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# Hypoxia in the upper reaches of the Pearl River Estuary and its maintenance mechanisms: A synthesis based on multiple year observations during 2000–2008

Biyan He [a,b], Minhan Dai [a,*], Weidong Zhai [a], Xianghui Guo [a], Lifang Wang [a]

[a] State Key Laboratory of Marine Environmental Science, Xiamen University, Xiamen 361005, China
[b] School of Bioengineering, Jimei University, Xiamen 361021, China

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ABSTRACT

Based on our multiple year observations during 2000–2008 in the Pearl River Estuary, this study sought to synthesize the long-term pattern of hypoxia and its relationship to organic carbon and nutrient loading in this important world major estuary under significant human impacts. We confirmed previously observed year-round low dissolved oxygen (DO) of <63 μmol kg$^{-1}$ reaching the threshold of hypoxia in the upper reaches of the Pearl River Estuary, extended from the Guangzhou Channel to downstream of the Humen Outlet, in the surface water, covering a water body of ~75 km length. The surface DO concentration had a significantly negative correlation with dissolved and particulate organic carbon, and $NH_4^+$ concentrations. Both aerobic respiration and nitrification highly varied spatially in the water column. The highest rates of respiration and nitrification were observed in the Guangzhou Channel, which decreased downstream along with organic carbon and $NH_4^+$ concentrations. Seasonally, the highest rates of total oxygen consumption upon normalization to the substrate (TOC, total organic carbon; and $NH_4^+$) were observed in summer, suggesting that both the substrate availability and water temperature were major factors controlling the oxygen consumption rates. Oxygen mass balance calculations showed that in summer, the oxygen consumption rate in the water column by aerobic respiration ($21.3 \times 10^6$ mol $O_2$ d$^{-1}$) and nitrification ($14.5 \times 10^6$ mol $O_2$ d$^{-1}$) was almost balanced by the reaeration ($32.6 \times 10^6$ mol $O_2$ d$^{-1}$) and net advective complement ($2.3 \times 10^6$ mol $O_2$ d$^{-1}$). The contributions of other processes (e.g., sediment oxygen consumption and photosynthesis) appeared to be minor. We estimated that the on-site biogenically produced organic matter, or autochthonous organic material, contributed only 13% ± 10% of the TOC being respired in the hypoxic area, suggesting that the allochthonous organic material, primarily derived from sewage discharge, dominated aerobic respiration and the associated oxygen consumption. Meanwhile, $NH_4^+$ which was clearly reflective of sewage loadings (if not all) dominated the nitrification process and the associated oxygen consumption. Taken together, the hypoxia in the studied area was profoundly anthropogenic and this conclusion should have many implications towards regional environmental management.
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## 1. Introduction

Hypoxic waters, typically defined when dissolved oxygen (DO) concentration falls below 2–3 mg L$^{-1}$ (or 63–95 μmol $O_2$ kg$^{-1}$), have become one of the most pressing worldwide environmental problems in many estuaries and coastal areas (Diaz and Rosenberg, 2008). The formation, development and maintenance of hypoxia usually depend on both physical and biogeochemical conditions of a particular water body. Physical processes such as stratification, circulation pattern, and the flushing rate influence the horizontal and vertical transport of DO (Lin et al., 2008; Rabouille et al., 2008). Biogeochemical processes include the consumption (e.g. respiration of organic matter and nitrification) or production of DO (e.g. photosynthesis).

The majority of the studies on hypoxia have focused on the inner shelf regimes where anthropogenic nutrients drive excess algal biomass production, the subsequent accumulation of which in the bottom water fuels microbial-mediated organic matter decomposition. This consumes large amounts of oxygen and, if the water column was stratified with limited DO replenishment from the surface, DO in the bottom water could become depleted. This mechanism has explained the oxygen depletion in many shelf systems, e.g. the Long Island Sound, the northern Gulf of Mexico and Chesapeake Bay (Hagy et al., 2004; Justic et al., 2002; Lee and Lwiza, 2008; Scavia et al., 2003; Turner et al., 2005), where the linkage between anthropogenic nutrient loads and hypoxia is well documented.

* Corresponding author.
*E-mail address:* mdai@xmu.edu.cn (M. Dai).

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Another setting of hypoxia is increasingly recognized to occur in well-mixed estuaries (Verity et al., 2006), mostly in highly impacted upper estuaries such as the Pearl River Estuary (PRE), Scheldt Estuary and Seine Estuary (Dai et al., 2006; Frankignoulle et al., 1996; Garnier et al., 2001). In this type of settings, high loads of allochthonous organic matter and nutrients (especially $NH_4^+$) from wastewater discharge might directly stimulate microbial respiration and nitrification and result in oxygen depletion in the water column, often only in the confined upper estuary. However, the mechanistic understanding and quantification of the contribution of individual processes to the overall oxygen depletion in these well-mixed estuaries are not well demonstrated.

The Pearl River is the largest river in southern China. With the rapid economic development and urbanization in the Pearl River Delta, human activity has seriously affected the regional environment during the past few decades. A very low DO concentration was observed in water columns in the upper reaches of the PRE, or upstream of the Humen Outlet, which have been attributed to organic matter respiration and nitrification (Dai et al., 2006, 2008a; He et al., 2010b). However, the origin of organic matter in supporting microbial respiration has not yet been characterized. Neither have the relative contributions of microbial respiration and nitrification to the oxygen consumption been well quantified. This problem is significant because it is essential in guiding environment management policies. In this study, we synthesized observations from 2000 to 2008 based on multiple cruises in order to further define the oxygen depletion zone and to examine the seasonal and interannual variations in DO conditions in the upper reaches of the PRE. Multiple physical and hydrochemical parameters were simultaneously determined to evaluate the effects of the alterations in physical conditions, nutrient and organic carbon loads on hypoxic conditions. On-deck oxygen metabolic incubations were carried out to further elucidate the mechanisms controlling oxygen depletion. Finally, a mass balance model was adopted to quantify the relative contribution of individual processes to the formation and the maintenance of this oxygen depletion zone, and to evaluate the role of allochthonous versus autochthonous organic matter in supporting microbial respiration throughout the hypoxic region.

## 2. Materials and methods

### 2.1. Study area

The Pearl River is one of the world's 20 largest rivers, with an annual river discharge of ~330 × $10^8$ $m^3$, 80% of which is delivered during the wet season from April to September. The PRE consists of three sub-estuaries, namely Modaomen, Huangmaohai and Lingdingyang Bay. Among them, Lingdingyang Bay (traditionally regarded as the PRE) is the largest, and receives ~53% of the river runoff via the northern four outlets, i.e. Humen, Jiaomen, Hengmen, and Hongqimen (Dai et al., 2014 and references therein).

Our study focused on the upper reaches of the PRE; the upstream of Lingdingyang Bay, stretching from the Humen Outlet upward to the suburbs of Guangzhou with a total length of ~75 km; and four segments, the Guangzhou, Huangpu, Shiziyang and Humen Channels (Fig. 1). The Guangzhou Channel is ~32 km long with an average width of ~525 m and an average depth of ~5.0 m (Guangzhou Record, http://www.gzsdfz.org.cn). It runs across the city of Guangzhou, the most urbanized and heavily impacted district in southern China, with ~12.7 million inhabitants (http://www.gzatats.gov.cn/rkpc/) and numerous industrial and agricultural settings. The Huangpu to Humen Channel is ~45 km long with an average width of ~2.2 km and an average water depth of ~6.6 m (http://www.gzsdfz.org.cn). It receives inflows from the Guangzhou Channel and the East River, and two cities, Panyu and Dongguan, are in the area, where agriculture and countryside industry are well developed and, thereby, the anthropogenic loads have dramatically increased in the last few decades (Table 1). As a consequence of high organic carbon and nutrient loads, the aquatic environments of the upper reaches of the PRE have deteriorated in recent years. A serious year-round oxygen depletion in the water column is noted in this area (Dai et al., 2006, 2008a; Zhai et al., 2005).

### 2.2. Data sources and new observations

This study synthesized the historical data from July 2000, May–June 2001, November 2002, February 2004, January 2005, August 2005, March 2006, and the new observations in April 2007, and August 2008. The major parameters observed and the detailed data sources are shown in Table 2. These cruises covered four seasons, representing the cold and dry season with low water flow, the warm and flood season with high water flow and the transitional seasons with medium flow.

Sampling was carried out on board R/V Yanping II during 2000–2004, and on another vessel, the Yue Dongguang 00589, during 2005–2008. Underway pumping was performed for continuous measurements of temperature, salinity and DO. The details of our underway pumping system were described previously (Dai et al., 2006, 2009; Zhai et al., 2005; Guo et al., 2009). Discrete underway sampling was also conducted for salinity and DO measurements using this system guided by the salinity gradient within the estuarine mixing zone and by distance where no significant salinity gradient occurred upstream of the Humen Outlet. Surface samples for nitrogenous nutrients ($NH_4^+$, $NO_2^-$, $NO_3^-$) and dissolved organic carbon (DOC) were collected with another pumping system equipped with a FloJet® pump and an on-line acid-cleaned cartridge filter (He et al., 2010b).

In addition to the surface water sampling, water column samples for DO, DOC, particulate organic carbon (POC), total suspended matter (TSM), chlorophyll a (Chl-a), $NH_4^+$, $NO_2^-$, and $NO_3^-$ were collected using a SEACAT CTD (SBE19 Sea-Bird Co.) rosette system equipped with Niskin or Go-Flo bottles. Sub-samples for DOC, POC, Chl-a, TSM and nutrients are collected following the procedures described previously (Dai et al., 2006; He et al., 2010b).

At selected stations, we used incubations to determine the $O_2$ production from the primary production, and $O_2$ consumption from microbial respiration and nitrification. These stations are numbered in Fig. 1.

### 2.3. Analysis

#### 2.3.1. Underway measurements of surface temperature, salinity, DO and meteorological data

Temperature and salinity (conductivity) of the surface water were continuously measured using a SEACAT thermosalinograph system (CTD; SBE21, Sea-Bird Co.) for the first two cruises, and using a Yellow Spring Instrument multi-parameter meter (YSI® 6600) for the other cruises (see details in Dai et al., 2006; Zhai et al., 2005). Surface water DO was monitored continuously using a pre-calibrated DO probe assembled on the YSI® equipped to an underway pumping system (Zhai et al., 2005). Our CTD sensors were calibrated at the National Center of Ocean Standards and Metrology of China every year. Temperature and salinity probes of YSI were calibrated with CTD sensors just prior to the cruises. The DO probe of YSI was calibrated against water saturated air. Winkler DO samples including different levels of DO were occasionally taken for ground truth of the probe data. Meteorological data including wind speed were collected with an onboard weather station set at ~10 m above the sea surface.

#### 2.3.2. DO, Chl-a, nutrients, TSM, POC and DOC of the discrete samples

The DO concentration in discrete samples was determined on board following the classic Winkler procedure. A small quantity of $NaN_3$ was added during subsample fixation to remove possible interference from nitrites (Wong, 2012). Based on replicated measurements of the $NaS_2O_3$ titration reagent concentration, the uncertainty of our DO data was estimated to be at a satisfactory level of <0.5%. The DO saturation (DO%) was calculated from the field-measured DO concentration

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