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Distribution, degradation and dynamics of dissolved organic carbon and its major compound classes in the Pearl River estuary, China

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ABSTRACT

We investigated the distribution, degradation and dynamics of organic carbon and its major compound classes, carbohydrates and amino acids, based upon a cruise in the Pearl River estuary in April 2007. Dissolved oxygen (DO), nutrients, particulate organic carbon (POC), chlorophyll *a* (Chl a), dissolved organic carbon (DOC), total dissolved carbohydrates (TCHO, including monosaccharides, MCHO, and polysaccharides, PCHO) as well as total dissolved amino acids (TAA, both dissolved free, DFAA, and combined components, DCAA) were measured along a salinity gradient. Community respiration and biodegradable DOC were also determined via both short term (within 3 days) and long term (lasting 30 days) incubation. DOC, MCHO, TCHO, DFAA and TAA concentrations were high in the upper reach of the Pearl River estuary and decreased rapidly downstream. Anthropogenic sewage input appeared to be an important source of the DOC pool in the upper estuary. DOC distribution was non-conservative during the estuarine mixing, showing a net consumption of DOC in the upper reach and in the low salinity (S<20) region of the Pearl River estuary. Changes in the relative compositions of carbohydrates (MCHO vs. PCHO) and amino acids (DFAA vs. DCAA) along the salinity gradient further indicated that different processes (biodegradation, flocculation, and phytoplankton production) had different influences on distributions of organic compound classes in this estuarine system. Our one-month incubation experiment further revealed that a substantial portion (15–45%) of DOC from the estuary was biodegradable. Bacterial respiration rates were much higher (0.12–5.8 μmol O_2 L^{-1} h^{-1}) than the DOC consumption rates, suggesting that there were other oxygen consumption processes, such as nitrification besides the aerobic respiration of organic matter in the Pearl River estuary, as inferred by the distribution of NH_4^+ and NO_3^-. We estimated that 5.3×10^8 g C d^{-1} of DOC can be exported out from the Lingdingyang Bay (a major subestuary of the Pearl River estuary) to the continental shelf of the South China Sea during this low flow season.

1. Introduction

Terrestrial organic material transported by river runoff represents an important material source to the ocean. It is estimated that 0.4×10^{15} g yr^{-1} organic carbon is discharged to the ocean by the world rivers (Meybeck, 1982). This amount of riverine organic carbon is sufficient to support the entire organic carbon turnover in the ocean (Williams and Druffel, 1987). However, evidence from the carbon isotopic ratio ($\delta^{13}C$) of the bulk DOC in the ocean has shown little terrestrial signal (Druffel et al., 1992). It is therefore suggested that terrestrial organic carbon must undergo rapid removal and decomposition within the estuarine mixing (Hedges et al., 1997).

Biodegradation has long been recognized as an important process in the removal of riverine DOC in estuarine and coastal waters (Benner et al., 1995; Moran et al., 1999; Raymond and Bauer, 2001a). Many estuaries and coastal zones are considered to be net heterotrophic with respiration exceeding primary production (Gattuso et al., 1998; Gazeau et al., 2005; Smith and Hollibaugh, 1993), where the biologically reactive fraction of the riverine organic matter may be partially or completely mineralized (Moran et al., 1999; Raymond and Bauer, 2000, 2001a; Servais et al., 1987). While a net loss of riverine particulate organic carbon (POC) has now been reported in many estuaries worldwide (Abril et al., 2002; Keil et al., 1996; Servais and Garnier, 2006), DOC very often exhibits an apparent conservative mixing in the estuary (Hung and Huang, 2005; Laane, 1980; Mantoura and Woodward, 1983). At the same time, studies have shown that many rivers have "young" DOC (Guo and Macdonald, 2006; Raymond and Bauer, 2001b). This young DOC is partially derived from recently produced ^{14}C-enriched soil and litter-fall

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organic matter (Raymond and Bauer, 2001b) and/or in situ production of phytoplankton (Bianchi et al., 2004; Repeta et al., 2002). These young and presumably labile DOC compounds can be consumed in the time scale of estuarine mixing (Moran et al., 1999; Raymond and Bauer, 2001a; Servais et al., 1987). The apparent conservative behavior of DOC in estuaries is, therefore, often due to the existence of simultaneous sources and sinks that may appear with only small net changes in bulk concentrations (Cifuentes and Eldridge, 1998; McKenna, 2004; Raymond and Bauer, 2001a).

Carbohydrates and amino acids are, among others, the major components of identified organic matter in the ocean. Carbohydrates account for 3% to 30% of the bulk DOC (Gueuen et al., 2006; Hung et al., 2003; Pakulski and Benner, 1994), while amino acids generally account for 2% to 15% of the bulk DOC (Ittekkot, 1982; Murrell and Hollibaugh, 2000) in estuarine and marine surface water. They are among the most labile fractions of bulk organic matter and may play key roles in the geochemical cycle of organic matter (Benner et al., 1992; Burdige and Zheng, 1998; Middelboe et al., 1995). Therefore, examination of DOC compound classes in addition to the bulk DOC is essential to better understand DOC cycling in marine environment.

The Pearl River is the largest river in southern China, the lower reach of which is located in a highly populated and industrialized area. Limited though, studies have been involved in organic matter in this important and complex estuarine system. Dai et al. (2000) report a first data set of size fractionated dissolved organic carbon, and Callahan et al. (2004) examine the distribution of both DOC and chromophoric dissolved organic matter (CDOM), which are not conservative in the mixing zone. Chen et al. (2004) investigate the spatial variation of dissolved and particulate amino acids in the Pearl River estuary plume and the adjacent coastal area during two high flow seasons, and suggest that phytoplankton is the main source of particulate amino acids in the estuarine and coastal water. Prior studies have also shown a persistent low oxygen zone down to <30 μmol O_2 kg^{-1} in the upper estuary, likely associated with high loads of organic matter and ammonia (Dai et al., 2006; Dai et al., 2008). However, the sources of DOC and its degradation in light of the oxygen consumption remain unknown. This study therefore aimed to examine the sources, degradation and biogeochemical behavior of dissolved organic carbon and its major compound classes, including carbohydrates and amino acids, in the Pearl River estuary. The export of bulk DOC and its major compounds, TCHO and TAA, to the shelf from the Lingdingyang Bay were also estimated.

2. Materials and methods

2.1. Study area

The Pearl River is the 13th largest river in the world in terms of freshwater discharge with an annual average of 3.26×10^{11} m^3 yr^{-1}, of which 80% occurs in the wet season from April to September (Dai et al., 2008 and references therein). It has three main tributaries, namely Xijiang (West River), Beijiang (North River) and Dongjiang (East River). The Pearl River water discharges into the South China Sea through eight outlets. Around 53% of the river runoff empties into the Lingdingyang Bay through the eastern four outlets (PRWRC/PRRCC, 1991), namely Humen, Jiaomen, Hongqimen and Hengmen (Fig. 1). Humen is the largest outlet of the eastern four outlets and is responsible for ~60% of the tidewater among all of the eight outlets (Dai et al., 2008 and references therein). The Pearl River estuary includes three sub-estuaries, among which the Lingdingyang Bay is the largest and traditionally regarded as the Pearl River estuary. This study thus focuses on the Lingdingyang Bay and its upstream channels (Guangzhou Channel, Huangpu Channel and Shiziyang Channel).

The Pearl River Delta region is surrounded by a number of metropolises such as Guangzhou, Shenzhen, Macau and Hong Kong. Up to 4.45×10^9 m^3 of domestic wastes and 2.46×10^9 m^3 of industrial effluents were discharged from Guangdong Province in 2007 with a domestic treatment rate of ~50% (Environmental Status Bulletins of Guangdong Province, http://www.gdepb.gov.cn). These high loads of organic matter and nutrients along with the high potential for microbial activities are believed to be responsible for the year-round depletion of oxygen in the water column (Dai et al., 2006; Dai et al., 2008) and significant degassing of CO_2 in the upper parts of the estuary (Zhai et al., 2005).

2.2. Sampling

Water samples were collected from 33 stations along a salinity gradient covering the Pearl River estuary as well as the three branches of the Dongjiang in April 2007 (Fig. 1). Salinity, temperature, DO, NH_4^+ and turbidity in the surface water were continuously monitored using a YSI® 6600 multi-parameter meter equipped to an underway pumping system. The details of our underway pumping system have been described previously (Dai et al., 2006; Zhai et al., 2005). Discrete underway sampling was also conducted for DO using this system. Surface (~1 m) samples for nutrients, DOC and organic compounds were taken with another pumping system equipped with a FloJet® pump, fitted with Teflon lined tubing with on-line acid-cleaned cartridge filters (pore size ~1 μm).

In addition to the surface water sampling, water column samples were also taken at selected stations using a 2.5 L Go-Flo sampler. Sub-Samples for DOC and organic compounds, carbohydrates and amino acids, were obtained by filtration of water samples through pre-combusted 0.7 μm GF/F filters and collected into 40 mL pre-combusted brown glass vials. Samples were frozen immediately at −20 °C until analysis. Samples for nutrients were obtained by filtration of water samples through 0.45 μm cellulose acetate filters. NH_4^+ was analyzed on board the ship. Samples for NO_3^- were frozen until analysis in a land-based laboratory in Xiamen University. Samples for Chl a were filtered through 0.7 μm GF/F filters and stored in liquid nitrogen until analysis. The concentration of total suspended substance (TSS) was measured by filtering a certain volume of water through pre-weighed 0.7 μm GF/F filters. The sampling volume was determined based on the TSS concentration, with a volume of ~200–300 ml in the upper reach and ~2000 ml in the lower estuary.

Triplicate samples for determination of bacterial abundance were pre-filtered with a 20 μm pore size net and preserved with 2% formaldehyde and stored at −20 °C. Bacterial abundances were counted using an Olympus BX61 epifluorescence microscope after staining with 4′,6-diamidino-2-phenylindole (DAPI) (Porter and Feig, 1980).

2.3. Bacterial respiration and DOC consumption rate incubation

Short term (1–3 d) incubations were carried out on-deck for measuring the bacterial respiration and DOC consumption rates at seven stations (see Fig. 1 for locations). Water samples were filtered through acid-washed cartridge filters (~1 μm pore size) to remove particulate material and collected into a 20 L pre-cleaned carboy, which were subsequently sub-sampled into ~300 mL acid-washed BOD bottles and incubated in the dark at in situ temperature (23–25 °C) controlled by flowing surface water. The poisoned control treatments were also established with 0.1% (v/v) saturated $HgCl_2$ added at the initial time point of the experiment. Sub-samples were taken every 12–24 h during the incubation. Sub-samples for determination of DOC, DO and bacterial abundance were all in duplicates. Samples for determination of DOC concentrations (20–30 mL) were filtered through 0.7 μm pore-size GF/F filters and stored in pre-combusted glass vials at −20 °C.

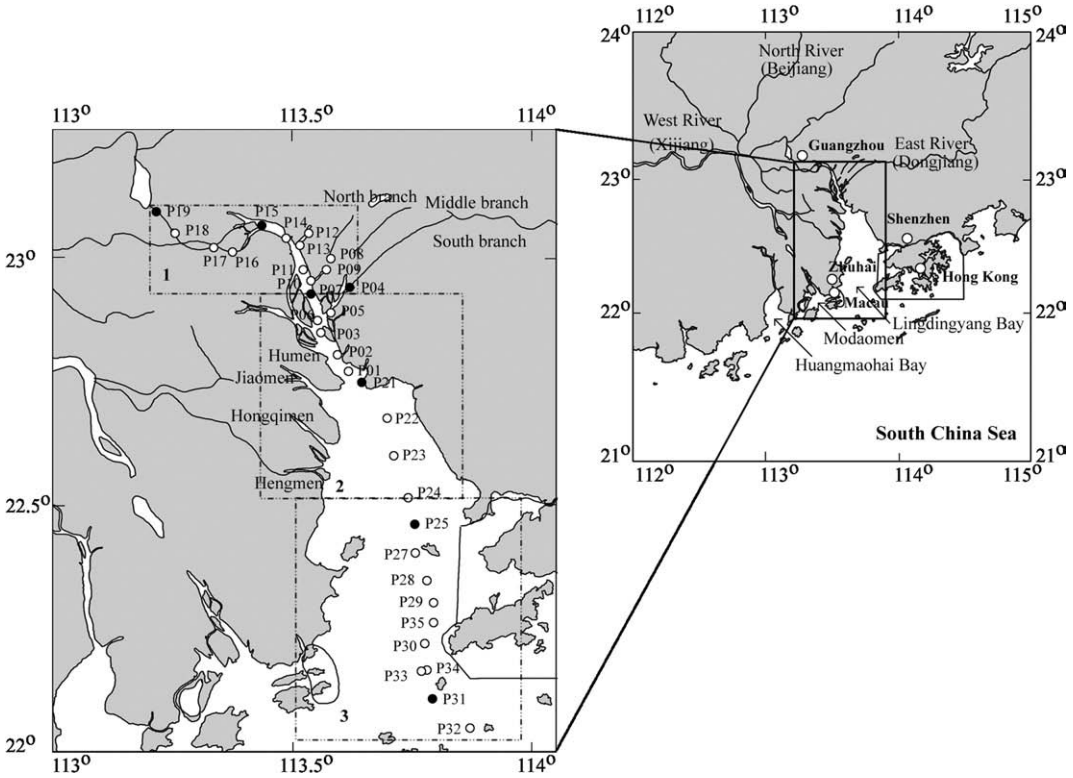

Fig. 1. Map of the Pearl River estuary showing sampling stations in April 2007. The closed circles showed stations where bacterial respiration and DOC consumption incubations were conducted. For ease of discussion, we divided the Pearl River estuary into three zones: 1—upper reach; 2—mixing-dominated zone; 3—lower estuary. Stations P19–P15 were located in Guangzhou Channel, stations P15–P11 in Huangpu Channel, and stations P11–P06 in Shiziyang Channel.

2.4. Biodegradable DOC (BDOC)

Long-term incubations were carried out at 12 stations to estimate BDOC concentrations following the methods of Servais et al. (1987). Approximately 300 mL of water was filtered into 500 mL pre-combusted brown glass bottles and incubated in the dark at ~20 °C for 30 d. Initial incubation water was bubbled and the incubation bottle contained enough air (~200 mL headspace) to ensure that the whole incubation was under aerobic conditions. BDOC concentrations were estimated as the difference of DOC concentrations measured before and after incubation.

2.5. Analysis for nutrients, DO, Chl a, POC and DOC

Nutrients were analyzed following our previously reported methods (Dai et al., 2008). DO was determined using the Winkler titration method. Chl a was determined using a Turner fluorometer after extraction of the membrane samples with 90% acetone (Herbland et al., 1985; Parsons et al., 1984). POC was analyzed on a Perkin Elam 2400IICHS/O elemental analyzer after removal of carbonate with fumes from HCl for 24 h. Concentrations of DOC were determined using high-temperature catalytic oxidation techniques using a Shimadzu TOC-V CPH TOC analyzer. Deep seawater DOC standard and low carbon water (Hansell's Laboratory, University of Miami) were used for quality control on a daily basis during sample analysis. Total blanks associated with DOC analyses were generally about 2–3 μmol C L^{-1} and the precision was better than 2% on replicate analyses.

2.6. Carbohydrates and amino acids analysis

Total dissolved carbohydrate concentrations (TCHO), including monosaccharides (MCHO) and polysaccharides (PCHO), were determined with the TPTZ (2,4,6-tripyridyl-s-triazine) method of Myklestad et al. (1997). Briefly, samples for TCHO measurements were hydrolyzed with 0.9 mol L^{-1} HCl in flame-sealed ampules at 100 °C for 20 h, and then the TCHO concentrations were measured by oxidizing the free reduced sugar with Fe^{3+} in alkaline conditions, followed by spectrophotometric analysis of a colored product of reduced Fe^{2+} and TPTZ. The concentrations of MCHO were directly measured without hydrolysis, and the concentrations of PCHO were obtained by the difference between TCHO and MCHO. The precision of replicate samples was better than 10%.

Amino acids were measured using the o-phthaldaldehyde (OPA) fluorescent derivatization method modified by Dauwe et al. (1999) and Murrell and Hollibaugh (2000). In this technique, samples for TAA measurements were hydrolyzed with 6 mol L^{-1} HCl inside flame-sealed ampules at 110 °C for 20 h under N_2, and then the total free amino acid concentrations were measured after neutralization and reaction with the OPA reagent to form fluorescent derivatization. The fluorescence was measured at excitation/emission wavelengths of 340/455 nm using a spectrofluorometer (Cary Eclipse 100, Varian). The DFAA concentrations were directly measured without hydrolysis, and the DCAA concentrations were obtained by the difference between TAA and DFAA concentrations.

We modified the sample preparation procedure to remove free ammonia which also reacts with OPA and may result in unstable fluorescence as suggested by Lindroth and Mopper (1979) and to prevent amino acids being oxidized by high concentrations of NO_3^- during hydrolysis (Robertson et al., 1987). Briefly, water samples were basified with 6 mol L^{-1} NaOH and incubated for 1 h at ~20 °C under continual N_2 purging in order to remove the free ammonia present in the sample (Dauwe et al., 1999). Excess ascorbic acid was added before hydrolysis to prevent the amino acids being oxidized during hydrolysis (Robertson et al., 1987). During OPA fluorescent derivatization, we chose a longer reaction time of 5 min rather than 2 min (Dauwe et al., 1999) in order to minimize the interference of the remnant ammonia.

Amino acid concentrations reported here were based on standard curves constructed from an amino acid mixture (Sigma Co.) following the method of Dauwe et al. (1999). Given an average molecular weight of 132 g mol^{-1}, total amino acid concentrations yielded are "amino acid mixture equivalent" concentrations. The method showed a detection limit of 0.1 μmol L^{-1}, and a spiked recovery of 96–102% with a relative standard deviation <10%.

3. Results

3.1. Hydrochemical settings

As compared to the flooding season (e.g., up to 17,100 m^3 s^{-1} in June 2007), April 2007 was a relatively low flow season with a discharge rate of ~5420 m^3 s^{-1} during the survey. (China NWR-BH, 2008). As a result of this low river flow, saline water intruded ~25 km into the upstream Humen Outlet at high tide during our upstream survey (Fig. 2a). The turbidity maximum was observed at ~20 km upstream of the Humen Outlet (Fig. 2b). Based on the salinity and turbidity gradient we divided the estuary into three zones: the upper reach, the mixing-dominated zone (hereafter referred to as the mixing zone) and the lower estuary (labeled in Fig. 1).

Also shown in Fig. 2 are the plots of individual chemical species against distance from the Human Outlet. These distributions are also shown against salinity (Fig. 3). The highest NH_4^+ concentration in surface water was observed at Sta. P19 with a concentration of 450 μmol L^{-1} and decreased rapidly downstream coinciding with a significant increase in NO_3^- concentrations reaching its maximum value of 174 μmol L^{-1} in the mixing zone (Fig. 2d). Such a distribution pattern has been observed in our previous studies indicating a significant nitrification reaction in the upper reach and in the mixing zone (Dai et al., 2006, 2008). In the lower estuary both NH_4^+ and NO_3^- concentrations gradually decreased due to the dilution by seawater with a lower nutrient content.

Pronounced oxygen depletion was observed in the upper reach of the estuary. The surface DO concentrations ranged from 9 μmol O_2 kg^{-1} (or 0.29 mg O_2 L^{-1}) in the upper reach near Guangzhou to 35 μmol O_2 kg^{-1} at the vicinity of the Humen Outlet. As observed in our previous cruises (Dai et al., 2006, 2008; Zhai et al., 2005), this hypoxic zone (DO<60 μmol O_2 kg^{-1} or 2 mg O_2 L^{-1}) extended>70 km in the whole upper reach from the Humen Outlet to the suburbs of Guangzhou (Fig. 2c). Downstream of the Humen Outlet, surface DO concentration increased with salinity, and DO supersaturation (up to 110%) was observed in the lower estuary (S>20).

Selected DO profiles (during a flood tide) are presented in Fig. 4. In the upper reach, bottom DO was 8–39 μmol O_2 kg^{-1}, slightly lower than in surface water (9—45 μmol O_2 kg^{-1}), suggesting rapid oxygen consumption in the water column and DO depletion throughout the whole water column. In the mixing zone vertical gradients of salinity were evident (S~2–6 and ~3–18 in surface and bottom water, respectively), reflecting the intrusion of the salt wedge. The DO profile patterns at the upstream of the Humen Outlet (Sta. P01 and Sta. P03) were similar to those in the upper reach. Downstream of the Humen Outlet (Sta. P23) the bottom water DO was distinctly higher than in surface water despite the aeration due probably to the higher oxygen consumption rate of the surface fresh water and/or to the bottom water mixing with high-DO seawater. In the lower estuary vertical gradients of salinity (thus stratification) were strong through to the estuary mouth at Sta. P31, where DO in both bottom and surface water was high, ranging from 190 to 245 μmol O_2 kg^{-1}.

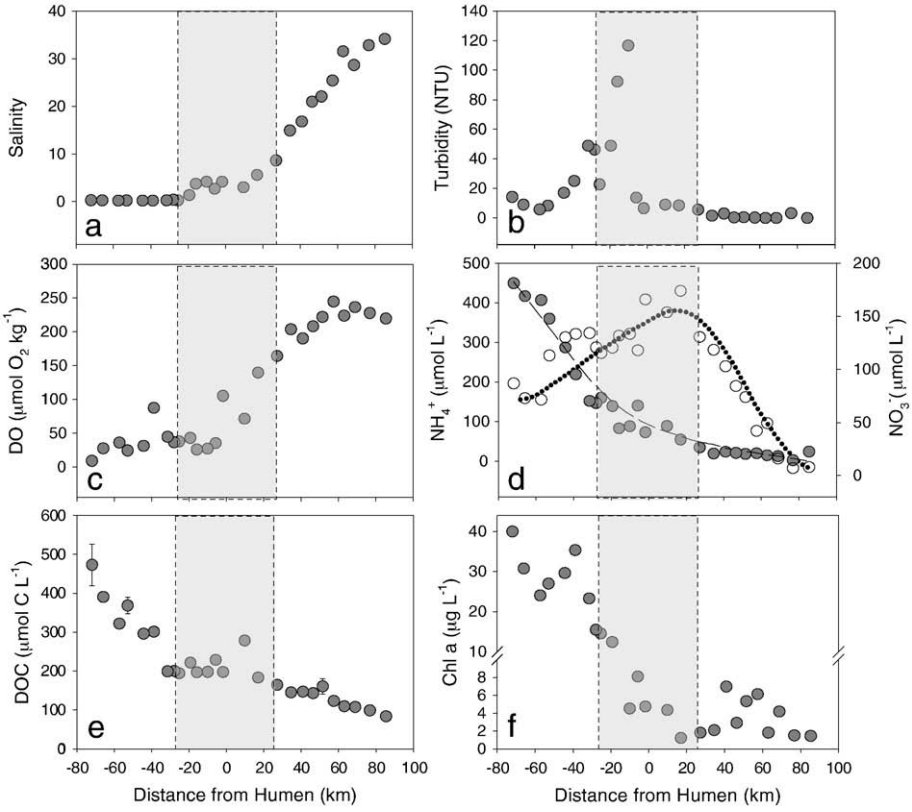

Fig. 2. Distribution of salinity, turbidity, DO, NH_4^+/NO_3^-, DOC and Chl a of surface water in the Pearl River estuary (exclusive of the Dongjiang tributary) along with the distance from Humen. (a) Salinity; (b) Turbidity; (c) DO; (d) NH_4^+ (closed circle), and NO_3^- (open circle); (e) DOC; (f) Chl a. Gray shadow represents the mixing-dominated zone. Dotted and dashed curves in (d) showed the fitting curves.

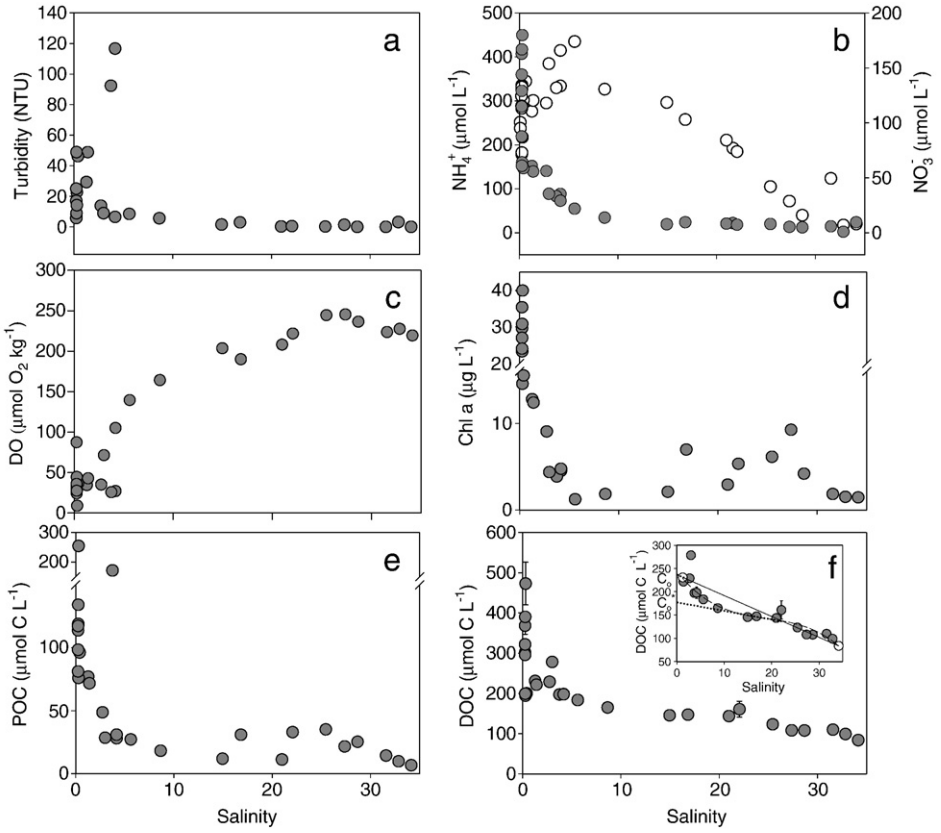

Fig. 3. Distribution of turbidity, NH_4^+/NO_3^-, DO, Chl a, POC and DOC along with the salinity in the Pearl River estuary (exclusive of the Dongjiang tributary). (a) Turbidity; (b) NH_4^+ (closed circle) and NO_3^- (open circle); (c) DO; (d) Chl a; (e) POC; (f) DOC. The inserted plot in Panel f was the DOC distribution in the Lingdingyang Bay. The open circles represented the two end-members, where the water after mixing with Dongjiang water was chosen as the river end-member (see text for details). The solid line showed the conservative mixing line. The dashed line showed the fitting curve, and the dotted line showed the tangent to the DOC-S fitting curve at $S = 22$.

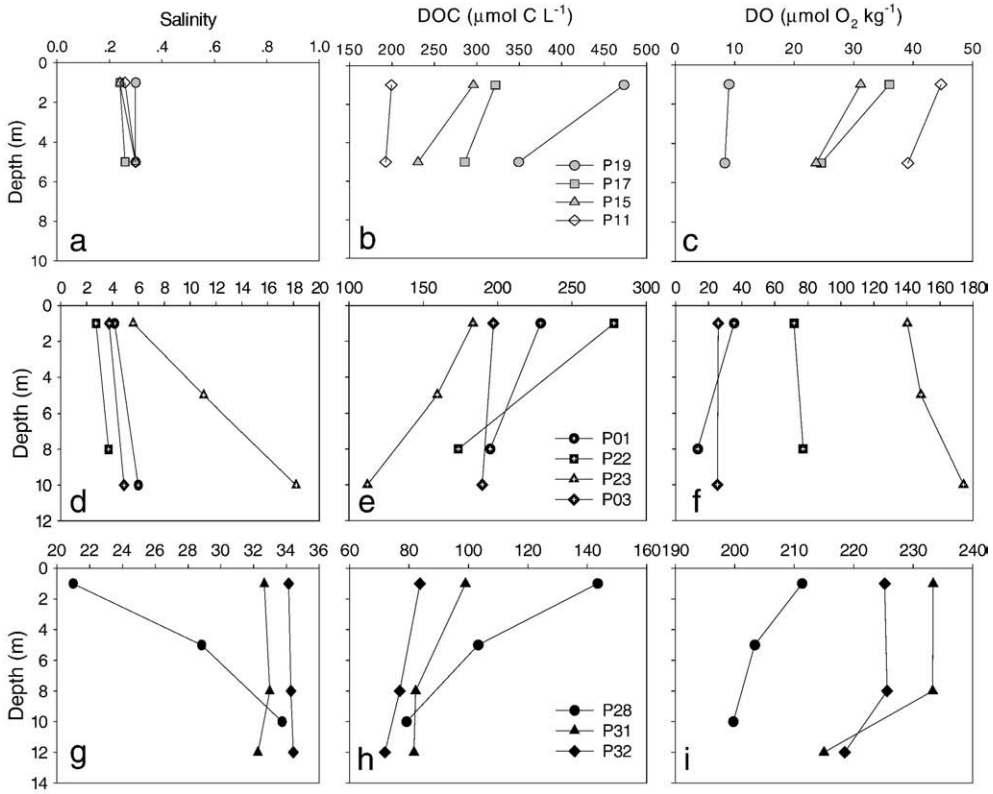

Fig. 4. Vertical profiles of salinity, DOC, and DO at selected stations in the upper reach (a, b, c), in the mixing zone (d, e, f) and in the lower estuary (g, h, i) of the Pearl River estuary.

3.2. Distributions of DOC, Chl a and POC

Surface water DOC concentrations ranged from 194 to 473, 165–278 and 84–161 μmol C L^{-1} in the upper reach, mixing zone, and lower estuary, respectively (Table 1). The highest DOC concentration (473 μmol C L^{-1}) along with the highest NH_4^+ concentration (450 μmol L^{-1}) was observed in the upper reach immediately downstream of the discharge points of the four main treated effluents of Guangzhou. Downstream DOC decreased rapidly with distance during Guangzhou Channel and Huangpu Channel. In Shiziyang Channel DOC was almost constant with distance, and then decreased again in the downstream of Humen Outlet due to the dilution by low DOC seawater (Fig. 2e). Such a trend was also shown in the concentration versus salinity plots, where both DOC and NH_4^+ were depicted non-conservatively during the estuarine mixing (Fig. 3). The removal of DOC was particularly pronounced in the upper reach and was extended to salinity ~20 (Fig. 3f).

Chl a concentration was high in the upper reach with the highest value of 40 μg L^{-1} at Sta. P19 near Guangzhou, in accordance with the highest DOC and NH_4^+ concentration (Figs. 2 and 3). Downstream the Chl a concentration decreased rapidly to its lowest value of 1.2 μg L^{-1} at the mixing zone (Sta. P23). Chl a was elevated again in the lower estuary at middle salinity (S ~ 20–30) likely due to the on-site primary production (Fig. 3d). Relatively high POC concentrations were observed in the Pearl River estuary during the present cruise, ranging from 6.7 to 254 μmol C L^{-1}, accounting for 7–35% of TOC (Total Organic Carbon). POC had an identical pattern with Chl a, with its highest concentration observed in the upper reach at Sta. P19 (254 μmol C L^{-1}), which decreased rapidly to a value of 12 μmol C L^{-1} in the mixing zone. POC was elevated again in the lower estuary at middle salinity (Table 1, Fig. 4e). POC strongly correlated with Chl a but not with TSS (Figs. 3 and 7), suggesting that phytoplankton were important to the POC pool.

3.3. Distributions of carbohydrate and amino acid species

Dissolved carbohydrate and amino acid concentrations are shown in Table 1 and Fig. 5. TCHO, MCHO, PCHO, TAA, DFAA and DCAA had similar distribution patterns, i.e., they were high in the upper reach and decreased with increasing salinity, suggesting an upper estuarine source of these constituents. Concentrations of TCHO ranged from 51 to 133 μmol C L^{-1} (20–28% of DOC), from 27 to 75 μmol C L^{-1} (16–28% of DOC) and 15 to 32 μmol C L^{-1} (18–23% of DOC) in the upper reach, in the mixing zone, and in the lower estuary, respectively. Within the TCHO pool, MCHO decreased gradually from a high value of 70 μmol C L^{-1} in the upper estuary to 6.0 μmol C L^{-1} in the lower estuary. In contrast, PCHO concentrations decreased from 63 μmol C L^{-1} in the upper reach to the lowest value 3.6 μmol C L^{-1} in the mixing zone, being elevated in the middle salinity area. As a result, the ratio of MCHO/PCHO was increased gradually along the estuary, reaching a maximum at the vicinity of Humen Outlet, and then declined in the lower estuary. Dissolved TAA ranged 33–103 μmol C L^{-1} (15–23% of DOC) in the upper reach, and 23–51 μmol C L^{-1} (12–20% of DOC) in the mixing zone, and 7.2–22 μmol C L^{-1} (8.5–15% of DOC) in the lower estuary. In contrast, DCAA dominated throughout the estuary.

The percentage abundance of both TCHO and TAA in the upper reach was unusually high due to the contribution of the wastewater inputs and phytoplankton production (see discussion below). In the

Table 1
Summary of hydrological data and the concentrations of organic carbon and its major compound classes in the three zones of the Pearl River estuary based on zonal and the Dongjiang tributary during April 2007.

Site	Station	Salinity	DOC	POC	Chla	MCHO	TCHO	PCHO	DFAA	TAA	DCAA	P_{MCHO} %	P_{PCHO} %	P_{TCHO} %	P_{DFAA} %	P_{TAA} %	P_{DCAA} %
Pearl River estuary: upper reach	P19	0.30	473	254	40.0	70	133	63	40	103	63	15	13	28	8.5	22	13
	P18	0.26	390	134	30.8	54	84	30	30	60	30	14	7.6	21	7.6	15	7.7
	P17	0.24	322	81	24.0	54	84	30	21	53	32	17	9.2	26	6.6	16	10
	P16	0.25	368	98	27.0	62	84	22	39	84	45	17	6.0	23	11	23	12
	P15	0.24	296	117	29.7	49	77	28	22	56	34	17	9.4	26	7.5	19	11
	P14	0.24	301	114	35.4	n.d.	n.d.	n.d.	23	56	32	16	3.2	20	7.7	19	11
	P11	0.26	199	119	23.3	41	55	14	12	35	23	20	7.2	28	6.0	17	11
	P10	0.40	200	96	15.5	39	51	12	13	33	20	20	5.9	26	6.7	17	10
Pearl River estuary: mixing zone	P07	0.29	194	76	14.6	40	55	15	13	36	23	20	7.7	28	6.6	19	12
	P06	1.40	222	72	12.4	38	54	16	17	39	22	17	7.1	24	7.6	18	10
	P05	1.23	231	77	14.6	40	61	21	19	45	26	17	9.0	26	8.2	20	11
	P03	3.75	197	143	3.9	34	45	11	6.0	24	18	17	5.5	23	3.0	12	9.4
	P02	4.17	198	28	4.5	33	37	4.2	11	33	22	17	2.1	19	5.5	17	11
	P01	2.73	229	49	8.1	34	60	26	6.0	33	27	15	11	26	2.6	15	12
	P21	4.17	198	31	4.8	27	33	5.5	6.4	30	24	14	2.8	17	3.2	15	12
	P22	3.00	278	28	4.4	46	75	29	16	51	35	17	10	27	5.6	18	13
	P23	5.60	183	27	1.2	31	36	5.1	5.6	25	19	17	2.8	20	3.1	13	10
	P24	8.65	165	18	1.8	23	27	3.6	3.2	23	20	14	2.2	16	1.9	14	12
Pearl River estuary: lower estuary	P25	14.95	146	12	2.1	22	32	10	2.8	22	19	15	6.4	22	1.9	15	13
	P27	16.82	147	31	7.0	19	31	12	n.d.	n.d.	n.d.	13	8.2	21	n.d.	n.d.	n.d.
	P28	20.99	143	11	2.9	21	30	9.4	5.2	20	15	15	6.1	21	3.6	14	11
	P29	22.07	161	33	5.3	17	32	15	3.2	20	16	11	9.0	20	2.0	12	10
	P30	31.58	110	14	1.8	8.5	25	17	4.0	14	10	7.7	15	23	3.6	13	9.1
	P31	32.85	99	9.8	1.5	9.3	22	13	0.8	8.4	7.6	9.4	13	22	0.8	8.5	7.7
	P32	34.14	84	6.7	1.5	6.0	15	8.7	1.2	7.2	6.0	7.1	11	18	1.4	8.6	7.2
	P33	28.68	108	25	4.2	13	23	10	2.8	12	9.2	12	9.1	21	2.6	11	8.5
	P34	27.37	108	22	9.3	7.7	26	18	n.d.	n.d.	n.d.	7.1	17	24	n.d.	n.d.	n.d.
	P35	25.45	123	35	6.1	17	26	9.0	2.8	16	13	14	7.9	21	2.3	13	10
Dongjiang tributary	P04	0.65	227	94	15.8	39	55	15	16	52	36	17	6.8	24	7.2	23	16
	P08	0.09	186	57	4.6	47	n.d.	n.d.	11	34	23	25	n.d.	n.d.	5.8	18	12
	P09	0.10	190	52	n.d.	43	71	28	18	35	17	22	15	37	9.2	18	9.0
	P12	0.21	219	104	19.9	51	65	14	18	54	36	23	6.4	30	8.0	24	16
	P13	0.23	209	104	13.5	41	50	9.2	13	29	16	20	4.4	24	6.1	14	7.6

Abbreviation: P_{MCHO} = percentage of monocarbohydrate carbon; P_{PCHO} = percentage of polycarbohydrate carbon; P_{TCHO} = percentage of total carbohydrate carbon; P_{DFAA} = percentage of free amino acid carbon; P_{DCAA} = percentage of combined amino acid carbon; P_{TAA} = percentage of total amino acid carbon; n.d. = no data.
Chla in μg L^{-1}. DOC, POC, carbohydrate and amino acid concentrations in μmol C L^{-1}, calculated assuming per mole "glucose equivalent" has 6 mol C, and per mole "amino acid mixture equivalent" has 4 mol C.

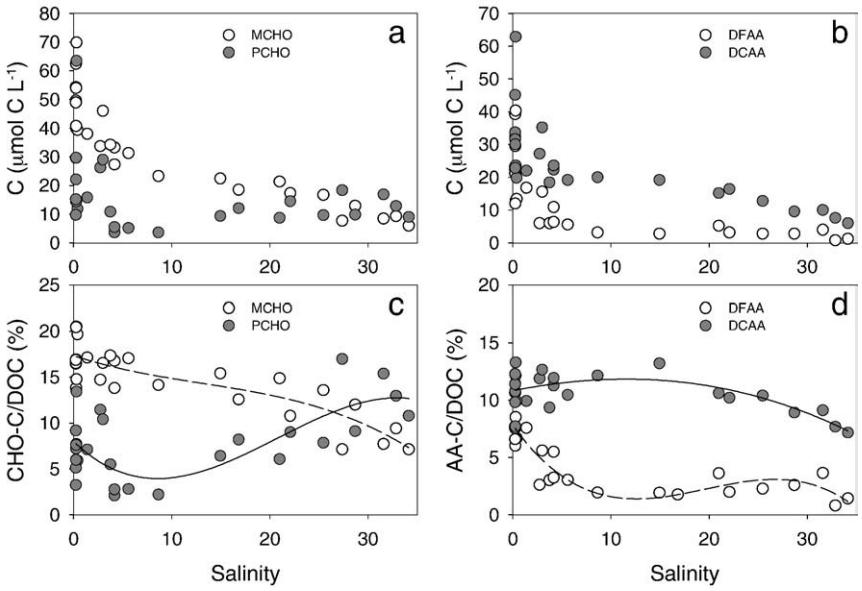

Fig. 5. Distribution of organic compound classes and their percentage abundance with respect to DOC in the Pearl River estuary. (a) MCHO and PCHO; (b) DFAA and DCAA; (c) Percentage of MCHO-C/DOC and percentage of PCHO-C/DOC; (d) Percentage of DFAA-C/DOC and percentage of DCAA-C/DOC.

Lingdingyang Bay, dissolved carbohydrate and amino acid concentrations were comparable to other estuarine systems such as in the San Francisco Bay (Murrell and Hollibaugh, 2000) and the Elorn estuary (Senior and Chevolot, 1991).

3.4. Bacterial respiration, bacterial abundance and DOC consumption

Bacterial respiration rates were based on standard dark-bottle O_2 consumption rate. DO declined linearly duration the incubations,

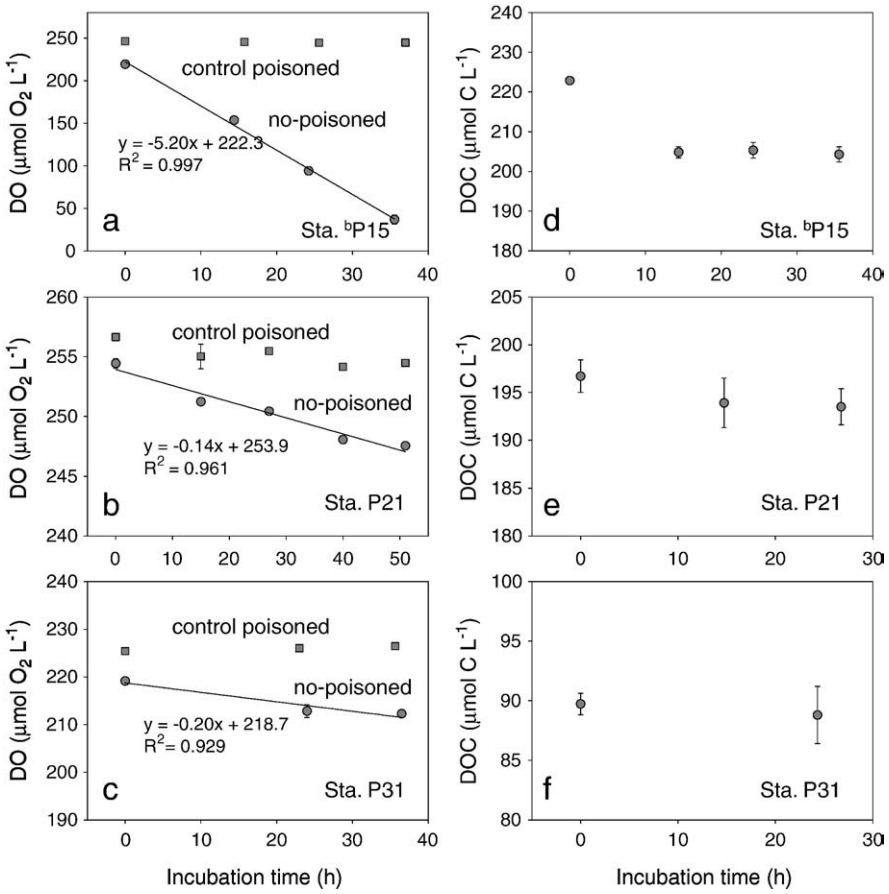

Fig. 6. Evolution of DO and DOC concentrations in the course of bacterial respiration rate (a, b, c) and DOC consumption rate (d, e, f) incubations at selected stations along the Pearl River estuary. The lines represent linear regressions of the data points. Note that all incubations were conducted with surface water (~ 1 m) except for the sample of ^{b}P15 which used bottom water taken at ~5 m.

whereas DO remained unchanged in the poisoned samples, indicating the experiments were in order (Fig. 6a–c). DO consumption rates (i.e. bacterial respiration rates) ranged from 5.8 μmol O_2 L^{-1} h^{-1} in the upper reach to 0.12 μmol O_2 L^{-1} h^{-1} in the lower estuary. In contrast, DOC consumption rates were significantly high in the first few hours of the incubations especially for samples taken from the upper reach (Fig. 6d–f), implying a more labile DOC pool that was utilized within the first few hours. In order to make the DOC consumption rate comparable between stations, we calculated the average DOC removal during the first 24 h of incubation, which revealed a range of 0.04–0.72 μmol C L^{-1} h^{-1}. Such DOC consumption rates were much lower than the DO consumption rates in the same incubation series (Table 2 and Fig. 6).

3.5. Distribution of BDOC

BDOC concentrations varied substantially along the estuary with a range of 19–202 μmol C L^{-1} (Table 2). High BDOC/DOC ratios (41 ± 3%) coupling with high DOC concentrations were found in the upper reach, suggesting that the riverine DOC was highly biodegradable. In the mixing zone, the average percentage abundance of BDOC was 27 ± 2%. These high levels of BDOC have been reported in other anthropogenic estuaries such as the Seine estuary, where ~40% and 23% of the DOC were biodegradable in the upper part and turbidity maximum zone, respectively (Garnier et al., 2001; Servais and Garnier, 2006). The lowest portion of BDOC (16%) in the present study was found in the lower estuary, a scenario similar to the observation by Raymond and Bauer (2000) at the lower York River estuary.

The exception occurred to Sta. P22 where an extraordinarily high DOC was measured and BDOC was up to 45%, the highest value observed in the cruise. The reason causing such an unusually high DOC concentration is unclear but might be associated with inputs from the Jiaomen Outlet (see Fig. 1 for location) or tidal flushing from the high pollution Humen fishing port immediately upstream. Considering that the DOC concentration decreased markedly with depth at this station (Fig. 4) we should exclude the contribution from the resuspended sediment. Note that we excluded this exceptionally high DOC value from the discussion hereafter. It is interesting that an elevated percentage abundance of BDOC (30%) was also observed in the high Chl a region (S>20) in the Pearl River estuary, likely due to the phytoplankton-derived labile DOC. It must be pointed out that during the long-term incubation the composition of bacterial populations and their ability to degrade residual DOC might have changed (Marmonier et al., 1995). These changes probably resulted in a slight overestimation of BDOC values. Long-term incubations may also have led to in situ processes, which may have created labile DOC on very short timescales, being overlooked (Raymond and Bauer, 2000).

Table 2
DOC, BDOC, bacterial abundance, bacterial respiration rates (R_B) and DOC consumption rates (R_D) in the Pearl River estuary during April 2007.

Site	Station	DOC μmol C L^{-1}	BDOC μmol C L^{-1}	BDOC/DOC %	Bacterial abundance cells mL^{-1}	R_B μmol O_2 L^{-1} h^{-1}	R_D μmol C L^{-1} h^{-1}
Upper reach	P19	473	202	43	1.69×10^7	2.8	0.37
	P16	369	160	43	9.78×10^6	n.d.	n.d.
	P15	296	111	38	1.11×10^7	5.8	0.14
	[b]P15	230	n.d.	n.d.	4.80×10^6	5.2	0.72
Dongjiang tributary	P10	200	41	21	6.89×10^6	n.d.	n.d.
	P04	227	69	30	9.60×10^6	1.1	0.24
Mixing zone	P07	195	49	25	1.05×10^7	1.1	0.28
	P01	229	66	29	6.43×10^6	n.d.	n.d.
	P21	198	53	27	4.73×10^6	0.14	0.12
	P22	278	126	45	3.31×10^6	n.d.	n.d.
Lower estuary	P25	146	23	16	1.42×106	0.12	0.04
	P31	99	30	30	2.05×106	0.20	0.04
	P32	84	19	23	8.30×105	n.d.	n.d.

Note:
1) n.d. denotes no data.
2) All samples were taken from surface at ~1 m except [b]P15 was taken from at ~5 m.

4. Discussion

4.1. Sources of organic carbon in the upper reach of the Pearl River estuary

As pointed out above, the upper reach of the Pearl River estuary is located in a highly populated and industrialized area, where a very high concentration of dissolved NH_4^+ occurred (Fig. 2d). In view of nitrogen loading being a good indicator of anthropogenic wastes (Cole et al., 1993) one can expect anthropogenic wastes to be a major source of organic matter in the study area. The fact was that the concentration of DOC in the upper reach near Guangzhou was 473 μmol C L^{-1}, comparable to what we observed in the Guangzhou sewage treatment plant effluents (DOC = 659 μmol C L^{-1}). The extremely high NH_4^+ concentration of 450 μmol L^{-1} near Guangzhou was also consistent with the standard ammonium concentration of waste plant effluents (~570 μmol L^{-1} according to the China National Standard #GB-18918), which demonstrated anthropogenic input to be the major source of DOC to the upper reach. The high relative abundance of carbohydrates and amino acids in the DOC pool observed in the upper reach may also suggest this. For example, TCHO and TAA accounted for 28% and 22% of DOC in the upper reach (Sta. P19) at the Guangzhou Channel (Table 1), which is comparable to the typical TCHO composition of domestic sewage DOC (31%) (Gray, 2004). In the carbohydrate pool, MCHO concentrations were more abundant than PCHO in the upper reach, which was also consistent with MCHO dominated sewage-derived carbohydrate (Gray, 2004), again suggesting a strong loading of anthropogenic waste-derived organic carbon in this area.

TOC concentrations (DOC + POC) were high in the upper reach at the Guangzhou Channel, with a range of 403–727 μmol C L^{-1} (Table 1). These values were significantly higher than the value suggested by Abril et al. (2002) for the unpolluted rivers (4 mg L^{-1} or 333 μmol C L^{-1}), once again indicating that the upper reach of the Pearl River estuary has been affected by sewage inputs. Note that about 46 km downstream of the region of source input (main treated effluents from Guangzhou) at Sta. P07 (Shiziyang Channel, S = 0.3), TOC dropped rapidly to 270 μmol C L^{-1}, suggesting that beyond this point, no significant anthropogenic input could be identified. Meanwhile, this sharp decline of TOC along with the high bacterial respiration rates and DOC consumption rates suggested that biodegradation should be an important process controlling the losses of organic matter in this zone. Note that downstream of the Guangzhou Channel, there also occurred dilution by fresh water from the Dongjiang tributary with lower DOC and POC contents.

In order to further assess the anthropogenic contribution to DOC and POC, we attempted to establish a natural background value. Previous observations show that the DOC concentrations in the three tributaries (Xijiang, Dongjiang and Beijiang) in the upstream (beyond the major sewage source areas) are 114, 125 and 117 μmol C L^{-1}, respectively (Wei, 2003), and POC concentrations are 69 μmol C L^{-1} in the Xijiang and 49 μmol C L^{-1} in the Beijiang during the spring season (Gao et al., 2001, 2002). Our own data collected at the middle branch of the Dongjiang during our spring cruise showed a POC concentration of 52–57 μmol C L^{-1}. Previous observations also suggest that DOC and POC concentrations in the Pearl River have a significant seasonal variation but without significant inter-annual variations (Gao et al., 2001; Wei, 2003). For example, DOC concentration was 93 μmol C L^{-1} in April 1998 (Gao et al., 2001) and 114 μmol C L^{-1} in March 2000 in Xijiang (Wei, 2003). We thus justified that these DOC and POC concentrations be of representative of the riverine background of the Pearl River in spring. Given the fact

that the above DOC and POC concentrations did not show a significant variation between tributaries, the arithmetic averages of the three tributaries (DOC ~119 μmol C L^{-1} and POC ~56 μmol C L^{-1}) were used as the land-derived DOC and POC concentration of the Pearl River.

At the same time, we adopted the ratio of POC/Chl a in the upper reach of the estuary to describe the relative contribution of algal POC to total POC. According to Eppley et al. (1992) the slope of linear regression of POC on Chl a by weight provides information of the carbon/Chl a ratio of the phytoplankton, while the intercept provides the non-algal POC. POC and Chl a had a significant positive correlation in the upper reach of the Pearl River estuary with a regression equation POC (μg L^{-1}) = 23.41 × Chl a (μg L^{-1}) + 684.7 (R^2 = 0.62, p < 0.001, n = 14; excluding the highest polluted Sta. P19, Fig. 7e). The slope of the POC/Chl a regression was 23.4 by weight, which is consistent with the value of estuarine phytoplankton in culture (range 21.5–46.5 μg C (μg Chl a)$^{-1}$) (Gallegos and Vant, 1996) and comparable to the value 27.8 used by Murrell and Hollibaugh (2000) for the northern San Francisco Bay. In this study we thus used the POC/Chl a ratio of 23.4 μg C (μg Chl a)$^{-1}$ to convert Chl a into algal-POC to estimate the contribution of autochthonous production to POC in the upper reach. Based on mass balance the contribution of the phytoplankton biomass to POC was estimated as ~42%, the land-derived accounted for ~40%, and wastewater input accounted for ~18% in the upper reach Guangzhou Channel. Downstream in the Huangpu Channel, the contribution of the wastewater input to POC pool decreased to ~5% while the land-derived POC increased to ~50%. Phytoplankton production was thus an important source of POC in the upper reach of the Pearl River estuary, despite the high turbidity that may limit the light available for photosynthesis. Our observation was similar to the previous study in the upper Scheldt estuary where high phytoplanktonic biomass was found in the turbid section of the estuary (Kromkamp and Peene, 1995). Moreover, our δ^{13}C values of POC observed in the upper reach of the Pearl River estuary in the low flow season (Feb. 2004) ranged from −25.29‰ to −31.45‰, well consistent with the δ^{13}C values for the net phytoplankton (−24.96‰ to −31.23‰, our unpublished data) collected in the same area, again suggesting that phytoplankton was the main source of POC during the spring season, which also had low flow.

Furthermore, we attempted to estimate the phytoplankton-derived DOC. Extensive studies have reported a wide range of photosynthetic DOC, ranging from <1% to 50% of the total carbon fixed (Hama and Yanagi, 2001; Ittekkot et al., 1982; Wiebe and Smith, 1977 and references therein). Here, we adopted 50% as an upper limit of phytoplankton contribution to the bulk DOC pool. The algae derived DOC was thus calculated as ~59 μmol C L^{-1}, which accounted for ~15% of total DOC pool at the most in the Guangzhou Channel. If we assumed that the average of the three tributaries DOC concentration (119 μmol C L^{-1}) represents the natural land-derived DOC of the Pearl River, we could establish the relative contribution of land-derived material to the DOC pool as ~31%, anthropogenic loads as ~54%, and phytoplankton contribution as ~15% in the Guangzhou Channel. It was clear that in contrast to POC, wastewater inputs here were major sources of DOC, whereas phytoplankton production was a minor source of DOC in the upper reach of the Pearl River estuary. It is worth noting that the contribution of sewage loads to the DOC shows a large variation, with a value of ~54% in the Guangzhou Channel down to ~32% in the Huangpu Channel. This highly dynamic feature of organic matter associated with the regional oxygen depletion again suggests rapid organic carbon consumption in the upper estuary (see discussion below).

4.2. BDOC, bacterial abundance and bacterial respiration

BDOC had a linear and positive relationship with the initial DOC concentrations (Fig. 7f). The offset of the regression line suggested that the DOC of 80 μmol C L^{-1} was non-labile within the time scale of the incubation (~1 month). The slope of the regression gave an estimate of the response of BDOC to the increasing initial DOC, with an average 0.5 μmol C L^{-1} of additional BDOC (excess over the 80 μmol C L^{-1}) for every 1.0 μmol C L^{-1} increase in bulk DOC. This value is consistent with the results given by Servais et al. (1987), who report that ~50% of the bulk DOC in the Scheldt estuary is biodegradable.

The DOC biodegradability can also be examined through the composition of the DOC pool. Given that both TCHO and TAA represent the dominant labile DOC, 27–50% of the bulk DOC in the Pearl River estuary can be readily utilized. These values matched well with BDOC abundance (16–45%) in the estuary, except in the

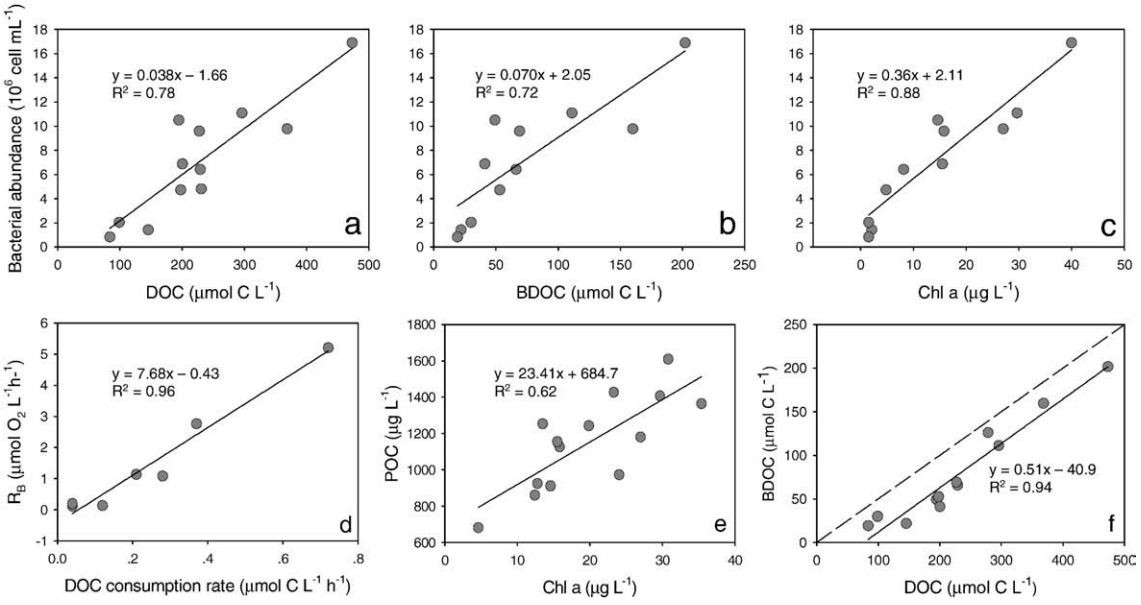

Fig. 7. (a) Bacterial abundance versus DOC; (b) Bacterial abundance versus BDOC; (c) Bacterial abundance versus Chl a; (d) Bacterial respiration rate vs. DOC consumption rate at selected incubation stations; (e) POC vs. Chl a in the freshwater part of the estuary (including the Dongjiang tributary); (f) BDOC concentration vs. initial DOC concentration at the selected incubation stations. The dashed line represented BDOC = 0.5 × DOC. These data are also shown in Table 2.

Dongjiang tributary where both TCHO and TAA accounted for 37–56% of the bulk DOC, significantly higher than the BDOC portions (21–30%). This discrepancy was probably due to the higher carbohydrate-like content in the water from the Dongjiang tributary, since organic carbon in this area was identified as being mainly contributed from natural land-derived material. Dongjiang tributary is located in a much less populated and less industrialized area. As a matter of fact, the upper reach of the Dongjiang is a main drinking water source for Hong Kong and Macau. This carbohydrate-like substance may be bound to, or a constituent of humic substances, and can be characterized by the TPTZ method. Senior and Chevolot (1991) also noted that a significant part of the dissolved carbohydrate pool in the Elorn estuary was refractory.

Bacterial respiration rates did not match well with the bacterial abundance within the estuary. Weak positive correlation of bacterial respiration versus bacterial abundance was also found in the Louisiana shelf and slop by Biddanda et al. (1994), who suggest that the dense bacterial biomass might constrain the respiration rate. Significant positive correlations were found between bacterial abundance and both DOC and BDOC concentration (Fig. 7a, b), implying that biodegradable labile DOC stimulated the bacterial growth. Strongly positive correlations were also found between bacterial abundance and Chl a (Table 2, Fig.7c), suggesting the algae-POC was another factor impacting the bacterial abundance besides the DOC availability. Oxygen consumption appeared to be perfectly linear for the duration of incubations, whereas DOC consumption was significantly enhanced in the initial hours. Moreover, the ratio of DO/DOC consumed ranged 1.2–7.6 (Note that incubation of the Sta.P15 surface water was excluded because this incubation did not start until ~6 h after the sampling, which might result in an underestimate of the DOC consumption rate). This ratio was far from the respiratory quotients, which varied between 0.9 and 1.4 depending on the composition of the substrates used according to Biddanda et al. (1994 and references therein), indicating that there were other oxygen consumption processes (e.g. nitrification) besides organic respiration in the Pearl River estuary. Although the bacterial respiration rate accounted for a low percentage (<15% at most stations) of total bacterial oxygen consumption, it had a strong correlation with the DOC consumption rate (Fig. 7d).

4.3. Behavior of DOC

In the Pearl River estuary, the longitudinal distribution of DOC showed a sharp removal in the low salinity zone (Fig. 3f). Such nonconservativity extended through the mixing zone. Due to the multiple end members in this complex estuarine regime (Cai et al., 2004; Guo et al., 2008), all of which affected the upper estuarine DOC behavior, we were not able to quantitatively evaluate the removal rate during the early estuarine mixing at low salinity. Nevertheless, considering the significant contribution of wastewater loads to total organic matter in the upper reach (see discussion above) and high turbidity in the upper reach and mixing zone of the Pearl River estuary, along with the depletion of DO (<30 μmol O_2 kg^{-1}) in surface water in this particular region, this DOC removal should be much related to bacterial degradation of this highly biodegradable sewage-derived material. Our on-deck incubation experiment showed that the bacterial respiration rates were very high in the upper reach (2.8–5.8 μmol O_2 L^{-1} h^{-1}, Table 2), along with high DOC consumption rate (0.37–0.72 μmol O_2 L^{-1} h^{-1}), demonstrating clearly that bacterial oxidation of organic matter was one of the most important mechanisms controlling the DOC removal in the upper reach of the estuary. The high proportion of biodegradable DOC (41 ± 3%) in the upper estuary may lend additional evidence pointing towards the potential for such a high removal of DOC. It was worth noting that DOC consumption rates were much lower than bacterial oxygen consumption rates in the upper reach. For example, if we assumed that oxidation of 1 mol DOC needed 1 mol O_2, DOC oxidation only accounted for 13–14% of total oxygen consumption. The reason for this discrepancy is unclear but might be at least related to other oxygen consumption processes besides organic matter respiration in this area. Considering the remarkable decrease in ammonium and increase in nitrate in the upper reach, nitrification must be another important oxygen consumption process as suggested by Dai et al. (2008).

Much higher percentage of POC (68%) was lost than DOC (32%) in the upper reach Guangzhou Channel. This high POC loss might be associated with bacterial degradation and dilution by the local streams with lower POC concentrations, deposition to sediment, and/or lower phytoplankton production downstream.

Having stated that it was difficult to estimate the removal of DOC in the very upper reach of the Pearl River estuary because the mixing scheme was complex with multiple end-members inputs (Fig. 1), we were able to estimate the removal of DOC in the Lingdingyang Bay. The water after mixing with the Dongjiang was chosen as the river end-member. The Lingdingyang Bay has a water residence time of ~5 days during low flow seasons (Wong and Cheung, 2000). It is unlikely that the end-member could change abruptly except with accidental inputs. Although there are four outlets, namely Humen, Jiaomen, Hongqimen and Hengmen in Lingdingyang Bay, the Humen and Jiaomen outlets discharge dominant river runoff (~66%) into the Lingdingyang Bay (Cai et al., 2004). Since the watershed of Jiaomen reach was similar to the lower Dongjiang tributary in terms of organic matter loads, one could expect that the DOC concentration at the Jiaomen Outlet was not significantly different from that at the Humen Outlet. In order to examine the steady state of the river end-member, we compared the DOC end-member of our two cruises determined in April 2007 and March 2006. The values were almost the same (DOC = 231 μmol C L^{-1} at $S = 1.2$ in spring 2007; and DOC = 232 - μmol C L^{-1} at $S = 1.1$ in spring 2006), which strongly argued for a near steady state condition in this case.

Based on a two-end member mixing model (Fig. 3f), we used Eq. (1), presented by Officer (1979) to estimate the removal of DOC in the Lingdingyang Bay.

$$\text{DOC loss fraction} = (C_o - C_o^*) / C_o \quad (1)$$

Where C_o is the point at which the conservative mixing equation intersects the y-intercept (i.e. the concentration at zero salinity), and C_o^* is the intercept of the regression line at $S = 0$ for the tangent to the DOC–S curve at $S = 22$, the intersection of C–S curve and the mixing line, as illustrated in the inserted plot of Fig. 3f. The concentrations of C_o and C_o^* thus estimated were 236 μmol C L^{-1} and 177 μmol C L^{-1}. The removal of DOC in the Lingdingyang Bay was estimated as ~25%. On-deck incubation showed that the rate of DOC biodegradation in this area was 0.15 ± 0.12 μmol C L^{-1} h^{-1}. Microbial degradation accounted for, on average, ~31% of the total DOC removal in the Lingdingyang Bay assuming that the water residence time is 5 days (Wong and Cheung, 2000). This value may represent the upper limit of bacterial degradation portion, because the DOC consumption rate adopted to estimate the bacterial removal was based on the first 24 h incubation.

As showed in Fig. 3f (inserted plot), the DOC removal in the Lingdingyang Bay mainly occurred in the mixing zone. Bacterial degradation was an important process, which controlled the DOC removal in this area. Other processes, such as flocculation, aggregation and adsorption, were also important processes, which controlled ~69% of the DOC removal in the mixing zone.

Similarly, we estimated removals of TCHO and TAA in the Lingdingyang Bay, which were 59% and 48%, respectively. Interestingly, the absolute removal of TCHO and TAA were 37 and 22 μmol C L^{-1}, respectively, both of which accounted for total DOC removal in the estuary, indicating that the humic substances should not be of

importance in the removal DOC pool. The plausible explanations were (1) relatively low portion of land-derived DOC transporting to the Bay; (2) low irradiance in this high turbidity estuary mixing zone; (3) relatively short water residence time. All these resulted in minimal humic organic carbon turnover within the estuary.

In the lower estuary, the DOC versus salinity showed an almost linear distribution. However, when we looked at the distribution of BDOC and the organic compounds, we found this linear distribution did not imply a conservative behavior. If there were no additional autochthonous inputs of labile DOC, the freshwater labile DOC pool would be removed during estuarine mixing, causing the percentage of BDOC to decrease with increasing salinity. There was a significant decrease of the BDOC portion from the upper reach to the mixing zone (Table 2). This decrease was expected with the utilization of the freshwater labile DOC during the first few days of transport. However, the percentage abundance of BDOC only decreased by ~4 %, from 27 ± 2% in the mixing zone to 23 ± 8% in the lower estuary along the Lingdingyang Bay. This value is much lower than the estimation based on the bacterial removal rate of DOC in the Lingdingyang Bay, indicating that there has been an additional input of labile DOC balancing the removal of BDOC in the lower estuary (S>20). Considering the elevated Chl a in this area (Fig. 3d), this labile DOC was most likely originated from phytoplankton production. These simultaneous sources and sinks also resulted in small net changes in the bulk DOC concentrations, which showed an apparently conservative behavior in the lower estuary though (Fig. 3f).

In contrast, these simultaneous sources and sinks could be distinctly identified with DOC compounds. The percentage abundance of both TCHO and TAA decreased with increasing salinity in the low salinity region, indicating selective removal of carbohydrates and amino acids (Table 1). In the middle salinity zone, the percentage of TCHO slightly increased, which was likely due to the contribution of local phytoplankton production. This phenomenon, coupled with an enhanced BDOC abundance (Table 2) and the higher Chl a concentrations observed in this area (see discussion above) further confirmed the autochthonous contribution of these labile DOC components.

Within the TCHO pool, the percentage of MCHO decreased with increasing salinity in the whole estuary without any elevated portion of MCHO/DOC in the middle salinity, indicating MCHO was preferentially removed within the DOC pool. As compared to MCHO, PCHO had an enhanced removal in the low salinity zone, and was significantly elevated in the middle salinity. This contrast in the distribution pattern between MCHO and PCHO may have been caused by the preferential flocculation of PCHO in the mixing zone (Fig. 5c). The fact is that PCHO is primarily composed of high molecule or colloidal organic matter (Aluwihare et al., 1997; Benner et al., 1992; Borch and Kirchmann, 1997; McCarthy et al., 1996), and flocculation has been demonstrated as a fundamental process of removing high molecular organic matter during estuarine mixing (de Souza Sierra et al., 1997; Mannino and Harvey, 2000). Alternatively, phytoplankton mainly releases polycarbohydrates rather than monocarbohydrates. Ittekkot et al. (1981) report that 75% of the carbohydrates exuded during an algal bloom in the northern North Sea are in combined forms.

Within the TAA pool, DCAA was dominant. The distribution pattern of DFAA/DOC was similar to MCHO/DOC, with a range of 6.0–11% in the upper estuary decreasing to 0.8–3.6% in the lower estuary (Table 1 and Fig. 5d), indicating the dominant removal of DFAA during estuarine mixing. In contrast with PCHO, the percentage of DCAA was almost constant in the mixing zone (Fig. 5d). And no elevation of DCAA was observed in the lower estuary where the Chl a and POC concentrations were obviously enhanced, suggesting that the phytoplankton exudates were predominately in the form of carbohydrates rather than amino acids, or amino acids were rapidly turned over. As a matter of fact, the relatively high average C/N ratio of ultrafiltered dissolved organic matter from phytoplankton cultures is reported in the literature (Biersmith and Benner, 1998), which implies that the phytoplankton-produced dissolved organic matter is rich in carbohydrates rather than amino acids.

4.4. DOC export from the Lingdingyang Bay

As mentioned above, a high proportion of bulk DOC in the Pearl River estuary was labile, which stimulated the high estuarine bacterial respiration rate. However the water residence time of the Pearl River estuary was short relative to the turnover time of the DOC pool, and thus a significant amount of riverine labile DOC should be exported to the adjacent northern South China Sea. The exported DOC from the Pearl River estuary must therefore be an important source of allochthonous organic matter that may fuel the heterotrophy in the South China Sea.

Although this study was conducted during a low flow season (April 2007) representing <5% of the annual outflow for 2007, extrapolating DOC export to the annual averages was difficult. We could only estimate seasonal export of DOC from the Lingdingyang Bay to the shelf area using Eq. (2).

$$\begin{aligned}\text{DOC export} &= \text{DOC input} - \text{DOC removal}\\ &= Q \times C_{in} - Q \times C_{in} \times \text{removal portion}\end{aligned} \quad (2)$$

Where Q is the freshwater discharge rate, C_{in} is the input DOC concentration (236 μmol L^{-1}) to the Lingdingyang Bay, and removal portion is the percentage of DOC removal in the Bay (25%).

Accordingly, the low flow seasonal flux of DOC into the continental shelf area from the Lingdingyang Bay was estimated as 5.3×10^8 g C d^{-1}, using a seasonal fresh water discharge rate of 5420 m^3 s^{-1} (China NWRBH, 2008), and assuming that Lingdingyang Bay receives 53% of the fresh water input (PRWRC/PRRCC, 1991). Similarly, the inputs of TCHO and TAA to the Lingdingyang Bay were 63 μmol C L^{-1} and 46 μmol C L^{-1}, respectively. The removal portions of TCHO and TAA in the Bay were 59% and 48%, respectively. So the fluxes of TCHO and TAA were estimated as 7.8×10^7 g C d^{-1} and 2.1×10^7 g N d^{-1}, respectively.

5. Conclusions

This study suggested that sewage inputs were the major sources of DOC in the upper reach of the Pearl River estuary. This portion of organic matter was highly biodegradable by heterotrophic bacteria. DOC concentrations had a non-conservative behavior with salinity during our observation at a low river flow condition, indicating a net consumption of this labile organic matter in the upper reach and the low salinity region of the Pearl River estuary. In the upper reach, microbial degradation was recognized as the major process controlling the DOC removal. This heterotrophic biodegradation of organic matter coupled with nitrification of ammonium supported the severe oxygen depletion in the upper estuary. In the mixing zone, microbial degradation was one of important processes controlling the behavior of DOC, which accounted for ~31% of total DOC removal. Other processes were also important reasonable for DOC removal. In the lower estuary, the heterotrophic removal almost balanced by the autotrophic production resulted in a linear distribution of DOC with salinity. Organic composition changed rapidly along the estuary, showing a selected removal of carbohydrates and amino acids within the DOC pool in the upper reach and mixing zone, and an autotrophic source of PCHO in the lower estuary, which gave an insight into the DOC estuarine process.

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