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Influence of seasonal monsoons on net primary production and CO_2 in subtropical Hong Kong coastal waters

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Abstract

Data from seven cruises in three different environments including the Pearl River estuary, sewage discharge outfall and eastern coastal/shelf waters, were used to examine the seasonal variations in net primary production (NPP) and the biologically active gases O_2 and CO_2. In the winter dry season, when monsoon-induced downwelling was dominant, NPP was low ($-60\pm50\,\mathrm{mmol\,C\,m^{-2}\,d^{-1}}$) in all three regions. The negative NPP corresponded to low O_2 influxes ($-100\pm50\,\mathrm{mmol\,O_2\,m^{-2}\,d^{-1}}$) and CO_2 effluxes ($24\pm10\,\mathrm{mmol\,C\,m^{-2}\,d^{-1}}$). In the summer wet season, when upwelling brought the bottom oceanic waters to the nearshore due to the southwest monsoonal wind, there was a 2 to 15-fold increase in integrated primary production (IPP) compared to winter. The increase in IPP was likely due to the favorable conditions such as stratification and the nutrient inputs from upwelled waters and the Pearl River estuary. NPP reached up to $240\pm100\,\mathrm{mmol\,C\,m^{-2}\,d^{-1}}$ in the wet season. However, accompanying the high positive NPP, we observed an influx of O_2 ($-100\pm60\,\mathrm{mmol\,O_2\,m^{-2}\,d^{-1}}$) and efflux of CO_2 ($25\pm15\,\mathrm{mmol\,C\,m^{-2}\,d^{-1}}$). The high positive NPP corresponding to a CO_2 source and O_2 sink could be explained by the influence of the southwest monsoon-induced upwelling, as the upwelling brought cold, low DO ($160\pm30\,\mu\mathrm{M}$) and high DIC ($1960\pm100\,\mu\mathrm{atm}$) water to the surface in the wet season. Hence, the subtropical Hong Kong coastal waters are generally a CO_2 source due to the monsoonal influence in both the dry and wet seasons.

1 Introduction

Urbanization and anthropogenic nutrients are known to result in eutrophication in many estuarine and coastal waters (Diaz and Rosenberg, 2008). The nutrient and organic matter inputs from riverine outflow and domestic sewage effluent have increased the occurrences of hypoxia or anoxia as well as high CO_2 release in many estuarine and coastal waters (Ducklow and McCallister, 2004; Diaz and Rosenberg, 2008; Borges et al., 2006).

Substantial attention has been paid to eutrophication impacts on biological activities (e.g. phytoplankton and bacteria), oxygen and CO_2 in temperate coastal and estuarine systems (Shiah and Ducklow, 1994; Borges et al., 2006), while subtropical coasts were less investigated. Many subtropical coastal waters are subjected to seasonal monsoons: northeast monsoonal winds in winter and the southwest monsoon in spring and summer, which considerably influenced biogeochemical cycling (Goyet et al., 1998; Mintrop et al., 1999; Yin, 2002, 2003). For examples, in the Arabian Sea and Northwestern Indian Ocean, seasonal variations in primary production and CO_2 release were closely associated with the influences of monsoon (Goyet et al., 1998; Mintrop et al., 1999). Similarly, the subtropical coastal waters adjacent to the Pearl River estuary were also reported to be influenced by the seasonal monsoon. As a result of monsoonal effects, there are marked seasonal and temporal variations in nutrients and phytoplankton biomass in the coastal waters adjacent to the Pearl River estuary (Yin, 2002, 2003).

Hong Kong subtropical waters are located on the southern coast of China, facing the northwestern part of the South China Sea (SCS) and lying to the southeast of the Pearl River estuary (PRE). Hence, this region is an interface where the Pearl River estuary, sewage discharge outfall and oceanic water meet and interact, and consequently a potential zone for transferring high amounts of terrestrial carbon to the atmosphere and/or deeper ocean in the South China Sea. Coupling with the monsoonal influence, the seasonal freshwater discharge from the Pearl River estuary further complicates the hydrodynamics and biochemical processes. Previous studies suggested that the anthropogenic inputs of nutrients and organic matter in the Pearl River estuary have led to a decrease in oxygen and increase in CO_2, especially in the upper estuary (Yin et al., 2004; Cai et al., 2004, Dai et al., 2006). Hong Kong coastal waters have also been reported to be generally a CO_2 source due to the influence of the Pearl River

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discharge and sewage effluent (Yuan et al., 2010). However, little is known about the seasonal variations in O_2 and CO_2 in responses to monsoonal winds.

In this study, several contrasting environments were studied: (1) western waters close to the Pearl River estuary (PRE); (2) Victoria Harbor (VH)– near a local sewage discharge outfall; and 3) eastern coastal/shelf waters – relatively far away from terrestrial or anthropogenic influences. By examining the air-sea fluxes of O_2 and CO_2, primary production and dark community respiration (DCR) in seven cruises, we examined: (1) the influence of the Pearl River estuary and sewage discharge on O_2 and CO_2 dynamics; (2) the seasonal variations in biological metabolism (e.g. primary production and respiration), and (3) air-sea fluxes of O_2 and CO_2 in response to monsoonal winds.

2 Materials and methods

2.1 Study area and sampling

The annual average Pearl River discharge is 10 524 $m^3\,s^{-1}$, with 20% occurring during the dry season in October to March and 80% during the wet season in April-September (Zhao, 1990), which carries heavy pollution and high nutrient inputs into the western Hong Kong waters (Cai et al., 2004; Yin et al., 2004). In addition, Hong Kong waters receive >2 million tons of sewage effluent daily from the local sewage discharge in Victoria Harbor (VH).

During 2005 and 2006, sampling was conducted at 8 stations (Fig. 1) at the surface (1 m), middle (4 m) and bottom (2 m above the bottom) in four seasons: winter (March in 2006), spring (April in 2006), summer (June in 2005 and July in 2005–2006) and fall (November in 2005 and 2006). Based on nutrient sources and salinity, the 8 stations represent three main regions: western waters (S1–S2) which are close to the Pearl River estuary; Victoria Harbour (S3–S6) which is close to the sewage discharge outfall sites; and eastern coastal/shelf waters (S7–S8). Water samples were taken using a custom-made 5-L Plexiglas sampler. The vertical profiles of salinity and temperature were measured with a YSI®6600 sensor. Monthly data on salinity, temperature, primary production, dark community respiration, DO, DIC and $p\mathrm{CO}_2$ are found in Ho (2007) and Yuan et al. (2010).

2.2 DO, dark community respiration (DCR) and primary production

Dissolved oxygen (duplicate) was determined by the Winkler titration, as outlined in the JGOFS protocols (Knap et al., 1994). After 4 to 5 volumes of water were allowed to overflow from the 60 ml BOD bottles, Winkler reagents were added. Winkler titrations were carried out in the laboratory with an automated titration apparatus (716 DMS Titrino, Metrohm®) that analyzed the samples with a potentiometric detector to determine the endpoint.

DCR (duplicate) was determined from the changes in dissolved oxygen in BOD bottles (60 ml) during a 24-h dark incubation period. The linearity of DO decrease over 24 h was verified in a separate time series experiment (Yuan et al., unpublished data). Samples were incubated in a water circulation tank simulating in situ temperature (±1 °C). For DCR, the average variation coefficient was 7±5%, which was considered to be precise enough to measure respiration in coastal waters, although 5 replicates for respiration measurements have been recommended for oceanic waters where respiration is often $<3\,\mu\mathrm{M\,d^{-1}}$ (Robinson et al., 2002).

Seawater samples for the primary production measurements were pre-screened through a 200-µm mesh, and then a 50 ml sample was transferred to acid-washed glass tubes to which 0.4–2 µCi (14.8–74 kBq) of ^{14}C-labelled sodium bicarbonate ($\mathrm{NaH^{14}CO_3}$) was added (see details in Ho et al., 2010). Duplicate tubes were wrapped with different layers of screening providing light fields corresponding to approximately 100, 55, 30, 10, and 1% of surface irradiance. Samples were incubated for 4 h between 10:00 to 14:00 on-deck in running surface seawater. The incubation was terminated after 4 h by filtering sequentially through a GF/F filter (i.e., 0.7 µm size fraction). Filters were put into a scintillation vial, and HCl (0.25 ml, 0.1 N) was added to the scintillation

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vials to remove the inorganic $NaH^{14}CO_3$. Counting was carried out using a liquid scintillation counter (LKB Rack Beta). Net primary production (NPP) was calculated by primary production minus dark community respiration. The integrated primary production (IPP), dark community respiration (IDCR) and NPP was calculated by averaging the measured production between two depths and multiplying by the depth interval (Ichimura et al., 1980). Carbon and O_2 units were converted into each other by using the classic Redfield ratio of 106:138.

2.3 DIC and $p\mathrm{CO_2}$

Water samples (50 ml) were preserved with saturated $HgCl_2$ (20 µl) for DIC analysis and stored in a cooled dark chamber at 4 °C. DIC was measured within 1 week by acidification and subsequent quantification of CO_2 with an Infra-red (IR) detector (Li-Cor 6252) using a DIC analyzer (AS-C2, Apollo SciTech). This method has a precision of 0.1 to 0.2% in coastal water (Cai and Wang, 1998). DIC was calibrated against Certified Reference Material from A. Dickson, Scripps Institution of Oceanography, and a duplicate analysis was made every tenth sample (Dickson and Goyet, 1994). pH was measured with an Orion Ross combination glass electrode that was calibrated against three NBS standards (Dickson and Goyet, 1994). Precision of pH measurements was ∼0.01. $p\mathrm{CO_2}$ was calculated from measured pH values and DIC concentration for estuarine and coastal waters (Cai and Wang, 1998). In order to remove the temperature effect, $p\mathrm{CO_2}$ was normalized to an annual average temperature, using the equation of Takahashi et al. (2002):

$$p\mathrm{CO}_{2\ \mathrm{mean\ SST}} = p\mathrm{CO}_{2\ \mathrm{in-situ\ SST}} \exp\left[0.0423\,(\mathrm{mean\ SST} - \mathrm{in-situ\ SST})\right] \tag{1}$$

where the mean SST is the mean value of the area-averaged sea surface temperature in all of the sampling months.

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2.4 Air-sea fluxes of CO_2 and O_2

The CO_2 and O_2 fluxes across the air-sea interface are calculated by following the one-dimensional stagnant-film model:

$$CO_2 \text{ flux} = k_{CO2} \quad \beta(pCO_{2w} - pCO_{2a}) \tag{2}$$

$$O_2 \text{ flux} = k_{O2} \left([O_2] - [O_2]_S\right) \tag{3}$$

where k_{CO2} and k_{O2} are the gas transfer velocities for CO_2 and O_2, respectively; β (Bunsen coefficient) is the solubility of CO_2 at a given temperature and salinity; pCO_{2w} and pCO_{2a} represent the partial pressure of CO_2 in surface water and overlying air, respectively. $[O_2]$ and $[O_2]_S$ represent the measured concentrations and estimated solubility, respectively. The gas transfer velocity (k) was empirically estimated from the surface wind speed at 10 m (Wanninkhof, 1992), which was obtained from the Hong Kong observatory (http://www.weather.gov.hk/contente.htm). The atmospheric pCO_2 was ∼370 µatm in the northern South China Sea (Zhai et al., 2005).

2.5 Statistical analyses

The significance of difference (e.g. seasonal and spatial variations in DO and CO_2) was assessed using an analysis of variance followed by a means comparison (t-test). The error bars for the bioassay represent a pooled sample standard deviation of the means. The Pearson test was used to obtain the correlation coefficient and the significance of the correlation. A significance level of 0.05 was used to determine statistical differences. All statistical analyses were performed using SPSS statistical software (SPSS Inc.).

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3 Results

3.1 Seasonal variations in salinity and temperature

Surface salinity exhibited a clear seasonal variation due to the seasonal freshwater discharge from the Pearl River. Surface salinity was high (∼33) in the dry season (October to March) in all three regions, and reached a minimum (15–31) in summer (Figs. 2 and 3). Spatially, surface salinity was not significantly different between the regions in the winter dry season (p >0.05), but increased from ∼15 near the Pearl River estuary to ∼31 in eastern coastal/shelf waters in the spring and summer wet season indicating a strong influence of freshwater discharge from the Pearl River estuary ($p<0.05$) (Figs. 2 and 3). Surface temperature also varied seasonally from ∼18 °C in the dry season to ∼27 °C in the wet season at all stations (Figs. 2 and 3).

Vertically, salinity at the surface and bottom were not significantly different in the winter dry season indicating a strong vertical mixing ($p>0.05$), while strong stratification was present in the summer wet season (Fig. 3). In the summer wet season, the stratified depths decreased from 10 m near the Pearl River estuary to ∼4 m in the eastern waters (Fig. 3), suggesting strong upwelling effects and less influence of freshwater discharge in the eastern coastal/shelf waters.

3.2 DO, DIC and air-sea fluxes of O_2 and CO_2

There were no significant seasonal variations in surface DO concentrations in all regions ($p>0.05$) (Fig. 4a). Lower surface DO concentrations (180–220 µM) were usually found in Victoria Harbour near the sewage discharge outfall (Fig. 4a). In contrast, bottom DO concentrations exhibited a clear seasonal variation, which decreased from 210–230 µM in the dry season to 150–210 µM in the summer wet season ($p<0.05$) (Fig. 3).

Surface water oxygen was generally undersaturated and thus there was an O_2 influx from the atmosphere in all regions (Fig. 4b). Influx of O_2 exhibited no significant difference between the wet and dry season (p>0.05), but it was spatially variable with the low influx in eastern coastal/shelf waters (−14±90 mmol O_2 m^{-2} d^{-1}) and high in Victoria Harbour (−100±120 mmol O_2 m^{-2} d^{-1}) (Fig. 4b).

Similar to salinity, DIC concentrations were vertically homogenous in the dry season, while became stratified in the wet season (Fig. 3). Surface pCO_2 exhibited a seasonal variation near the Pearl River estuary, with higher pCO_2 in the spring and summer wet season (800±100) than in the dry season (500±90 µatm) (p<0.05) (Fig. 4c). However, pCO_2 did not exhibit significant seasonal variations in the other two regions (p>0.05) (Fig. 4). Air-sea effluxes of CO_2 were higher near the Pearl River estuary and Victoria Harbour (30±20 mmol C m^{-2} d^{-1}) and decreased to 10±5 mmol C m^{-2} d^{-1} in eastern coastal/ shelf waters (Fig. 4d) (p<0.05).

There was a significant correlation between air-sea fluxes of CO_2 and O_2 (p<0.05) (Fig. 5). The slope (0.17) indicated that the flux speed of CO_2 was ∼6-fold slower than O_2. In addition, the flux direction of CO_2 usually was opposite to O_2, but they were episodically in the same direction (see data in the rectangular box) (Fig. 5). Overall, the dataset mainly concentrated on the first quadrant of CO_2 degassing and O_2 ingassing.

3.3 Primary production and dark community respiration

The integrated primary production (IPP) also exhibited seasonal and spatial variations. A seasonal comparison revealed that IPP was the lowest (50–200 mmol C m^{-2} d^{-1}) in winter, moderate (70–300 mmol C m^{-2} d^{-1}) in spring and fall, and the highest (up to 1500 mmol C m^{-2} d^{-1}) in summer (Fig. 6a). In summer, IPP was 2 to 15-fold higher in eastern costal/shelf waters (approximately 250–300 mmol C m^{-2} d^{-1}), compared to other regions (Fig. 6a). IPP was relatively low (<300 mmol C m^{-2} d^{-1}) near the Pearl River estuary in both the wet and dry seasons (Fig. 6a). In contrast, IDCR was not as seasonally variable as IPP, since the maximum increase in IDCR was only 3-fold in summer wet season in comparison with the dry season (Fig. 6b).

In parallel with IPP, net primary production (NPP) was lower (-60 ± 50 mmol C m^{-2} d^{-1}) in winter than summer (240 ± 100 mmol C m^{-2} d^{-1}) in Hong Kong waters ($p<0.05$) (Fig. 7). In general, NPP was positive in the wet season, while negative in the dry season (Fig. 6b), indicating that Hong Kong waters shifted from autotrophy in the wet season to heterotrophy in the dry season.

4 Discussion

4.1 The influence of the Pearl River discharge and sewage effluent

Hong Kong waters are influenced by the summer Pearl River discharge in the west, and year-round domestic sewage effluent in the Victoria Harbour area. Hence, these two regions receive large amounts of inorganic nutrients as well as terrestrial organic matter from the Pearl River and sewage discharge. Previous studies have reported that there was a significant increase in NO_3 and SiO_4 concentrations (up to 17–56 and 18–40 µM, respectively) due to the freshwater discharge near the Pearl River estuary (PRE) (Ho et al., 2008), while continuous year round discharge of sewage efluent resulted in high NH_4 (7 to 20 µM) and PO_4 (and 0.7 to 1.4 µM) in Victoria Harbour (VH) and its vicinity (Ho et al., 2008). DOC also increased to 200 µM in Victoria Harbour in both the dry and wet seasons (Yuan et al., unpublished data). Hence, the increase in inorganic nutrients and organic carbon not only increased primary production in summer (Ho et al., 2010), but also produced an increase in bacterial production (BP) and respiration (BR) (Yuan et al., 2010). Our results showed that the eutrophication increased primary production more than bacterial respiration and resulted in a positive NPP in Victoria Harbor and eastern waters in the wet season, except for near the Pearl River estuary in summer (Fig. 6). Figure 4 showed that surface pCO_2 and air-sea fluxes of CO_2 were higher near the Pearl River estuary and in Victoria Harbor than eastern waters in all seasons ($p<0.05$), indicating that the Pearl River estuary and sewage effluent increased pCO_2 (Yuan et al., 2010).

However, the high freshwater input from the Pearl River discharge in western waters also increased the horizontal flushing and reduced the water residence time, as the annual average freshwater discharge from the Pearl River is 10 524 $m^3 s^{-1}$, with 80% occurring during the wet season in April–September (Zhao, 1990; Yin, 2002). The residence time is much shorter (~1.5 to 2.5 days) in the wet season, and hence there is strong horizontal advection (Kuang and Lee, 2004). Therefore, abnormally low or high oxygen waters caused by high phytoplankton production or bacterial respiration could be replaced quickly by a water mass from the Pearl River estuary and bottom oceanic waters due to the short residence time. Harrison et al. (2008) concluded that there is no massive hypoxia in the lower Pearl River estuary due to a short residence time of the seawater. Hence, the dissolved oxygen (DO) remained >150 µM and $p\mathrm{CO_2}$<1200 µatm near the Pearl River estuary, and the eutrophication impact in Hong Kong waters was not as severe as expected for such a eutrophic area in the wet season (Ho et al., 2008; Yuan et al., 2010).

4.2 O_2 and CO_2 in relation to heterotrophy

An important question concerning estuarine ecosystem functionality is whether it is autotrophic or heterotrophic. Sea surface CO_2 uptake or release is also often taken as an indicator of net autotrophy or heterotrophy (or net biologically metabolic balance) in marine systems. In addition, the variability in DO is also indicative of ecosystem metabolism. For example, the percent oxygen saturation (or air-sea influxes) can be used to infer respiration by planktonic organisms in the ocean by assuming that surface oxygen concentration is close to saturation with the overlying atmosphere (Ito et al., 2004).

However, our results indicated that O_2 influxes and CO_2 effluxes might not always be a good indicator of heterotrophy or autotrophy (i.e. production vs. respiration) in the Hong Kong coastal waters, since O_2 and CO_2 concentrations are regulated not only by biological processes, but also by strong physical factors such as water mass mixing, salinity, temperature, and air-sea exchange (Emerson et al., 1987; Chen, 2010). The

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relative contribution of each factor has been a widely debated topic and is probably variable in different regions.

In our study, high positive NPP corresponded to a CO_2 source in the spring and summer wet season, which seems to be a paradox if the physical regulations were not considered. In addition, our data showed that air-sea fluxes of O_2 and CO_2 were generally in the opposite direction suggesting a biological control (e.g. phytoplankton photosynthesis and bacterial respiration) (Fig. 4b and d), although air-sea fluxes were in the same direction episodically in 8% of total dataset (Fig. 5). The negative correlation between O_2 and CO_2 fluxes was also due to the relatively strong biological control ($p<0.05$) (Fig. 5). Furthermore, the correlation coefficient between O_2 and CO_2 fluxes is equal to 0.4 (Fig. 5), which may statistically suggest that the biological control contributed to only 40% of the variations in O_2 and CO_2 fluxes. Therefore, although the biological control considerably affected O_2 and CO_2 fluxes, other processes (e.g. physical mixing) should also be taken into account.

4.3 Monsoonal influences

We now offer an explanation for the apparently inconsistent observations of positive NPP and the ingassing of O_2 and degassing of CO_2. We suggest that a more important regulating factor of O_2 and CO_2 fluxes is the physical mixing such as downwelling and upwelling due to seasonal monsoons. The responses of O_2 and CO_2 fluxes to the seasonal monsoons have not been addressed in previous studies, although the strong seasonal changes in salinity, temperature, chl *a* and nutrients have been reported to be closely coupled with seasonal monsoons (Yin, 2002, 2003).

In the winter dry season, prevailing northeastern monsoonal winds cause downwelling due to the Coriolis effect, and the downwelling results in the shoreward movement of surface offshore waters (Yin, 2002, 2003). Hence the Pearl River estuary and the adjacent coastal waters are dominated by offshore waters, which results in low temperature, nutrients, chl *a* and high salinity (Yin, 2002, 2003). In the summer wet season, surface waters flow offshore (southwards) due to the southwest

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monsoon-induced winds which draw the bottom oceanic waters from the continental shelf to the nearshore, and hence high salinity and low temperature were present at the bottom (Fig. 3). The shallow and weakly stratified depths (~4 m) in eastern coastal/shelf waters were also likely due to the strong upwelling (Fig. 3).

Similarly, monsoonal influence and the freshwater discharge from the Pearl River estuary also exerted important influences on net primary production (NPP). As described in the conceptual carbon transport model (Fig. 7), cold offshore water moves shoreward with high DIC and moderate DO in the winter dry season. Light availability was reduced due to strong vertical mixing (Ho et al., 2010), which resulted in a low NPP (-60 ± 50 mmol C m^{-2} d^{-1}) in all three areas (Fig. 7). Correspondingly, O_2 influxes and CO_2 effluxes were also low (-100 ± 50 mmol O_2 m^{-2} d^{-1} and 24 ± 10 mmol C m^{-2} d^{-1}, respectively) due to the dominance of offshore waters at both the surface and bottom (Fig. 4). In the spring and summer wet season, the freshwater input increased nutrient availability and resulted in stratification at the surface (Yin, 2002, 2003). Coupling with high nutrient inputs from the Pearl River estuary and the upwelling, IPP increased by 2 to 15-fold in summer in comparison with winter (Fig. 6). However, the high IPP and NPP did not reverse the air-sea exchange directions of O_2 and CO_2 (Figs. 4 and 7). There was not enough time for the positive NPP to reverse the directions of O_2 and CO_2 fluxes, since the water residence time was only ~2 days during summertime (Kuang and Lee, 2004). In addition, the low DO (160 ± 30 µM) and high DIC (1960 ± 100 µatm) upwelled waters would offset an increase in DO and decrease in CO_2 by the high phytoplankton photosynthesis (Figs. 3 and 7). Therefore, surface DO, pCO_2 and their air-sea fluxes fluctuated with much less seasonality, compared to salinity, temperature and IPP ($p<0.05$) (Figs. 2, 4 and 6).

In previous studies, the effect of mixing on DO and DIC mass balance has seldom been investigated. In order to quantify the contributions of the physical mixing, we conducted a mass balance analysis of DIC. The DIC and DO concentrations reflect a balance between the influence of mixing of the Pearl River estuary, sewage discharge and the coastal waters, degassing to the atmosphere and net internal regeneration

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(i.e., water column and benthic respiration versus primary production). The change in the DIC concentrations is given in Eq. (4) (revised from Cai et al., 2003):

$$\frac{d\mathrm{DIC}}{\mathrm{d}t} = \left(\sum \mathrm{DIC}_{\mathrm{input}} - \sum \mathrm{DIC}_{\mathrm{outport}}\right)_{\mathrm{mixing}} - F_{\mathrm{air-sea}} + (R - P) \tag{4}$$

where $\mathrm{DIC}_{\mathrm{input}}$ is oxygen input; $\mathrm{DIC}_{\mathrm{output}}$ is DIC export due to mixing; $F_{\mathrm{air-sea}}$ is air-sea CO_2 exchange; R is the total ecosystem respiration; P is the gross primary production. Thus, the mixing contribution to the variations in surface DIC is: $\mathrm{DIC}_{(\mathrm{mixing})}=\mathrm{DIC}_{(\mathrm{pelagic\ NPP})}+\mathrm{DIC}_{(\mathrm{air-sea\ fluxes})}+\mathrm{DIC}_{(\mathrm{benthic\ respiration})}$. Benthic respiration has been estimated to be 13 to 40 mmol C m^{-2} d^{-1} in Hong Kong coastal waters (Hu et al., 2001), and hence benthic respiration was only equal to 3 to 20% of pelagic integrated dark community respiration (IDCR). As pelagic net primary production (NPP) and air-sea fluxes have been measured in this study, the estimates of the mixing contribution to DIC variations are presented in Fig. 6d. The mixing contribution to DIC was seasonally variable, which was positive (20 to 110 mmol C m^{-2} d^{-1}) in winter and generally negative in summer (−930 to 198 mmol C m^{-2} d^{-1}) (Fig. 6d). On the other hand, although the air-sea gas exchange of O_2 was ∼6-fold faster than CO_2, the mixing contribution to O_2 was estimated to be in the same magnitude by using the same calculation as for DIC mass balance, which varied from −20 to 160 mmol O_2 m^{-2} d^{-1} in the dry season to −920 to 130 mmol O_2 m^{-2} d^{-1} in the wet season (data not shown). Overall, the mixing contribution to DIC in Hong Kong waters was 49 mmol C m^{-2} d^{-1} in the dry season and −230 mmol C m^{-2} d^{-1} in the wet season (Fig. 7). The negative mixing contribution to CO_2 in the wet season suggested that bottom offshore waters increased DIC concentrations due to upwelling in Hong Kong waters (Fig. 7). Hence, high phytoplankton photosynthesis (or high NPP) would significantly decrease DIC concentrations by −230 mmol C m^{-2} d^{-1} in the wet season if no mixing occurred ($p<0.05$). However, due to the short water residence time (∼2 days) in summer (Kuang and Lee, 2004), 90% of the decrease in DIC due to NPP was offset by the high DIC inputs from the bottom offshore waters (Fig. 6d).

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4.4 Comparison with global coastal estimates and other upwelling coastal waters

Longhurst et al. (1995) have reported their estimate of global coastal net ecosystem production to be 32.1 mol C m^{-2} yr^{-1}, while Gattuso et al. (1998) estimated coastal gross primary production to be 17.4 mol C m^{-2} yr^{-1}. The annual NPP is 130 mol C m^{-2} yr^{-1} in Hong Kong waters, indicating a high net production capacity due to eutrophication. In contrast to the relative consensus on positive NPP, whether coastal waters are sinks or sources of atmospheric CO_2 is still very controversial as was suggested by Ducklow and McCallister (2004).

In terms of CO_2 (or O_2) sink and source, upwelling is a "double-edged sword." Some previous studies showed that upwelled nutrients indirectly decreased pCO_2 by providing a source of new nutrients for photosynthesis in the upwelling system off the Galician coast (Borges and Frankignoulle, 2002). In the northern South China Sea, Zhai et al. (2009) also observed that there was biological drawdown of pCO_2, which resulted in a CO_2 sink in coastal upwelling areas near Hainan Island in July 2004. However, some studies in the Arabian Sea suggested that CO_2 degasses into the atmosphere due to coastal upwelling, by bringing cold and CO_2-rich deep water to the surface, where NPP increases considerably during the southwest monsoon compared to northeast monsoon (Barber et al., 2001; Dickson et al., 2001; Goyet et al., 1998). Takahashi et al. (2002) even concluded that, because most of the upwelling occurs in low altitudes, these regions tend to be CO_2 source areas, whereas high latitudes are sink regions of CO_2 uptake. Therefore, the balance between biological draw down and physical release of CO_2 determined whether CO_2 was a source or sink in coastal upwelled waters. Our results were consistent with the scenario that intensive upwelling regions may be autotrophic and still release CO_2 to the atmosphere (Chen, 2010), due to the strong influence of upwelling in summer.

5 Conclusions

We present the first study to simultaneously estimate the biological and physical contributions to the O_2 and CO_2 in Hong Kong coastal waters. Coupled with the seasonal discharge of the Pearl River estuary, monsoons not only regulated the biological activities (e.g. net primary production), but also the dynamic variations in O_2 and CO_2 (Fig. 7). In the dry season, when strong vertical mixing resulted in light limitation due to the monsoon-induced downwelling, primary production (50–200 mmol C m^{-2} d^{-1}) was lower than community respiration (~200 mmol C m^{-2} d^{-1}). Hence, the heterotrophic status corresponded to low levels of O_2 influxes and CO_2 effluxes. In the wet season, southwest monsoon-induced upwelling brought cold, low DO and CO_2-rich deep water to the surface, which offset the DO increases and DIC decreases due to high positive net primary production (600–1000 mmol C m^{-2} d^{-1}). Hence, despite the seasonal shifts between heterotrophy and autotrophy, Hong Kong waters were a CO_2 source to the atmosphere. This study may have similar implications for other coastal areas of the South China Sea, which are also subject to the same physical forcing by seasonal monsoon winds.

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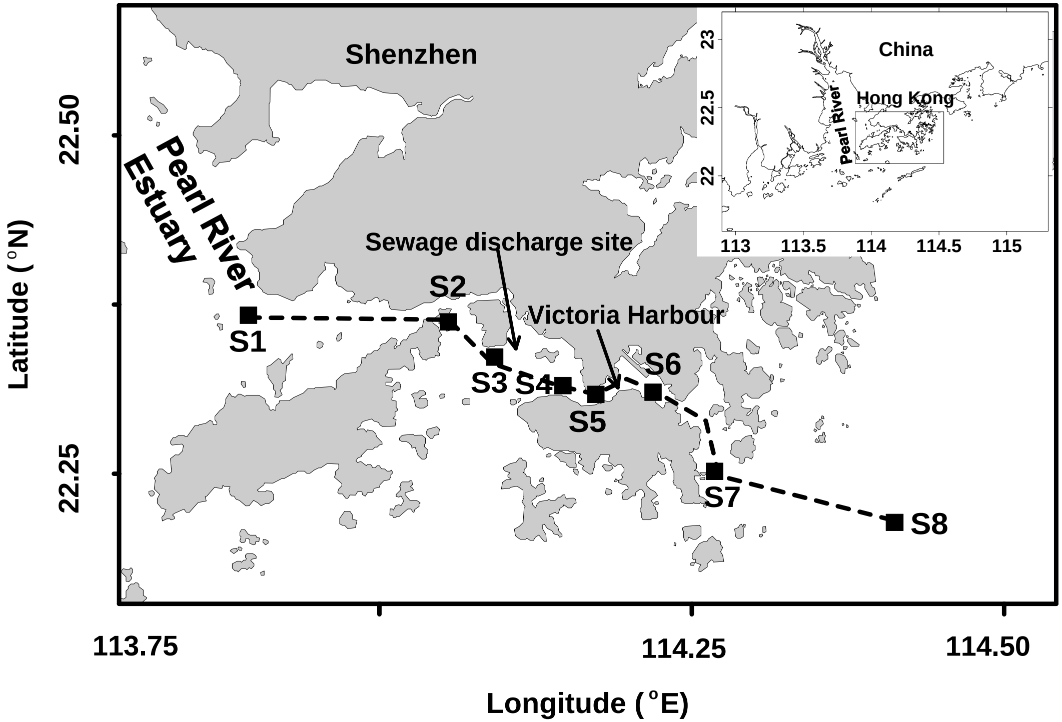

Fig. 1. Map and sampling stations along a transect from S1 near the Pearl River estuary to S8 in eastern coastal/shelf waters. The sewage discharge site is located between S3 and S4.

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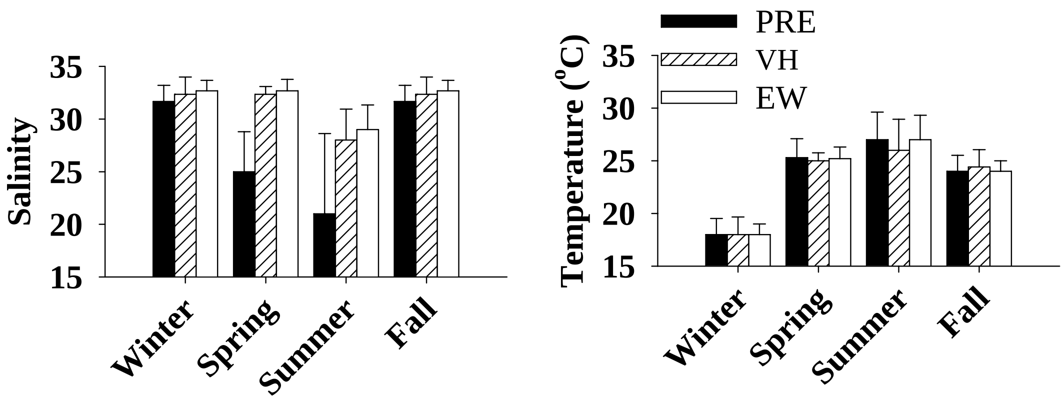

Fig. 2. Seasonal average surface salinity and temperature at S1 to S2 (PRE), S3 to S6 (VH) and S7 to S8 (EW) during 2005 and 2006. Salinity and temperature data are obtained from Hong Kong Environmental Protection Department. Error bars = ±1 SD and n=4 to 12.

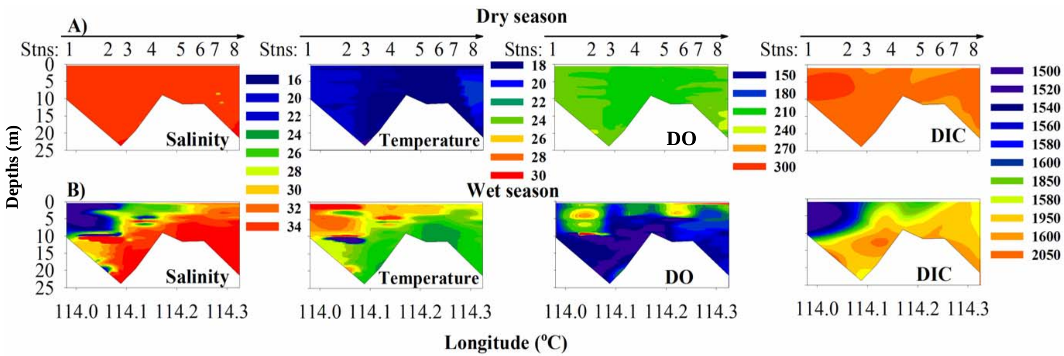

Fig. 3. Vertical contour of salinity, temperature (°C), dissolved oxygen (DO, µM) and dissolved inorganic carbon (DIC, µM) from S1 near the Pearl River estuary to S8 in eastern coastal/shelf waters in **(A)** the winter dry season (March 2006) and **(B)** the summer wet season (July 2006).

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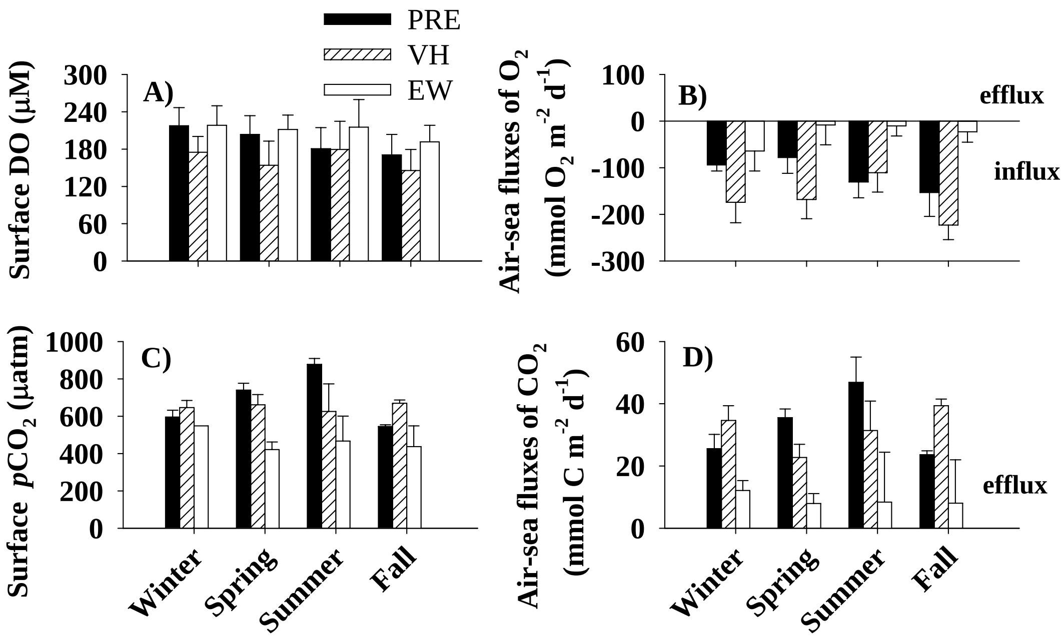

Fig. 4. Seasonal variations in **(A)** surface DO, **(B)** air-sea fluxes of O_2, **(C)** surface pCO_2 and **(D)** air-sea fluxes of CO_2 near the Pearl River estuary, sewage discharge outfall and eastern coastal/shelf waters during 2005 and 2006. Error bars = ±1 SD and n=4 to 12.

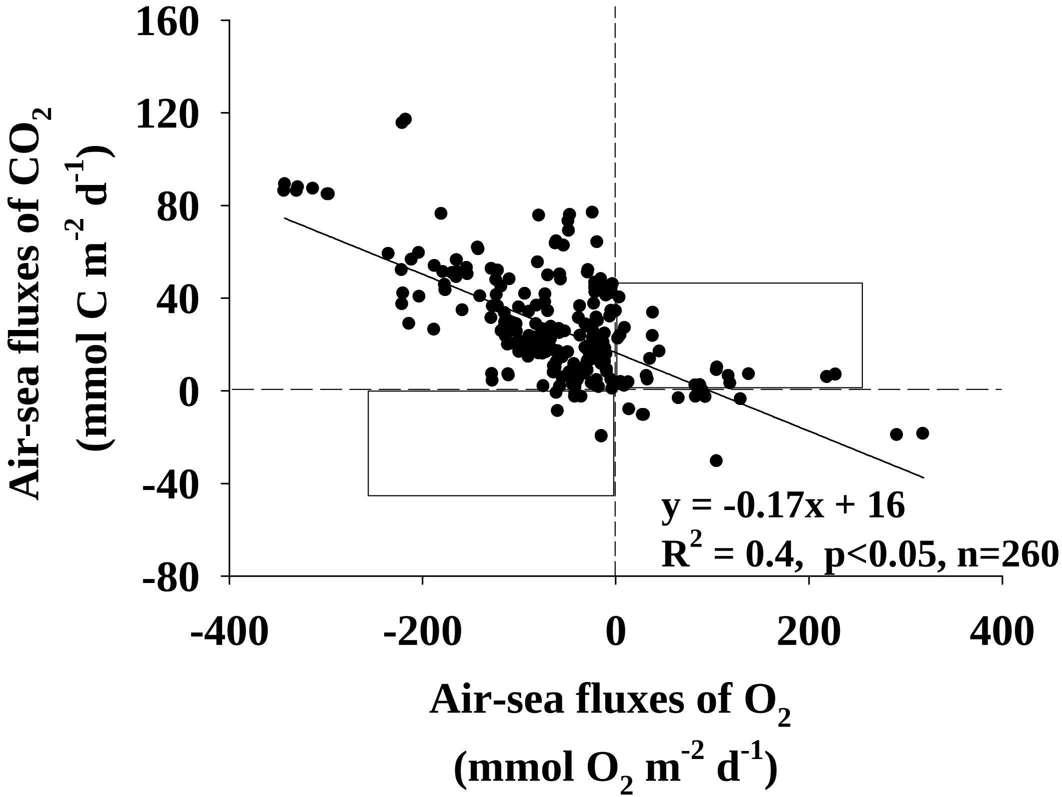

Fig. 5. Air-sea fluxes of O_2 versus CO_2 along the west to east transect at the surface between 2005–2006. The correlation coefficient (R^2) and significant value (p) are given.

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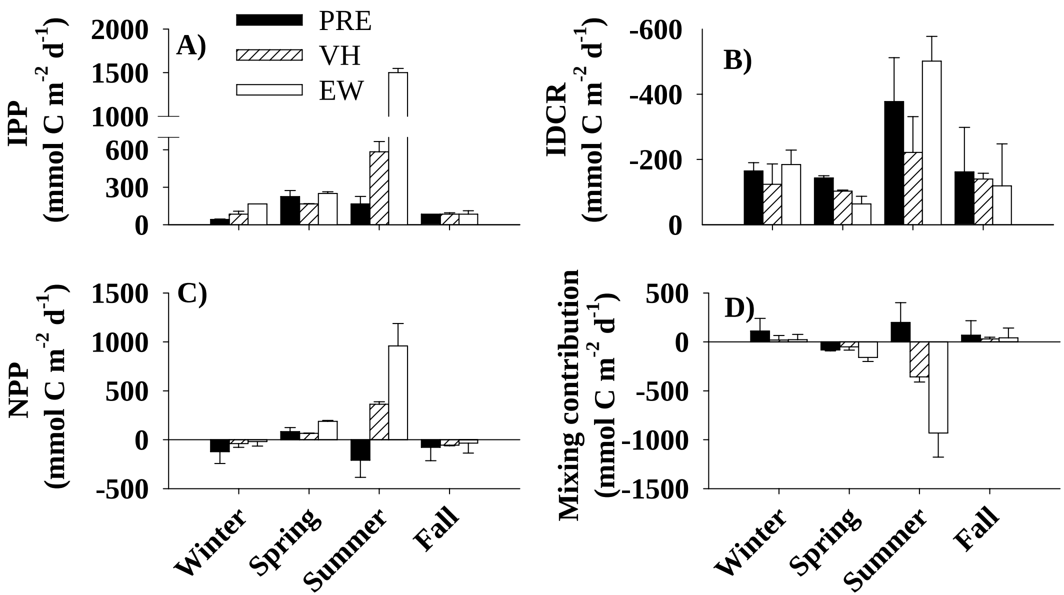

Fig. 6. Seasonal variations in **(A)** integrated primary production (IPP), **(B)** dark community respiration (DCR), **(C)** net primary production (NPP) and **(D)** mixing contribution to CO_2 in three regions during 2005 and 2006. IPP data were obtained from Ho et al. (2010). Error bars = ±1 SD and *n*=4 to 12.

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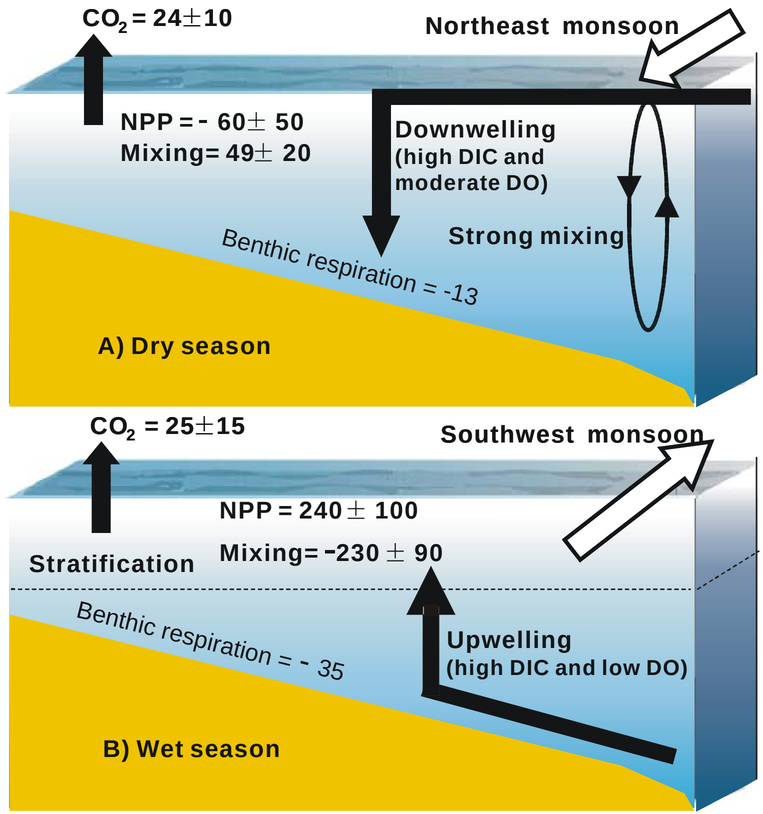

Fig. 7. A conceptual carbon transport model and a mass balance analysis in the **(A)** dry and **(B)** wet seasons. Units are in mmol C m^{-2} d^{-1}. Net primary production (NPP), CO_2 effluxes and the contributions of mixing (e.g. downwelling and upwelling) were estimated with overall average in the three regions (the PRE, VH and EW), respectively. Estimates of benthic respiration were based on Hu et al. (2001). Positive values represent CO_2 losses and negative values are CO_2 releases into water column. Error bars = ±1 SD and n=14 to 21.

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