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Sources and transport of organic carbon from the Dongjiang River to the Humen outlet of the Pearl River, southern China

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Abstract: Transport of organic carbon via rivers to estuary is a significant geochemical process in the global carbon cycle. This paper presents bulk total organic carbon (TOC) from the Dongjiang catchment to the adjacent Humen outlet, and discusses the applicability of $\delta^{13}C$ and ratio of carbon to nitrogen (C/N) as indicators for sources of organic matter in the surface sediments. Survey results showed that organic carbon concentration in summer were higher than in the winter. An elevated trend of TOC occurred along the river to the Humen outlet in both surveys, and the highest mean values of dissolved and particular organic carbon (DOC~279 μmol L^{-1} and POC~163 μmol L^{-1}) were observed in the urban deltaic region in summer flood flow. Winter samples had a wide range of $\delta^{13}C$ and C/N ($\delta^{13}C$ –24.6‰ to –30.0‰, C/N 4–13), and summer ones varied slightly ($\delta^{13}C$ –24.2‰ to –27.6‰, C/N 6–18). As results suggest that POC in the three zones of upstream-delta-outlet dominantly came from riverbank soil, phytoplankton and agricultural C3 plants in winter, whereas main sources were from the riverbank and mangrove soil in summer. Moreover, anthropogenic sewage inputs had 11% and 7% contribution to POC in the deltaic and outlet. Transport accompanied with seasonal freshwater variation, phytoplankton production and degradation, and removal behavior caused variation of organic carbon concentration. The results also discovered that TOC export bulk in Dongjiang was approximately one quarter of Humen flux in the dry flow, and anthropogenic activity significantly impacted the river export contribution.

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1 Introduction

Transport of organic carbon via rivers is a significant process in global carbon cycling (Ouyang, 2003). Fluxes of organic carbon provide essential information on the rate of continental yield and reflect the biogeochemical processes within catchments. Soil properties, extreme climatic and hydrological events, and anthropogenic activities lead to rapid changes of the amount of organic carbon that is imported into rivers (Spitzy *et al.*, 1991; Hedges, 1992; Hedges *et al.*, 1997). The rivers are not passive water pipelines but are active components of the global carbon cycling that store terrestrially derived carbon in river sediments and release CO_2 emissions into the atmosphere (Cole *et al.*, 2007). Loss of terrestrial organic matter delivered by the upper rivers play a key role in global carbon cycling (Saliot *et al.*, 2002). Geochemical processes include biodegradation, flocculation, phytoplankton production (Abril *et al.*, 2002; He *et al.*, 2010), and removal behavior transform and vary river organic carbon over time and space (Jiao *et al.*, 2008). Human activities also influence these transformations, especially in the deltaic and coastal regions (Gao *et al.*, 2008; Jia *et al.*, 2013). Moreover, total organic carbon (TOC) of natural river origin, composed of dissolved organic carbon (DOC) and particulate organic carbon (POC), can be used as an indicator of water quality and organic contamination (Wu *et al.*, 2007; Ni *et al.*, 2008). Therefore, quantifying riverine inputs of TOC is crucial for better understanding the biogeochemical processes within catchments and for assessing the variation in transport of organic carbon from the upper mountain rivers to downstream deltaic regions.

Dongjiang River, Beijiang River, and Xijiang River are three main tributaries of the Pearl River which is the second longest river in China and the 13th longest river in the world. Approximately 53% of the Pearl River runoff empties into the Lingdingyang Bay through the eastern four outlets (PRWRC/PRRCC, 1991), namely Humen, Jiaomen, Hongqimen and Hengmen (Figure 1). As the upper Pearl River channel, the Humen outlet receives all of the Dongjiang freshwater, 60% of the Beijiang discharge, and little of the Xijiang. The recent research including the distribution and source of organic matter in the Pearl River, has been focused on estuarine and coastal areas outside the shelf of the South China Sea (Cai *et al.*, 1990; Zhang *et al.*, 1999; Yin *et al.*, 2001; Yin *et al.*, 2004; Callahan *et al.*, 2004; Chen *et al.*, 2004; He *et al.*, 2004; Hu *et al.*, 2006). Yu *et al.* (2010) discussed the applicability of $\delta^{13}C$ and C/N as indicators of the source of organic matter in upstream channels and estuarine regions. While previous research on the three tributaries has mainly focused on TOC in the upper-mountain rivers, the bulk of organic matter and source from catchment to estuary are not well known (Hu *et al.*, 2006; Gao *et al.*, 2002; Wei *et al.*, 2003; Tao *et al.*, 2011; Sun *et al.*, 2010). Dongjiang covers areas of subtropical monsoon climate with intense continental erosion and has been disturbed deeply by anthropogenic activities in the last two decades, such as riverbed sand mining (Zhang *et al.*, 2007), in-stream damming and basin reclaim (Zhang *et al.*, 2009; Bai *et al.*, 2011), and anthropogenic nutrients inputs, especially in estuarine city groups (Hu *et al.*, 2006). Such events could be an important trigger for coastal environmental problems and could lead to variations in river organic carbon. This paper provides an investigation for bulk of organic carbon and its source in upstream-delta-outlet areas in two surveys, and aims to discover the river transport variation characteristics and flux export to the Humen outlet under human disturbance.

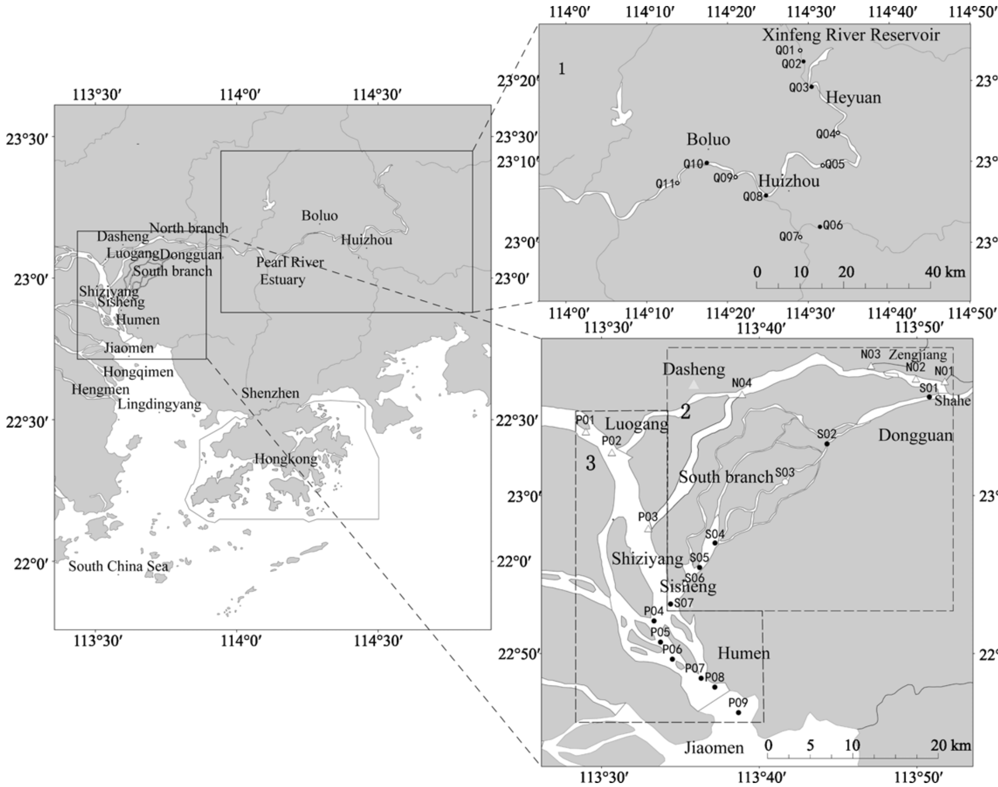

Figure 1 Map showing the sampling stations in the Dongjiang upper reach (zone 1), delta (zone 2, 20–60 km away from the Humen outlet) and Humen outlet (zone 3) in November 2009 and June 2010. Zone 2 is the upper boundary of the estuary tide in winter.

2 Materials and method

2.1 Study area

The Dongjiang catchment (22°38′–25°14′N, 113°54′–115°52′E) is located in the northeast of the Pearl River Delta (Figure 1). There are areas about 35340 km^2, 23540 km^2 in Guangdong Province. The catchment has a hot, humid, and rainy subtropical climate. There are about 1757.1 km^2 of severe soil erosive areas located mainly in the low-mountain granite hilly region. The vegetation type is mostly C3 covers but also includes C4 vegetation (Wei *et al*., 2010). With the destruction of forests in recent decades, grasses and broad-leaved forest have been replaced by sparse grass slopes and farmland in the upper reach (Wei *et al*., 2004). Vegetation covers in the Dongjiang catchment decreased from 42.1% in 1990 to 37.2% in 1999.Grasslands and bare soils accounted for 13.8% and were mainly distributed in the upper reaches. Farmland accounted for 9.7% and was distributed in the middle-stream region (SYG, 2000).

The downstream deltaic region is surrounded by a number of metropolises such as Guangzhou, Shenzhen, Huizhou and Dongguan. Up to 5.7×10^9 m^3 domestic waste and

2.6×10^9 m^3 industrial effluent were discharged into the Dongjiang River (Bai *et al*., 2011; He *et al*., 2010; STY, 2005). The Boluo hydrological station was the upper boundary of estuary tide. The monthly water discharge recorded in Boluo in June 2010 accounted for 38% of the total annual discharge, and the discharge rate (~1920 m^3/s) was 6.6 times that in November 2009 (http://www.zwsw.gov.cn). Additionally, the sediment loads were a similar case. The sea water intrusion can reach back to the Dongjiang river delta in low-flow season, whereas it only reaches the Humen outlet during flood-flow periods.

2.2 Sampling and analyses

Samples of river organic matter include seasonally collected DOC, POC and other hydrochemical settings (Figure 1). A total of 92 samples covering three zones of upstream-delta-outlet areas were collected at 35 stations in the winter dry- flow (29th, November 2009) and 40 stations in the summer flood (9th, June 2010), respectively. The monthly precipitation at Boluo (Q10) and Sisheng (S07) were 42 mm and 49 mm in November 2009, and 171 mm and 415 mm in June 2010, respectively. According to seasonal characteristics, most of the stations had two seasonal samples. Some stations in the Dongjiang northern branch were involved in the previous survey with few samples. Water samples were all collected from the surface (0.5 m below) in three zones, and then from the middle layer and 1 m above the bottom in zone 2 and zone 3 due to deep water level. Salinity, temperature, dissolved oxygen (DO), Chl-a and turbidity were also monitored using an YSI®6600 VⅡ multi-parameter, which was calibrated daily. In the calibration process, all parameters had to be within 10% of the calibration standard value. Water samples were collected using a 2.5 L Go-Flo sampler and 5 L Niskin bottles. Samples were frozen immediately at −4°C until laboratory analysis. Sub-samples for DOC and organic compounds were obtained by filtration of the water samples through pre-combusted 0.7 μm GF/F filters, and were collected into 40 mL pre-combusted brown glass vials (Wang *et al*., 2004).

TSS (total suspended sediments) was measured by filtering a volume of water through pre-weighed 0.7 μm GF/F filters. The sampling volume was determined based on TSS concentration. The volume used for samplings of upper reach and deltaic region were 2000 mL and 300–400 mL in flood-flow condition, and 2500 mL and 500–750 mL in dry-flow condition, respectively. POC was analyzed on a Perkin Elam 2400IICHS/O elemental analyzer after removal of carbonate with HCl fumes for 24 h. DOC was determined using high-temperature catalytic oxidation techniques and a Shimadzu TOC-VCPH TOC analyzer. The uncertainty of the DOC concentration range was 2%–3% for replicated analyses.

The isotopic ratios of POC are expressed as $\delta^{13}C$ in delta notations against the references of PDB, in units of per mille (‰). After removing carbonate by HCl , the $\delta^{13}C_{POC}$ was measured on an EA-continuous flow isotope ratio mass spectrometer (Flash EA 1112 Series—Finnigan Delta Plus XP). The samples were combusted in an elemental analyzer and the combustion products (CO_2) were introduced into an isotope ratio mass spectrometer for determination. The analytical precision was better than 0.2‰ for $\delta^{13}C$. The weight ratio of total organic carbon (TOC %) to total nitrogen (TN %), giving C/N, is usually measured alongside $\delta^{13}C$ and helps to distinguish carbon sources. The TOC and TN contents of bulk POM were performed on an elemental analyzer (VARIO EL III) with analytical precisions better than ±5%. All these measurements were performed at the State Key Laboratory of Environmental Geochemistry, Institute of Geochemistry, Chinese Academy of Sciences, Guiyang.

3 Results

Longitudinal sections across the estuary illustrate variations of the hydrochemical properties in the two seasonal surveys (Figure 2). The plots of the relation of organic carbon with Chl-a, TSS and salinity are also analyzed. Mean values of samples in the three zones are listed in Table 1.

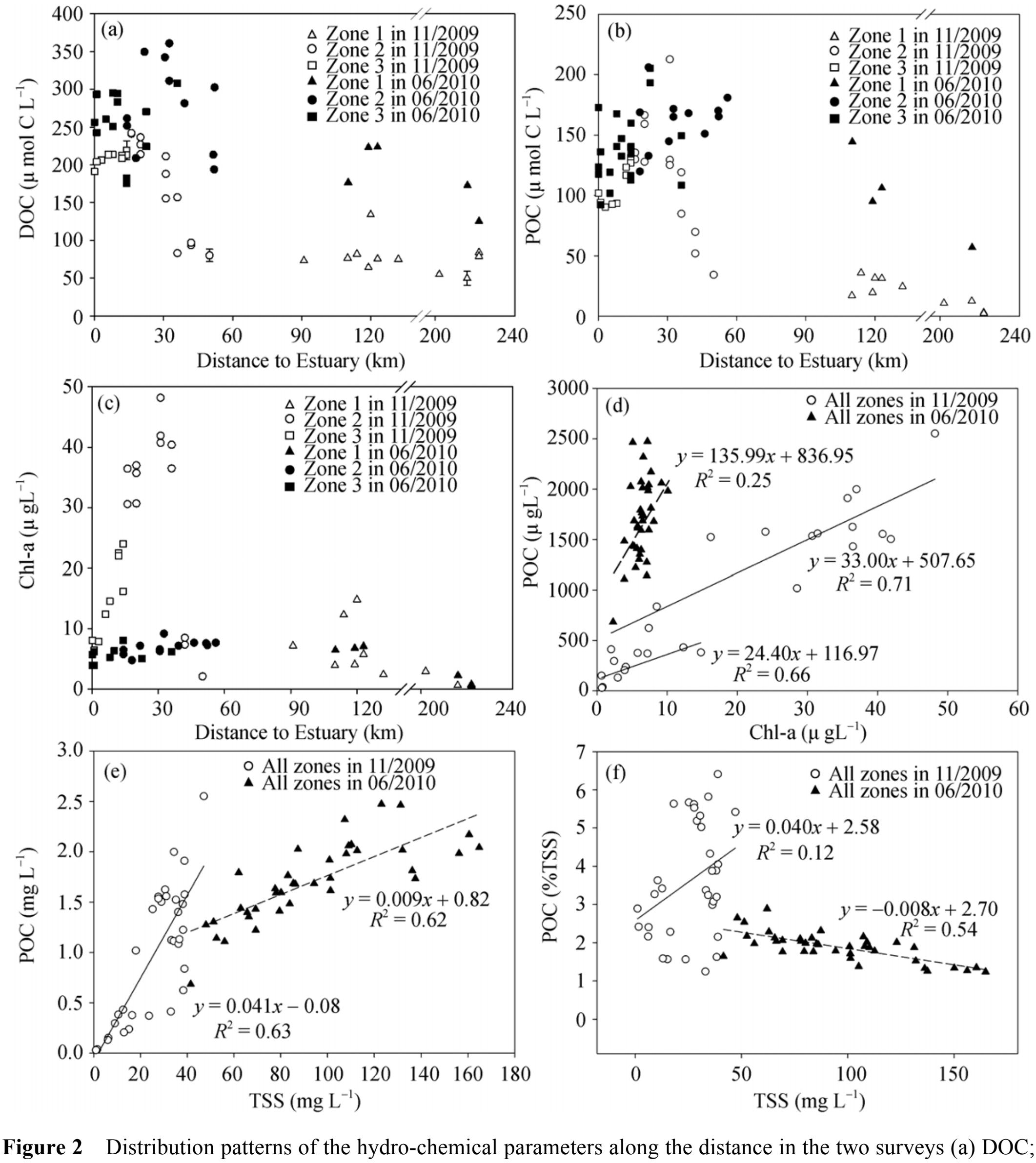

Figure 2 Distribution patterns of the hydro-chemical parameters along the distance in the two surveys (a) DOC; (b) POC; (c) Chl-a; and relations between (d) POC and Chl-a; (e) TSS and POC; and (f) TSS and POC%

Table 1 Mean values and standard deviation of the samples in the river catchment, delta and Humen outlet

Winter									
Zone	DOC	POC	δ^{13}C	C/N	Chl-a	TSS	pH	Sal	DO
Zone 1	77±22	97± 12	–26.3±1.1	6.5±1.8	5.1±4.7	10.7±3.8	7.0±0.2		8.3±0.4
Zone 2 (Southern)	178± 62	120± 45	–27.4±0.7	8.6±1.5	31.4±10.8	39.9±5.8	6.8±0.2	5.1±2.9	8.8±1.0
Zone 3	207± 7	102± 13	–25.2±0.6	9.6±1.6	9.3± 3.0	31± 5.6	6.8±0.06	12±2.6	7.9±0.6
Summer									
Zone	DOC	POC	δ^{13}C	C/N	Chl-a	TSS	pH	Sal	DO
Zone 1	184±41	101±36	–25±0.8	6.6±0.9	4.7±3.0	62.8±6.8	6.0±1.5		7.1±0.2
Zone 2 (Southern)	279± 62	163±25	–26.6±1.0	10.7±1.9	7.3± 1.7	105.5±7.2	4.7±1.3	0.7±0.3	7.2±1.4
Zone 2 (Northern)	273± 91	153±23	–25.5±0.5	8.3±1.3	7.2± 0.7	108.9±11	4.4±0.8		7.1±1.0
Zone 3	256± 39	138± 31	–25.8±0.5	13.1±2.1	5.9± 0.9	85.6±3.3	5.3±1.2	3.0±0.5	7.1±0.2

DOC, POC concentrations in μmol C L^{-1}, Chl-a in g L^{-1}, TSS (total suspended sediments) in mg L^{-1}, Sal (salinity), DO (dissolved oxygen) in mg L^{-1}

3.1 Distribution of DOC

As shown in Figure 2a, DOC values in summer were all larger than in the winter. An increasing trend of DOC occurred in both seasons along the river. The ranges varied widely, and the highest DOC values were in the downstream delta. The average DOC has lower value and narrow range in zone 1 (average of 77±22 μmol L^{-1} in winter, 184±41 μmol L^{-1} in summer) compared to in zone 2 (average of 178±62 μmol L^{-1} in winter, 279±62 μmol L^{-1} in summer) (Table 1 and Figure 2a). In the Humen outlet, the average DOC varied from 207 to 256 μmol L^{-1} in the two seasons. The summer surface DOC in the Humen outlet (P09, 256 μmol L^{-1}) was greater than in the Guangzhou channel (P01, 149 μmol L^{-1}).The case demonstrates that Dongjiang had an important contribution to the Humen outlet. Previous studies reported the river outlet DOC to be about 188 μmol L^{-1} in November, 2002 (Callahan *et al.*, 2004) and 202 μmol L^{-1} in March, 1987 (Cai *et al.*, 1990).

3.2 Distribution of POC

POC are also elevated and widely variable along the river (Figure 2b). As Table 1 shows, average POC have lower value in zone 1 (average of 97±12 μmol L^{-1} in winter, 120±45 μmol L^{-1} in summer) compared to in zone 2 (average of 101±36 μmol L^{-1} in winter, 163±25 μmol L^{-1} in summer), and also lower than average DOC. The lowest DOC (approximately 50 μmol L^{-1}) and POC (approximately 85 μmol L^{-1}) were observed in Heyuan (Q03) in the winter. In the deltaic region (zone 2), the mean POC value hit 120 μmol L^{-1} in the winter. High TSS (approximately 150–160 mg L^{-1}) together with high POC (160–180 μmol L^{-1}) occurred at the entrances of zone 2, including Shahe (S01) and Zengjiang (N01). In the Humen outlet, POC concentration had dropped to 114 μmol L^{-1} in dry flow and 138 μmol L^{-1} in flood flow, most likely due to dilution by other branches.

3.3 Chl-a, TSS and salinity

In contrast with high organic carbon in the summer samples, Chl-a concentrations in the winter samples had high values and ranged widely from 5.1–31.4 μg L^{-1} (Figure 2c). Taking S03 with the maximum Chl-a as an example, the value was 41.9 μg L^{-1} in the winter and only 3.9 μg L^{-1} in summer. Positive correlations (POC (μg L^{-1}) = 24.40× Chl-a (μg L^{-1}) + 116.97 (R^2 = 0.66, p < 0.001, n =11) and POC (μg L^{-1}) = 33 × Chl-a (μg L^{-1}) + 507.65 (R^2 = 0.71, p < 0.001, n = 15) (Figure 2d) were found in the Dongjiang upstream and delta in the winter of 2009.

Fluctuations of the Dongjiang discharge vary seasonally and result in changes in Chl-a, TSS and organic carbon. With the flood discharge, mean TSS of summer samples varied within 62.8–108.9 mgL^{-1} and were higher than in the winter. Along longitudinal sections, POC concentration had a positive correlation with TSS, as shown in Figure 2e (R^2 = 0.63, p<0.001, n=35 in November 2009, and R^2 = 0.62, p<0.001, n=40 in June 2010). The percentage content of POC (POC %) in TSS was approximately 4.11% in winter and 0.94% in summer (Figure 2f), suggesting a relatively complex source and a simple source for river POC, respectively. A similar comparable POC% was found in the Pearl River, which was 4.69% in winter and 1.09% in summer (He *et al*., 2010). Moreover, the decreased POC% with increasing TSS concentration for samples in the summer flood flow can be explained by several possible mechanisms (Meybeck *et al*., 1999; Ludwig *et al*., 1996; Gao *et al*., 2007; Balakrishna *et al*., 2005). Firstly, a high TSS concentration meaning reduced light availability can restrict the growth of phytoplankton. Secondly, a high surface runoff leads to intensified erosion in the deeper soil horizons with lower contents of organic carbon.

As shown in Figure 3, DOC and POC varied with salinity from delta to the Humen outlet. DOC increased with the rising salinity gradient until salinity more than 8.5 (R^2 = 0.95, p<0.001, n=11), and decreased with salinity range of 8.5–16.7 (dashed line R^2=0.97, p<0.001, n=5). The sudden decrease is likely due to dilution by the sea water intrusion and the organic carbon removal behavior (salinity approximately 12) (Figure 3). The similar DOC removal behavior was reported in the estuaries (Wang *et al*., 1998; He *et al*., 2010). A similar pattern of DOC was not seen in June 2010 due to less sea water intrusion.

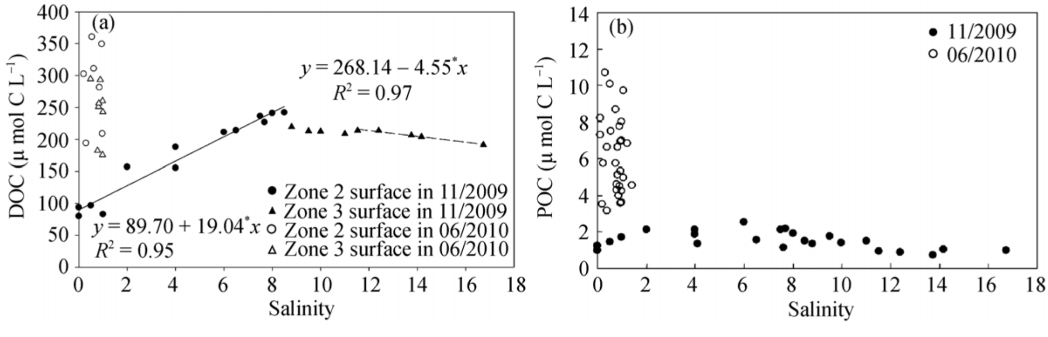

Figure 3 Relation of DOC (a) and POC (b) with the salinity gradient in two surveys

3.4 $\delta^{13}C_{poc}$ and C/N

The carbon isotopic compositions of the river particulate organic matter (POM) are listed in

Table 1 and Figure 4. The average $\delta^{13}C_{poc}$ from zone 1 to zone 3 were –25.2‰, -26.3‰, and -27.4‰, respectively in winter, while in summer, these average were –25.8‰, –25‰, and –26.6‰, respectively. The average C/N increased along the river in both seasons. Almost all of the $\delta^{13}C$ and C/N in summer were greater than in winter. Similar $\delta^{13}C$ and C/N results in the winter and summer seasons were found by Dai *et al*. (2008) and Yu *et al*. (2010). The distinct C/N characteristics in the three zones varied widely with considerable overlap, indicating different sources.

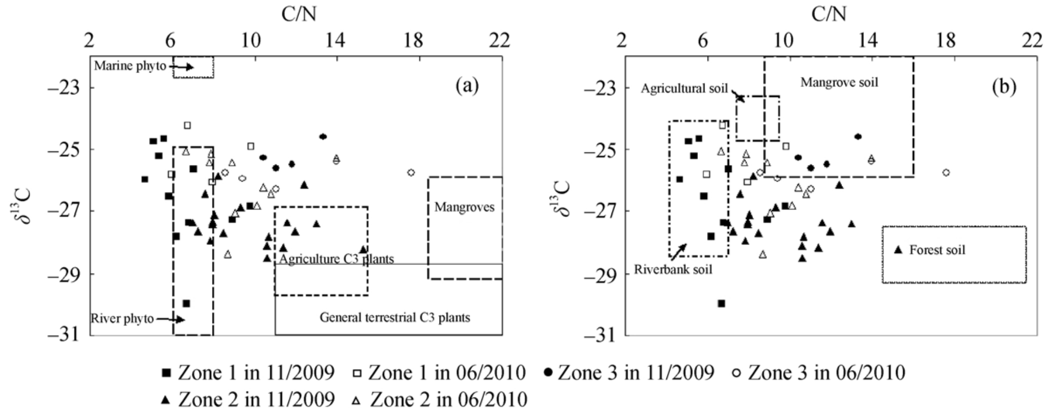

Figure 4 Plots of $\delta^{13}C$, C/N with phytoplankton, terrestrial plants (a) and soils (b)

3.5 Flux in the two seasonal cruises

The seasonal flux of DOC and POC of the Dongjiang tributary exported to the Humen outlet can be estimated using Formula (1).

$$\text{Flux} = Q \times C \tag{1}$$

where Flux is the river seasonal flux export rate (in 10^8 g C d^{-1}) of DOC or POC with an input concentration C (in g m^{-3}) to Humen, and Q is the freshwater discharge rate (m^3 d^{-1}). The study was conducted in Dongjiang (Q approximately 289 m^3/s in winter, and 1920 m^3/s in summer flood), and discharge in April 2007 (Q ~947 m^3/s) together with the organic carbon (He *et al*., 2010) were used to estimate the flux in spring. The average DOC and POC of the southern branch outlet (S07) and northern branch outlet (P02) in zone 2 were inputted as C for flux estimation of Dongjiang. As results shown in Table 2, the seasonal DOC flux rate of the Dongjiang is estimated as 1.82×10^8 g C d^{-1}, 4.69×10^8 g C d^{-1}, and 0.66×10^8 g C d^{-1}, respectively, in normal discharge (April 2007), flood flow (June 2010) and dry flow (November 2009), which held 34%, 21%, and 25% of the total Humen flux with a river freshwater ratio of 33%, 23%, and 22%. The corresponding seasonal POC flux hit 0.92×10^8 g C d^{-1}, 3.02×10^8 g C d^{-1}, and 0.38×10^8 g C d^{-1}, and its contribution was approximately 32%, 28% and 27%, respectively.

As mentioned above, approximately 53% of the total discharge of the three tributaries empties into the Lingdingyang Bay through the four eastern outlets (PRWRC/PRRCC, 1991). The Humen outlet is the dominant river runoff outlet (~66%) (Cai *et al*., 2004) and has a similar organic matter loads to the Jiaomen, Hongqimen and Henmen (Ni *et al*., 2008; He *et al*., 2010). Therefore, the flux export ratio of Humen outlet was estimated by the concentration in P09 and 53% of the total discharge of the three tributaries. When water discharge (Q) was estimated as 2871 m^3/s, 8544 m^3/s, and 1336 m^3/s in April 2007, June 2010 and November 2009, respectively, the corresponding seasonal TOC flux rate of the Humen outlet was estimated as 8.16×10^8 g C d^{-1}, 33.64×10^8 g C d^{-1}, and 4.07×10^8 g C d^{-1}. As a matter of fact, the results are also representative of the flux of eastern four outlets.

Table 2 Comparison of organic carbon export flux rate in Dongjiang, Humen, and other rivers

River	Month, year	Freshwater discharge (m^3/s)	DOC (10^8 g C d^{-1})	POC (10^8 g C d^{-1})	TOC (10^8 g C d^{-1})	DOC/POC	Study area	Distance to outlet (km)	Reference
Yangtze River	April, 1997	27970	24.66	60.27	84.93	0.41	Nantong	188	Wu *et al.*, 2007
Yangtze River	June, 1998*	78202	150.68	246.58	397.26	0.61	Datong	400	Duan 2000
Yellow River	1989	963	15.62	61.92	77.54	0.25	Kenli		Cai *et al.*, 1993
Pearl River	March, 1987	4136	14.70	8.50	23.20	1.59	estuary		Han *et al.*, 1990
Xijiang River	June, 2005*	18328	2.22	5.22	7.44	0.43	Gaoyao	240	Sun *et al.*, 2007
Xijiang River	March, 2005	1520	2.08	0.24	*2.32*	8.67	Gaoyao	240	Sun *et al.*, 2007
Beijiang River	October, 2000	1300	1.92	0.36	*2.28*	5.34	Hekou	140	Wei, 2003
Dongjiang River	November, 2000	395	0.53	0.13	0.66	4.07	Boluo	110	Wei, 2003
Dongjiang River	April, 2007	947	1.82	0.92	*2.74*	1.99	Sisheng	22	He *et al.*, 2010
Dongjiang River	June, 2010*	1920	4.69	3.02	7.71	1.55	Sisheng	22	This study
Dongjiang River	November, 2009	289	0.66	0.38	*1.04*	1.74	Sisheng	22	This study
Humen	April, 2007	2871	5.30	2.86	*8.16*	1.85	Outlet		He *et al.*, 2010
Humen	June, 2010*	8544	22.72	10.92	33.64	2.08	Outlet		This study
Humen	November, 2009	1336	2.65	1.42	*4.07*	1.87	Outlet		This study

*Observed in the flood period. Flux rate of Humen (representative flux of eastern four outlets) is estimated by 53% freshwater discharge of the three tributaries to Humen outlet. The flux of the Pearl River estuary is the total discharge of the three main tributaries exporting into the SCS (South China Sea).

4 Discussion

4.1 Sources and variation of organic matter

Anthropogenic waste is a major source of organic matter in the urbanized watershed (Tucker *et al.*, 1999) and in estuarine rivers, such as the Pearl River estuary and the Danshuei estuary (Hu *et al.*, 2007; He *et al.*, 2010; Liu *et al.*, 2007). Dongjiang is a highly urbanized watershed with its downstream linking to the Humen estuarine. Inputs of waste sewage elevated the river organic carbon and major ions Cl^- and SO_4^{2-} here (Hu *et al.*, 2007; Zhang *et al.*, 2007). As reported in previous study, river and estuarine algae exhibit a rather broad range of stable carbon isotopic values (–22‰ to –28‰) and C/N (approximately 6–8), while typical marine phytoplankton exhibit intermediate $\delta^{13}C$ values (–18‰ to –22‰) and similar C/N values (e.g. Fry and Sherr, 1984; Meyers, 1997; Goni and Thomas, 2000; Jia and Peng, 2003). Moreover, rivers highly contaminated by urban sewage had $\delta^{13}C$ (–22‰ to –25‰) and C/N (7–10) (Wu *et al.*, 2007; Xiao *et al.*, 2010; Griffith *et al.*, 2009, Barros *et al.*, 2010), which have obvious overlay compared to the observed $\delta^{13}C$ and C/N. It is demonstrated that the potential source of algae and sewage input here.

4.1.1 Potential sources and its contributions

As above stated that the organic carbon variations occurred in upstream-delta-outlet, the natural terrestrial background of the river POC, the positive correlation, and the POC/Chl-a value were used to identify the potential sources. Due to far from urban sewage inputs, Heyuan (Q03) in the upstream had $\delta^{13}C$ (–24.7‰), C/N (9.1) and Chl-a 0.7 (μg L^{-1}) values which suggested the main terrestrial contribution. So POC in Q03 (approximately 70 μmol L^{-1}) in winter normal discharge was indicated as the riverine background of Dongjiang. The POC/Chl-a in zone 1 and zone 2 (zone 3) of 24.4 and 33.0 μg C (μg Chl-a)$^{-1}$ were used to estimate the algal-POC, respectively. The contribution of land-derived POC in the upper reach accounted for 73% which was obtained by dividing the natural background value by the average POC. Based on mass balance, the phytoplankton contribution (dividing average algal-POC value by average POC) was estimated as 16%, and the sewage input accounted for 11%. In zone 2, the land-derived POC decreased to 47%, the algal-POC increased to 46%, and the wastes input to POC pool decreased to 7%. It is confirmed that the similar study of average algal-POC contribution in Pear River estuary is 47.21% (Wang *et al.*, 2011).Sewage inputs from urban groups such as Huizhou and Dongguan provided nutrients for the fertility of the algal boom, especially in the low turbidity water of the dryflow. The autochthonous and terrestrial sources are significant for POC here, and the impacts of sewage inputs also cannot be ignored.

4.1.2 Indicator of $\delta^{13}C$ and C/N

Terrestrial organic matter is an important source in Asian monsoon rivers. The $\delta^{13}C$ and C/N of plants and sediment samples in the Pearl River Delta region were examined and reported in the concerned research (Wei *et al.*, 2010b; Yu *et al.*, 2010; Zong *et al.*, 2010). C3 plants are dominant vegetation in the Dongjiang catchment and have lower overall average $\delta^{13}C$ (average of –24.6‰ to –29.7‰) compared to C4 plants (average of –11.7‰ to –12.9‰). The general C3 plants have the lowest $\delta^{13}C$ of –29.9±1.3‰ , followed by the agricultural C3 plants (e.g. rice, lotus and banana) and then mangroves C3 plants, with $\delta^{13}C$ values of –28.2±1.4‰ and –27.1±1.7‰ respectively (Figure 4a). C/N of C3 and C4 plants are widely variable (7.4–61.8 for C3 plants and 8.2–40.3 for C4 plants) and overlap significantly. Moreover, soil samples were divided into four categories: forest soil, riverbank soil, agricultural soil and mangrove soil in the estuarine, depending on the sample locations as well as the dominant vegetation type. As shown in Figure 5b, river autogenously and terrestrial organic matters are the main sources for two seasons.

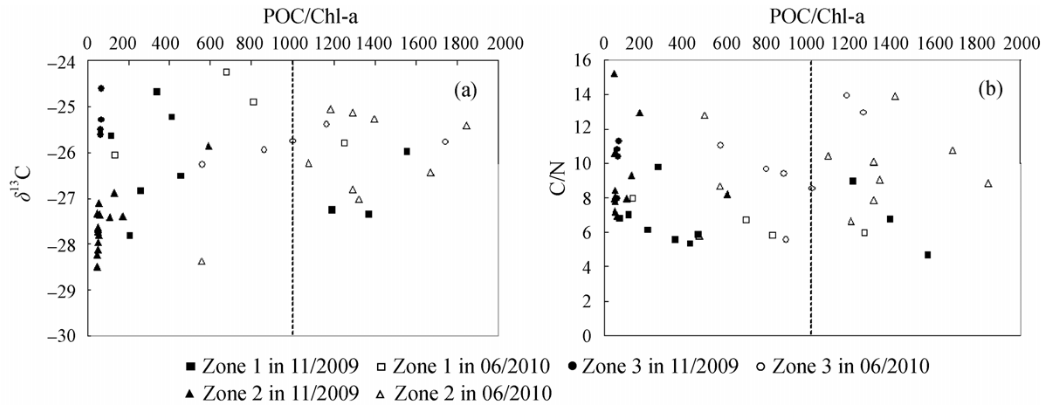

Figure 5 Stable carbon isotope ratio ($\delta^{13}C$) (a) and C/N (b) vs. particulate organic carbon: chlorophyll a ratio (POC/Chl-a)

As is indicated in Figures 4a and 4b, the main sources of the winter samples were from riverbank soil, river phytoplankton and agriculture C3 plants, and mangrove soil, each of which had distinct distribution ranges. There are more positive $\delta^{13}C$ mean values and lower C/N values in the upper reach than in the other zones, which is consistent with the soil erosion characteristics in the upper reaches of Dongjiang River (Wei *et al*., 2010b). A special case of Q7 in one tributary had a high Chl-a of 14.8 g L^{-1} and a low $\delta^{13}C$ value of –30.0‰ with C/N of 6.8, suggested the impact of agricultural nitrogen fertilizer. An average $\delta^{13}C$ of –27.4±0.7‰ and C/N of 8.6±1.5 in the downstream delta indicated two additional sources of agricultural C3 plants and phytoplankton. There are croplands and urban areas distributed along the downstream deltaic region. As estimated above, 46% contribution was derived from river phytoplankton sources in these zones. After entering the Humen outlet, the samples mainly fell into the range of mangrove soils due to the mangrove cover here.

As a result, the summer samples have higher $\delta^{13}C$ and C/N values in the three zones than the winter samples. Variation of the $\delta^{13}C$ was clustered between –24.2‰ and –25.8‰ and C/N of 6.6–13.1, suggested sources of riverbank, agricultural, and mangrove soils by flood flushing. POM in the upper reach still comes from the riverbank and agricultural soils which were brought into the rivers, and mangrove soils in the Humen outlet. River phytoplankton in the downstream contributes relatively little. Compared with Xijiang and Beijiang, more positive $\delta^{13}C$ and C/N in the Dongjiang upstream suggests high intensity soil erosion (Wei *et al*., 2010a). The distinct transport and seasonal variation of organic carbon were highly related to the catchment land use/cover change and downstream urban expansion (Li *et al*., 1997).

4.1.3 Influence on sources of river organic matter

As a matter of fact, carbon isotope measurements alone often cannot identify influence of various sources on the organic carbon pool. Combination of isotopes with other tracers had been considered, such as POC/PN ratios (Goonnea *et al*., 2004), POC/Chl-a ratios (Cifuentes *et al*., 1996), or other biochemical tracers such as lignin-derived phenols (Dittmar *et al*., 2001). The POC/Chl-a ratio reflected the contribution of nonliving sources to the POC (Fogel *et al*., 1993; Cifuentes *et al*., 1996). As Figure 5 illustrates, three winter samples in zone 1 and almost all of the summer samples in zone 2 had POC/Chl-a values more than 1000, high δ^{13}C (approximately of −26±1‰), and high C/N (approximately 12.5±3.5) values. It is suggested comparatively larger contribution of allochthonous detritus rather than river and marine detritus (Cifuentes *et al*., 1996; Bouillon *et al*., 2009).The case thus proved that Heyuan was selected as reasonable terrestrial background to estimate land-POC contribution. Moreover, the other samples with POC/Chl-a less than 1000 might be associated with bacterial degradation and dilution by the local streams with lower POC concentrations, deposition to sediment, and/or autochthonous detritus from phytoplankton production downstream (He *et al*., 2010; Yu *et al*., 2010). As observed in Figure 3, removal of DOC and dilution of POC with low POC/Chl-a and δ^{13}C in the downstream are another important impact of intrusion marine.

Seasonal variations in freshwater discharge resulted in changes of the above geochemical process and thus cause the relative contribution of different sources in the mass balance estimation. The agricultural C3 plants and phytoplankton, and sewage inputs in the deltaic region brought about rich organic carbon. During flood-flow periods, as POC% and δ^{13}C indicated, the leaching and erosion of soil organic matter was dominantly responsible for the increased organic carbon and TSS, also including other anthropogenic organic matter on the riverbank. A similar case has been observed in most of the river systems around the world (Meybeck *et al*., 1999; Balakrishna *et al*., 2005; Gao *et al*., 2007; Sun *et al*., 2007). Identifying the sources, thus, will be helpful for knowing about the variation of organic carbon and its flux that is exported to the SCS.

4.2 Comparison of the seasonal flux

Little estimation of the carbon fluxes in recent years has been published for the Humen outlet. In Table 2, a number of previous reports including the estuaries of Yangtze River, Yellow River, Pearl River and its three tributaries are listed here for comparison. Among the three longest rivers in China, DOC and POC flux of the Yangtze estuary is the greatest (Wu *et al*., 2007). POC flux of Huanghe (Cai *et al*., 1993) and Pearl River (Cai *et al*., 1990) have the second and third one, respectively,and DOC flux of the Pearl River (22.68×10^8 g C d^{-1}) is larger than that of Huanghe (15.62×10^8 g C d^{-1}). Within the three tributaries, Xijiang (Tao *et al*., 2011; Sun *et al*., 2010) and Beijiang (Wei *et al*., 2003) had more river discharge compared with Dongjiang during the observation periods, but have a similar total organic carbon flux (Italics in Table 2) for the three rivers. As calculated above, the TOC fluxes of Dongjiang accounted for one quarter of the Humen outlet and thus indicate similar export contribution from four parts to the Humen outlet, including Xijiang, Beijiang, Dongjiang and Guangzhou channel.

The global POC and DOC inputs are estimated as 170×10^6–195×10^6 tons C/yr and 200×10^6–215×10^6 tons C/yr, respectively (Meybeck *et al*., 1999; Ludwig *et al*., 1996). So the dry and wet seasonal flux proportion of Humen to the worldwide rivers can be estimated using the November and June survey results. It is approximately 0.019% in the dry season and 0.050% in the wet season, so with a mean value of 0.035% of all worldwide rivers exported from the Humen outlet in both seasons. The similar TOC contribution of the Pearl River to the world oceans was reported within a range of 0.2%–0.3%, and that of the Humen outlet to the world oceans is 0.037% (Ni *et al*., 2008).

During the last decades, DOC/POC in the Pearl River and its tributaries (seen in Table 2) was larger than the global average of 1.18 (Ludwig *et al*., 1996), which was different from other Asian monsoon rivers such as Lanyang His in Taiwan (Kao *et al*., 1997), Yangtze (Wu *et al*., 2007), and Huanghe (Cai *et al*., 1990). The dominance of DOC flux over POC flux was a result of the impacts of humans' behaviors. By 2008, more than 300 large- and medium-sized reservoirs with a total capacity of 85.2 billion m^3 have been constructed in the Dongjiang watershed (PRWRC website http://www.pearlwater.gov.cn) and many sewage inputs entered into the rivers. Reservoir building can result in lower turbidity and velocity of freshwater and thus an increased invasion of estuarine water. Together with the anthropogenic effluents, these events accelerated the phytoplankton blooming and changed the riverine inputs and transports as well as the flux and DOC/POC.

5 Conclusions

As the observed result along the Dongjiang catchment to the Humen outlet, there are elevated DOC and POC concentrations which in summer is greater than in winter. The ratios of DOC to POC along Dongjiang were larger than the global average level (1.18), whereas DOC values were notably lower than the global river DOC (average of 479 μmol L^{-1}) (Meybeck, 1982), suggesting deeply anthropogenic impacts in such an Asian monsoon river. In addition, the following conclusions can be drawn as follows:

(1) Terrestrial organic matter, river phytoplankton and anthropogenic sewage inputs were demonstrated to have distinct contributions to the upstream-delta-outlet of the river. Especially in the downstream delta, the land-derived POC decreased to 47%, the algal-POC increased to 46%, and 7% sewage contribution to POC pool is also significant.

(2) $\delta^{13}C$ and C/N further indicated river organic carbon sources were from riverbank and mangrove soil, and river phytoplankton, and agricultural C3 plants in winter while from soils in summer. Analysis of POC/Chl-a with $\delta^{13}C$ and C/N can identify influences on transport of organic carbon by seasonal freshwater variation, phytoplankton production and degradation, removal behavior and thus change TOC flux significantly.

(3) By comparison, there was similar export flux from four parts including Xijiang, Beijiang, Dongjiang and Guangzhou channel to the Humen outlet under normal discharge in the winter survey. The summer flux was increased about 3-fold of the winter one in flood discharge. Significantly, Dongjiang brought into about one quarter of the Humen flux pool which accounted for a proportion of 0.035% of worldwide river exports.

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