl River estuary (PRE), and (b) computational cross-sections for 1-D model and model grids for 3-D model. The red numbers in Fig. 1a represent islands which are not marked on the map: 1-Qi'ao island; 2-Hengqin Island; 3-Gaolan Island.

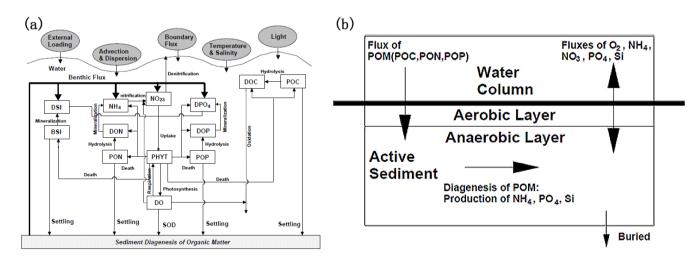


Fig. 2 A conceptual framework for (a) RCA model and (b) sediment flux model (revised from (Di Toro, 2001)):
dissolved oxygen (DO); phytoplankton (PHYT); particulate organic carbon (POC); dissolved organic carbon (DOC);
ammonia nitrogen (NH₄); nitrite and nitrate nitrogen (NO₂₃); particulate organic nitrogen (PON); dissolved organic
nitrogen (DON); dissolved inorganic phosphorus (DPO₄); particulate organic phosphorus (POP); dissolved organic
phosphorus (DOP); dissolved silica (DSi); biogenic silica (BSi); sediment oxygen demand (SOD).

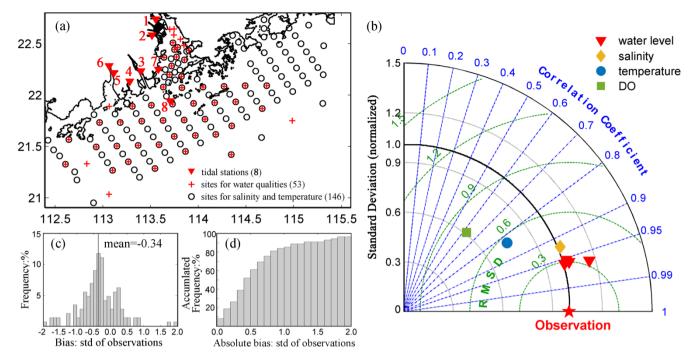


Fig. 3 (a) Survey stations of water levels (red triangles), salinity and temperature (black circles), and water quality 2 variables (red crosses) during July and August 2006. (b) Normalized Taylor diagram illustrating the model skills of 3 4 simulating the water levels (red triangles), salinity (orange diamonds), temperature (blue circles), and DO (green 5 squares). (c) Frequency and (d) accumulated frequency distribution as a function of the biases and absolute values of 6 the biases normalized by the standard deviation of observations between the simulated and the observed DO 7 concentrations. Note that positive values represent model's overestimations on the DO concentrations, while negative 8 values represent underestimations. 1-Jiaomen; 2-Hengmen; 3-Modaomen; 4-Jitimen; 5-Hutiaomen; 6-Yamen; 9 7-Zhuhai; 8-Wanshan Island.

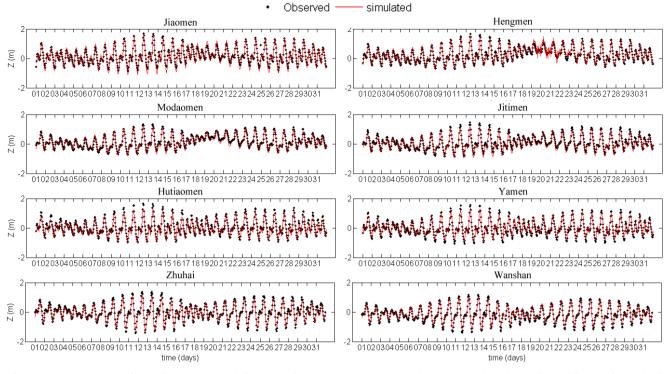


Fig. 4 Comparisons of the simulated (red lines) and the observed (black dots) water levels at eight tidal stations during
July 2006. Locations for the tidal stations are shown in Fig. 3a.

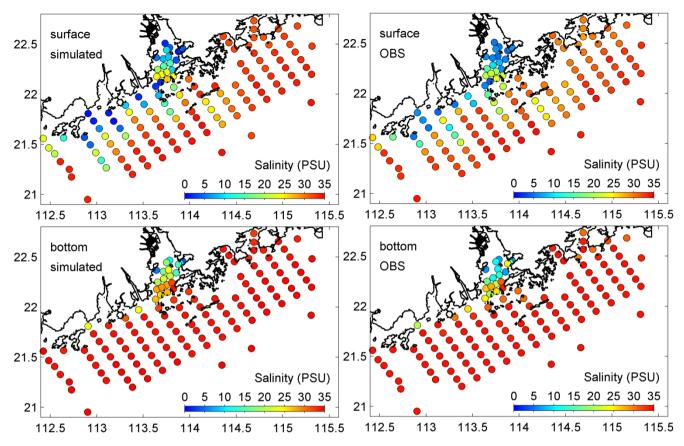


Fig. 5 Comparisons of the simulated (left panels) and the observed (right panels) salinity at the surface layer (upper panels) and the bottom layer (lower panels) during July and August 2006.

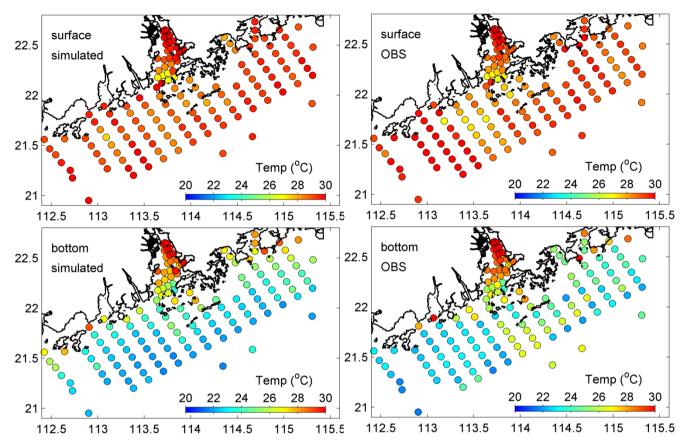


Fig. 6 Comparisons of the simulated (left panels) and the observed (right panels) temperature at the surface layer (upper panels) and the bottom layer (lower panels) during July and August 2006.

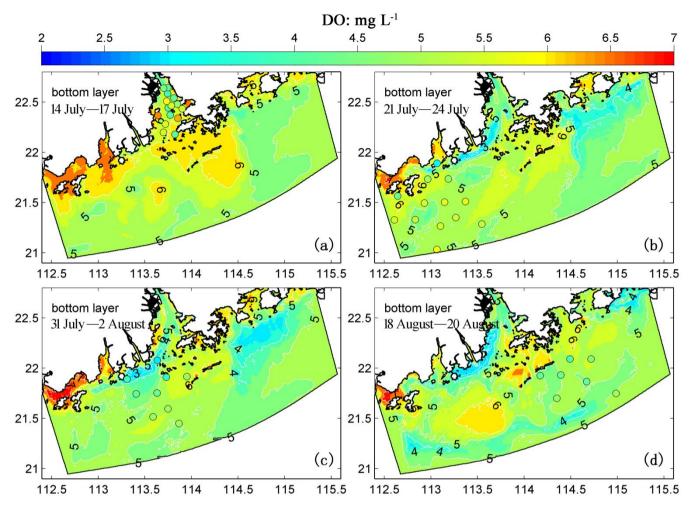


Fig. 7 Comparisons of the simulated (colored map) and the observed (colored dots) DO concentrations at the bottom layer during July and August 2006.

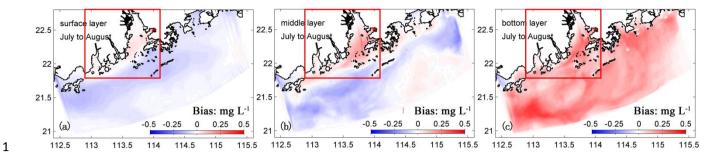


Fig. 8 Spatial distributions of the biases of the simulated DO concentrations (averaged over July-August 2006) between the physical modulation method and the water quality model (RCA). Note that positive values (red) indicate that the physical modulation method overestimates the DO concentrations simulated by RCA, while negative values indicate underestimations. The red box represents the main part of the Pearl River estuary (PRE), which is the area of interest in this study.

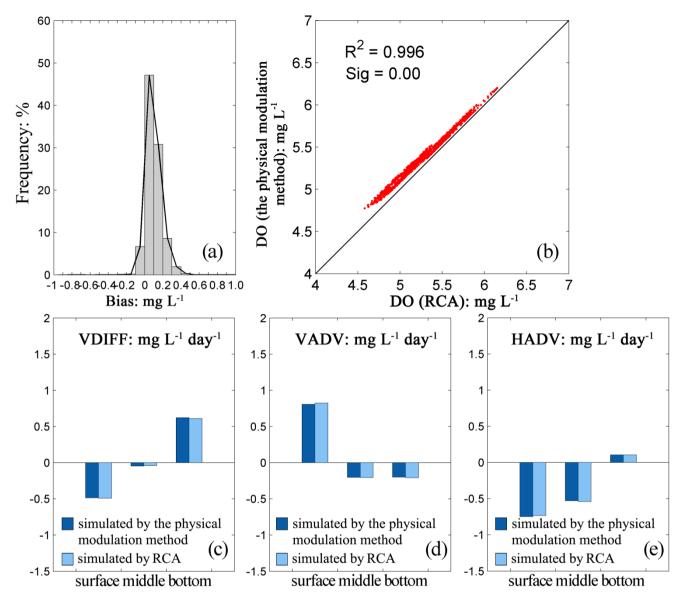


Fig. 9 Comparisons for the physical modulation method and RCA: (a) frequency distribution as a function of the biases of the simulated DO concentrations; (b) the DO concentrations in the main PRE (denoted by the red box in Fig. 8); (c) the vertical DO diffusive fluxes; (d) the vertical advective DO fluxes; (e) horizontal advective DO fluxes.

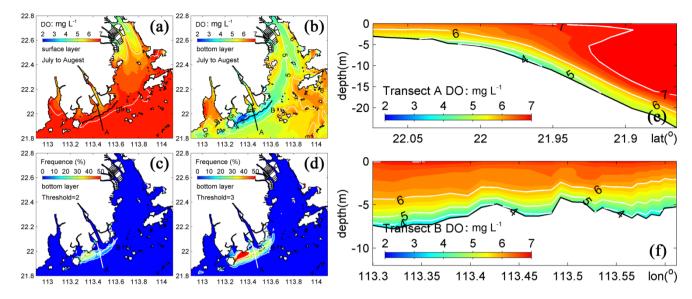
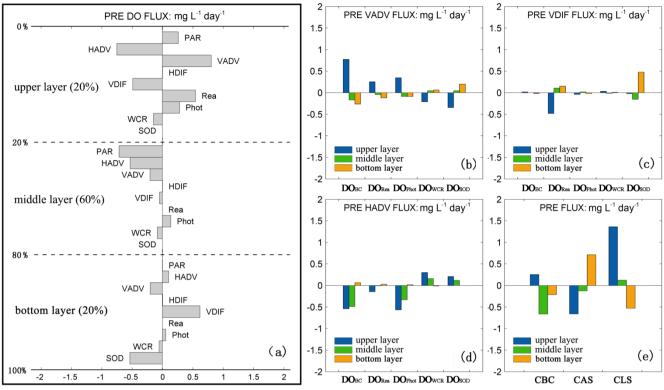


Fig. 10 Spatial distributions of the monthly averaged DO concentrations at (a) the surface layer and (b) the bottom layer in the PRE. Spatial distributions of hypoxic frequency during July and August using DO thresholds of (c) 2 mg L^{-1} and (d) 3 mg L^{-1} for hypoxia. Vertical distributions of the DO concentrations along two transects (see their locations in Fig. 10 a-d).



2 Fig. 11 (a) The simulated DO mass balance (averaged over July-August 2006) for the PRE. All the diagnostic terms are given for the upper layer above the 20% of depth, for the middle layer, and the bottom layer which covers 20% of 3 4 depth over the sediment. Contributions of each source and sink process as well as boundary conditions to (b) the vertical advective DO fluxes, (c) the vertical diffusive DO fluxes, and (d) the horizontal advective DO fluxes. (e) 5 6 Contributions of boundary conditions (CBC), adjacent source and sink terms (CAS), and local source and sink terms 7 (CLS) to the DO balance. Abbreviation PAR represents localized partial derivatives of DO; SOD and DO_{SOD} 8 represent the sediment oxygen demand and the changes of DO concentrations due to the effects of sediment oxygen 9 demand, respectively; WCR and DO_{WCR} represent the water column respiration and the changes of DO concentrations due to the effects of water column respiration, respectively; Phot and DO_{Phot} represent the 10 photosynthesis and the changes of DO concentrations due to the effects of photosynthesis, respectively; Rea and 11 12 DO_{Rea} represent the re-aeration and the changes of DO concentrations due to the effects of re-aeration, respectively; DO_{BC} represents the changes of DO concentrations due to the effects of boundary conditions; VADV represents the 13 14 vertical advection of DO; HADV represents the horizontal advection of DO; VDIFF represents the vertical diffusion of 15 DO; and HDIFF represents the horizontal diffusion of DO.

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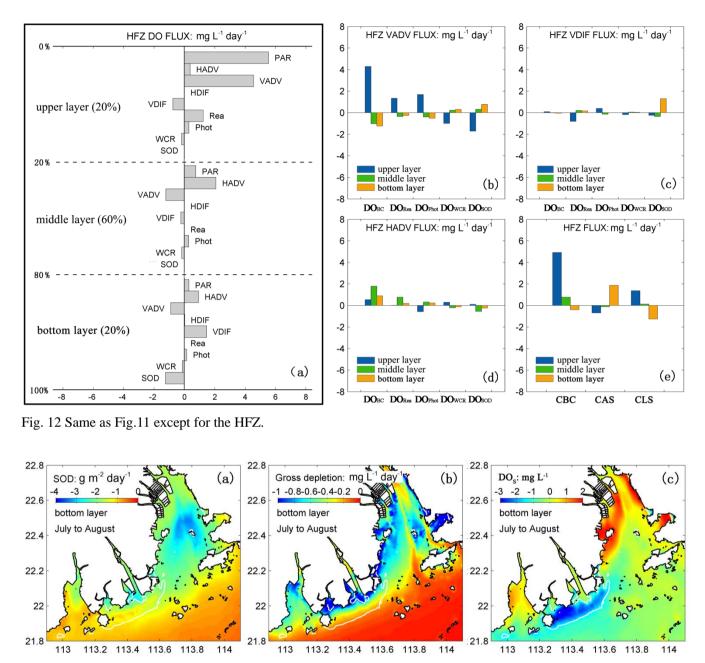


Fig. 13 Spatial distributions of the monthly averaged (a) SOD, (b) gross depletion rates of DO, and (c) the concentrations of DO_S at the bottom layer. Note that the HFZ is also shown here (denoted by the area encompassed by white lines).

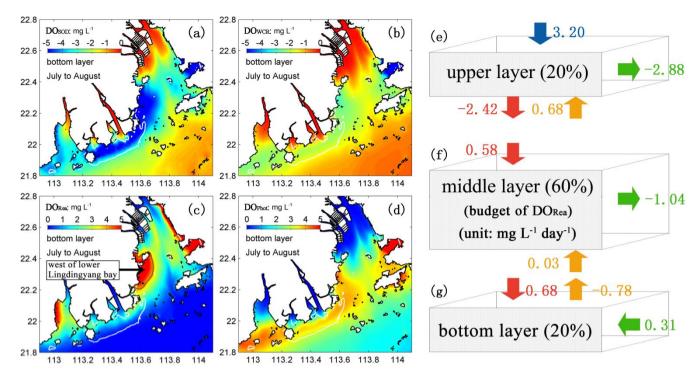


Fig. 14 Spatial distributions of the monthly averaged (a) DO_{SOD} , (b) DO_{WCR} , (c) DO_{Rea} , and (d) DO_{Phot} at the bottom layer. Note that the HFZ is also shown here (denoted by the area encompassed by white lines). The DO_{Rea} balance analysis for (e) the upper layer, (f) the middle layer, and (g) the bottom layer to the west of the lower Lingdingyang bay (the western shoal near the Qi'ao Island and encompassed by a DO_{Rea} isoline of 4 mg L⁻¹; as shown in Fig. 14c). Blue arrows represent the re-aeration rates; red arrows represent the vertical diffusive fluxes of DO_{Reg} ; orange arrows represent the vertical advective fluxes of DO_{Rea}; green arrows represent the horizontal advective fluxes of DO_{Rea} . Note that positive values indicate sources of DO, while negative values indicate sinks of DO (unit: mg L⁻¹ dav^{-1}).

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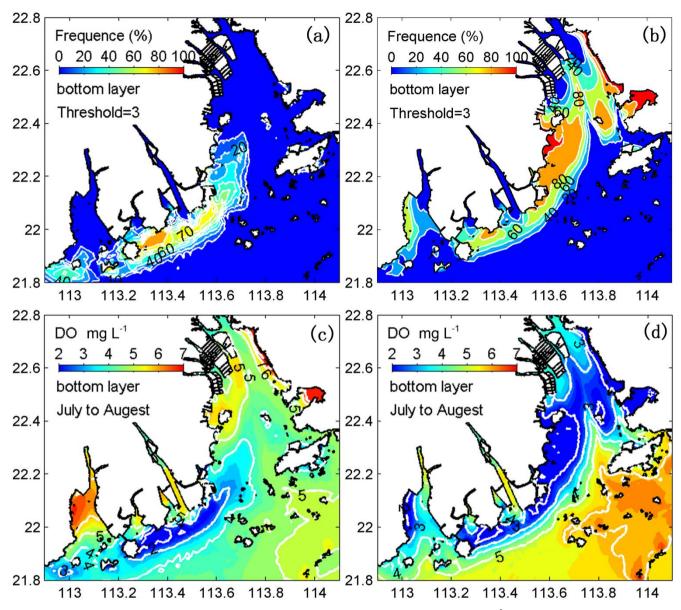


Fig. 15 Spatial distributions of hypoxic frequency (using a DO threshold of 3 mg L^{-1} for hypoxia) and the monthly averaged DO concentrations at the bottom layer for the numerical experiments by turning off (a, c) photosynthesis and water column respiration and (b, d) the re-aeration, respectively.

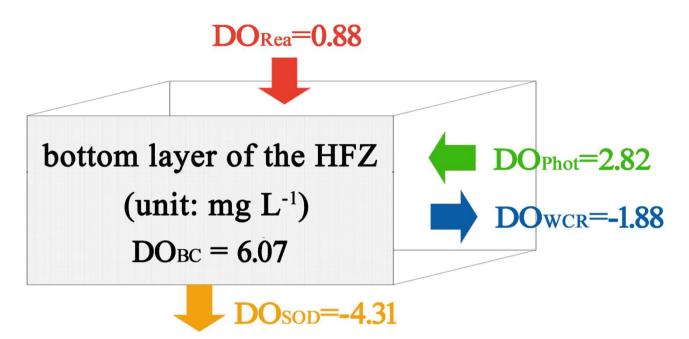


Fig. 16 The simulated mass balance for the bottom DO in the HFZ. Note that positive values indicate positive effects on the DO concentrations, while negative values indicate negative effects (unit: mg L^{-1}).