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Key Points:

- Isotopic evidence shows a clear decoupling of DOC and DON dynamics
- DOC undergoes substantial removal in the salinity range of 5 to 22
- Estuarine DON dynamics are influenced by both biotic and abiotic processes

Supporting Information:

- Supporting Information S1

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The Sources and Transformations of Dissolved Organic Matter in the Pearl River Estuary, China, as Revealed by Stable Isotopes

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Abstract To investigate the sources and transformation processes of bulk marine dissolved organic matter (DOM), seasonally collected water samples from the Pearl River Estuary (PRE), south China, were analyzed for concentration and stable isotopic ratios ($\delta^{13}\text{C}$ and $\delta^{15}\text{N}$) of DOM. The $\delta^{13}\text{C}$ values clearly indicated a shift of dissolved organic carbon (DOC) sources from terrigenous material in the river to predominantly plankton in the lower estuary. The distribution of $\delta^{13}\text{C}$ during the estuarine mixing, in combination with the notable deviation of DOC concentration, provided strong evidence for a substantial DOC removal in the salinity range of 5 to 22. In contrast to $\delta^{13}\text{C}$, the $\delta^{15}\text{N}$ of DOM exhibits a strong seasonality, implying a clear decoupling of estuarine DOC and dissolved organic nitrogen (DON) dynamics. During dry periods with low river discharge, sewage-derived DON contributed significantly to the riverine loading. While freshwater-saltwater mixing is important in regulating the distribution of DON, the distribution of $\delta^{15}\text{N}$ along the salinity gradient provided strong evidence for active sediment-water interaction and adsorption/desorption processes at the middle to high salinities. During wet periods, severe soil loss and erosion, and/or in situ biological production, adsorption onto suspended particles dominate the riverine DON fluxes, whereas the DON dynamics might be governed by different biogeochemical processes between spring and summer, as reflected by distinct $\delta^{15}\text{N}$ patterns in the estuarine zone. In spring, highly degraded DON originating from soil experienced little further biological alternation during estuarine mixing, whereas there was a tight coupling of DON production and consumption in summer.

Plain Language Summary Isotopic evidence shows a clear decoupling of DOC and DON dynamics in the Pearl River Estuary, south China. DOC undergoes substantial removal in the salinity range of 5 to 22. Estuarine DON dynamics are influenced by both biotic and abiotic processes.

1. Introduction

Dissolved organic matter (dissolved OM, DOM) is often the dominant form of OM transported from land to sea by rivers, but it is considered to be largely refractory and behaved conservatively in many estuaries (Bronk et al., 2007; Seitzinger & Sanders, 1997; Wiegner et al., 2006). DOM is also a carrier of large quantities of carbon (C) and nitrogen (N). However, seawater contains little terrestrial organic carbon (OC) signal, as evidenced by the $\delta^{13}\text{C}$ of bulk dissolved OC (DOC) in the ocean, which suggests that terrestrial OC must undergo rapid removal and decomposition during estuarine mixing. Moreover, recent studies have demonstrated that a considerable portion of dissolved organic nitrogen (DON) is bioavailable to algae and bacteria, including both low-molecular-weight (LMW; <1 kDa; e.g., amino acids and urea) and high-molecular-weight (HMW) components (>1 kDa; e.g., humic substances) (Berman & Bronk, 2003; De Galan et al., 2004; Veuger et al., 2004; G. Zhang et al., 2015). Perhaps more importantly, some DON compounds could be the main source of N supporting algal bloom development and growth, especially for harmful algal bloom species such as dinoflagellates and cyanobacteria (Altman & Paerl, 2012; Bronk et al., 2007; Fagerberg et al., 2009). An understanding of the sources and cycling processes of DOM in estuaries is therefore critical for constraining local C and N budgets and for evaluating the role of estuaries in regulating C and N fluxes between land and sea.

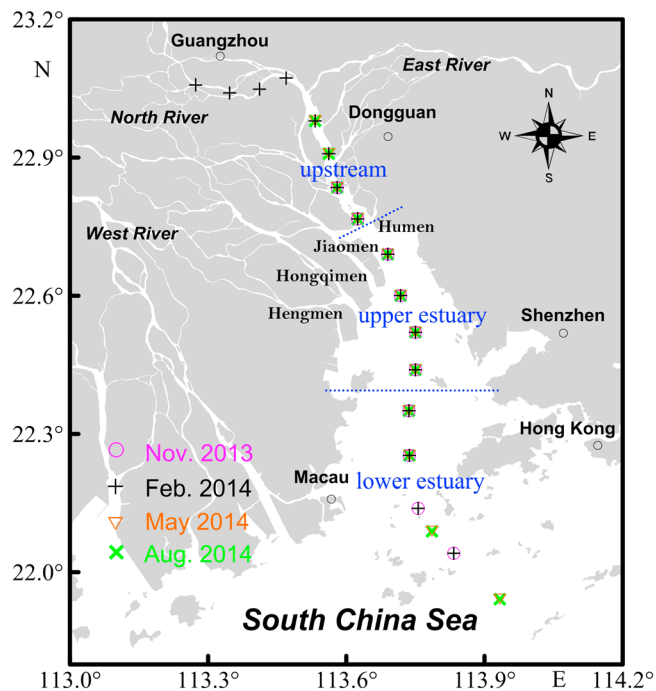


Figure 1. Map of the Pearl River estuary showing sampling stations for all seasons. Three zones are divided based on the geographic scope, that is, upstream, upper estuary, and lower estuary.

However, DOM inputs to the estuary come from multiple sources, including allochthonous sources (e.g., terrestrial OM from river input, runoff from land, domestic sewage, and atmospheric deposition) and autochthonous sources (e.g., in situ phytoplankton and bacteria production, and grazer input) (Berman & Bronk, 2003). In shallow estuarine systems, DOM released from benthic sediments can be an important contributor to the overlying water column (Burdige & Zheng, 1998, and references therein). Moreover, during the complex mixing dynamics within estuaries, DOM can be affected by numerous biotic and abiotic processes in response to the strong physiochemical and biological gradients from rivers to oceans. These processes mainly include photochemical oxidation, bacterial degradation, phytoplankton uptake, and adsorption/desorption from suspended particles (Bushaw et al., 1996; J. Chen Li, Yin, & Jin, 2004; Hedges & Keil, 1999; Veuger et al., 2004). Accordingly, quantification of DOM sources and understanding the biogeochemical processes controlling the DOM distributions in estuaries are challenging, due primarily to the large number of complex and overlapping interactions between sources and sinks.

More than concentration data alone, C and N stable isotope ratios ($\delta^{13}\text{C}$ and $\delta^{15}\text{N}$) can offer powerful insights into the sources and turnover processes of DOM in complex estuarine and coastal waters (Bauer & Bianchi, 2011; L. Guo et al., 2003; X.-C. Wang et al., 2004). In general, the $\delta^{13}\text{C}$ characteristics of DOM from fresh water and seawater are distinct, with much heavier $\delta^{13}\text{C}$ values for DOM derived from marine phytoplankton (-21‰ to -22‰) than for that of terrestrial origin (-25‰ to -32.4‰) (Bauer & Bianchi, 2011, and references therein). The $\delta^{15}\text{N}$ values of DOM can provide further information on the sources and cycling mechanisms of DON in estuarine and marine environments, as there can be distinct isotopic fractionation and enrichment processes during production, transformation, and degradation pathways (L. Guo et al., 2003; Knapp et al., 2011, 2012; X.-C. Wang et al., 2004). For example, $\delta^{15}\text{N}$ -enriched DON moieties are likely to be selectively adsorbed onto suspended particulates, especially in the turbidity maximum zone (Schlarbaum et al., 2010), whereas there is a preferential loss of lighter $\delta^{15}\text{N}$ compounds during DON decomposition (L. Guo et al., 2003; Knapp et al., 2012).

The Pearl River Estuary (PRE) is a bell-shaped subtropical estuary in south China, located on the northern shelf of the South China Sea (Figure 1). It has a surface area of $2,000\text{ km}^2$ and a mean water depth of 4.8 m (ranging from 4 to 20 m). It receives freshwater discharge from the Pearl River (including the west, north, and east rivers), and is the second largest river system in China in terms of annual water discharge. The region has an East Asian climate with hot, wet summers and cold, dry winters, with about 80% of the total freshwater discharge occurring between April and September. The residence time of water in the estuary is estimated to be 2–5 days in the wet season and 2 weeks in the dry season (Dong et al., 2006; Yin et al., 2000). Wind stress is an important mixing force during dry periods and plays a significant role in sediment resuspension and the subsequent OM and nutrient cycling (L. Zhang et al., 2013). Due to the growing urbanization and intense agricultural activities in the Pearl River delta region, the inputs of terrestrial OM and nutrients into the PRE have increased markedly in past decades, causing frequent cultural eutrophication and harmful algal blooms (Harrison et al., 2008). Each year, the Pearl River carries 31.7×10^9 mol DOC and 6.9×10^9 mol DON into the northern South China Sea (Lu et al., 2009; Ni et al., 2008).

In contrast to dissolved inorganic C and inorganic N, less work has been conducted to determine the sources and cycling processes of DOM in this hydrodynamic complex estuary, and even fewer studies have investigated its potential role in estuarine N cycling. Limited concentration-based studies have reported significant DOC removals and DON additions in the mixing zone of the PRE (Callahan et al., 2004; Lin et al., 2004; X.-W. Wang et al., 2003). He et al. (2010), based on in situ incubations, suggested that the DOC removal within the estuary can be attributed to microbial degradation (31%) and other processes such as flocculation and aggregation (69%). More recent studies have suggested that a significant fraction of the DON pool is bioavailable

(~15.5%) (X. Li, Xu, et al., 2016) and that DON can even act as an important source of N to maintain harmful algal blooms (*Cochlodinium geminatum*) in the PRE (Pang et al., 2015). However, debate exists concerning the sources and transformations of DOM (especially DON) in this subtropical estuary, where sources and sinks can act simultaneously in combination with intensive physical mixing. For example, there seems to be disagreement about the significant bioavailability of DOC and DON and their approximately conservative behavior in this subtropical estuary (He et al., 2010; X. Li, Xu, et al., 2016). The exact reasons for these observations remain to be clarified.

This work uses DOM concentration and isotope data, coupled with other environmental data, to better constrain the sources and cycling processes of DOM in the PRE. It has been suggested that DON could undergo a more rapid turnover than DOC (Hopkinson et al., 1997, 2002); therefore, we are specifically interested in the linkages between DON and particulate nitrogen (PN) pools, both of which may be products of phytoplankton assimilation of dissolved inorganic nitrogen, or in the case of DON, may originate from PN decomposition. Taking into account that the bioavailability of DOM can vary depending on land use (anthropogenic vs. natural sources), climatic patterns (hotter summer vs. cold winter), and seasonally varying physical and biogeochemical processes within the estuary, the cycling processes of DOM are expected to exhibit seasonal variability, which can thus be traced by the isotopic signatures of DOM.

2. Materials and Methods

2.1. Sampling

Sampling was performed during four cruises in November 2013 and February, May, and August 2014, representing the cold and dry period with low water discharge (autumn and winter) and the warm and wet period with high discharge (spring and summer). To obtain the whole salinity gradient from 0 to >30, the sampling locations in the wet season were slightly different from those in the dry season, but we do not expect this difference to cause cruise-to-cruise differences in chemical and biological processes (W. Guo et al., 2015).

At each site, surface water samples (0.5 m below the water surface) for nutrient and DOM analysis were filtered through precombusted (450 °C for 4 hr) glass fiber filters (47 mm, Whatman GF/F) onboard. Filtrates were split into two fractions: one for nutrient analysis (200 ml) was preserved with HgCl₂ and stored in HCl-rinsed polypropylene bottles, and another for DOM analysis (1–2 L) was acidified to pH 2–3 with 2 M HCl and stored at –20 °C in the dark until analysis within 6 months. An aliquot of this acidified filtrate (100 ml) was sampled for quantification analysis of the DOM; the remainder was used for isotopic analysis of the DOM. The filters were wrapped in aluminum foil and frozen immediately for analyses of chlorophyll *a* (*Chl a*) and suspended particulate matter (SPM; Ye et al., 2016).

2.2. Analytical Methods

2.2.1. Environmental Parameters

Temperature and salinity were determined onboard using a conductivity-temperature-depth/pressure unit (miniCTD, Valeport, Devon, UK) that was calibrated before each cruise, with precisions of 0.01 °C and 0.01 for temperature and salinity, respectively. SPM was measured as the weight difference of material retained on the GF/F filter after passing 200–500 ml of water. The dissolved oxygen (DO) concentration was measured by Winkler titration. *Chl a* filters were extracted with 90% acetone at –4 °C in the dark for 24 hr and then measured using the fluorometric method (Parsons et al., 1984). In the laboratory, nutrient concentrations were analyzed on a Lachat QC8500 flow injection autoanalyzer (Lachat Instruments, Loveland, CO, USA) using standard colorimetric methods. Detection limits, estimated as 5 times the standard deviation of the blank concentration, were 0.05, 0.02, and 0.10 μM for nitrate (NO₃⁻), nitrite (NO₂⁻), and ammonium (NH₄⁺), respectively (see Ye et al., 2016).

2.2.2. DOC and DON Concentrations

Concentrations of DOC and total dissolved nitrogen (TDN) were measured via high-temperature oxidation on a total organic carbon analyzer equipped with a TDN module (Shimadzu TOC-L CPH/CPN, Kyoto, Japan). The combustion temperature was set at 720 °C. Ultrapure water (as a blank) and reference standards (1.0 mg/L potassium biphthalate for DOC and a mixture of 0.5 mg/L potassium nitrate and 0.5 mg/L urea for TDN) were injected every fifth sample to check the accuracy of the measurements. The system blank was found to be less than 0.8 ± 0.2 μM (*n* = 10), and blank corrections were applied to the TDN data. Duplicates for each

sample were divided over separate runs, and their results were averaged. The DON concentration ([DON]) was calculated as the difference between TDN and dissolved inorganic nitrogen (the sum of nitrite, nitrate, and ammonium). Propagation of error yields a precision on [DON] measurement of $0.5 \mu\text{M}$. While the certified reference materials (e.g., the deep Sargasso Seawater) used by Sharp et al. (2002) were not available in our laboratory, measurements of deep seawater ($>1,000 \text{ m}$) from the South China Sea (i.e., the South East Asian Time-series Study station) yielded 41.8 ± 3.5 , 39.5 ± 2.0 , and $38.0 \pm 1.7 \mu\text{M}$ for DOC, TDN, and NO_3^- ($n = 3$), respectively. These values are close to the reported values of $43 \pm 3 \mu\text{M}$ for DOC, $38.0 \pm 2.0 \mu\text{M}$ for NO_3^- , and about $1.2 \mu\text{M}$ for DON (Huang et al., 2007; Wu et al., 2003).

2.2.3. Stable Isotope Measurements

Isotopic compositions ($\delta^{13}\text{C}$ and $\delta^{15}\text{N}$) of DOM were measured for all samples according to the solid-phase extraction method (Dittmar et al., 2008). Briefly, DOM was extracted using modified styrene divinyl benzene polymer cartridges (PPL Agilent, USA), rinsed with acidified ultrapure water, dried by flushing with N_2 , and eluted with 6 ml of methanol. The resulting extracts were measured using an isotope ratio mass spectrometer system (DELTA plus XL, Thermo Finnigan, San Jose, CA, USA). The standard deviations associated with duplicate analysis of a sample for DOC $\delta^{13}\text{C}$ and DON $\delta^{15}\text{N}$ were $\pm 0.15\text{‰}$ and $\pm 0.3\text{‰}$, respectively. This method cannot completely isolate the total marine DOM due to the varying adsorption abilities of the complex DOM moieties, but the efficiency is better than or similar to that of other methods (Dittmar et al., 2008, and references therein). Moreover, recent studies have demonstrated that this procedure is efficient in isolating DOM from natural waters (62% of DOC on average) and that the extract is highly representative in terms of DOM characteristics (Y. Li, Harir, et al., 2016; Linkhorst et al., 2017). All samples were corrected for blanks and isotopic fractionation using several standard materials, including glycine, urea, 6-amino caproic acid (ACA), and EDTA, most of which have been used previously for seawater $\delta^{15}\text{N}$ precision and accuracy analyses. For further quality assurance of the results, we measured two in-house standards (glycine and acetanilide) with each batch of samples. The standard deviation for these in-house standards was within the same specification for $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ when DOC and DON concentrations were higher than 50 and 15 μM , respectively.

3. Results

3.1. Environmental Characteristics

Surface water temperature and salinity exhibited strong seasonal variations (Figure 2), with warmer temperature and lower salinity during the wet season relative to the dry season. In general, concentrations of SPM and *Chl a* were higher in the fresh end-members than in seawater on all cruises, and there were clear differences in the SPM-S relationships among seasons (Figure 2). The concentration of SPM was higher in spring than in the other seasons, whereas *Chl a* concentrations were lower in spring. During the dry period, however, elevated SPM concentrations were also observed at the middle to high salinities ($15 < S < 25$), probably due to an additional source of suspended particulates during this period. The DO concentration was relatively low in the freshwater end-member, then increased with increasing salinity (i.e., in the seaward direction). Approaching high-salinity waters ($S > 20$), the DO concentration decreased slightly. In contrast, NO_3^- and NH_4^+ concentrations generally decreased along the salinity gradient, but with significant deviations from conservative mixing at low salinities in all seasons (for more details, see Ye et al., 2016).

3.2. Concentrations of DOC and DON

Concentrations of DOC and DON ranged from 43.3 to 298.3 μM and 7.3 to 92.5 μM , respectively (Figure 3). These are consistent with previous findings for the PRE and adjacent waters (J. Chen, Li, Yin, & Jin 2004; X. Li, Xu, et al., 2016). The concentrations of DOC and DON were found to be relatively high (>160 and $>50 \mu\text{M}$, respectively) in the freshwater; they then declined sharply at an early stage of estuarine mixing ($S < 5.0$), and moderately decreased with increasing salinity. The latter decrease could be attributed mainly to mixing between the fresh and marine end-members. We observed negative deviations along the salinity gradient for both DOC and DON. Moreover, the DON concentration exhibited a strong seasonal variation in freshwater but remained largely constant in coastal waters at salinities of >30 . On average, the concentration of DOC was consistently higher in summer but lower in spring than in autumn and winter, whereas the DON concentration was slightly higher in winter than in the other seasons.

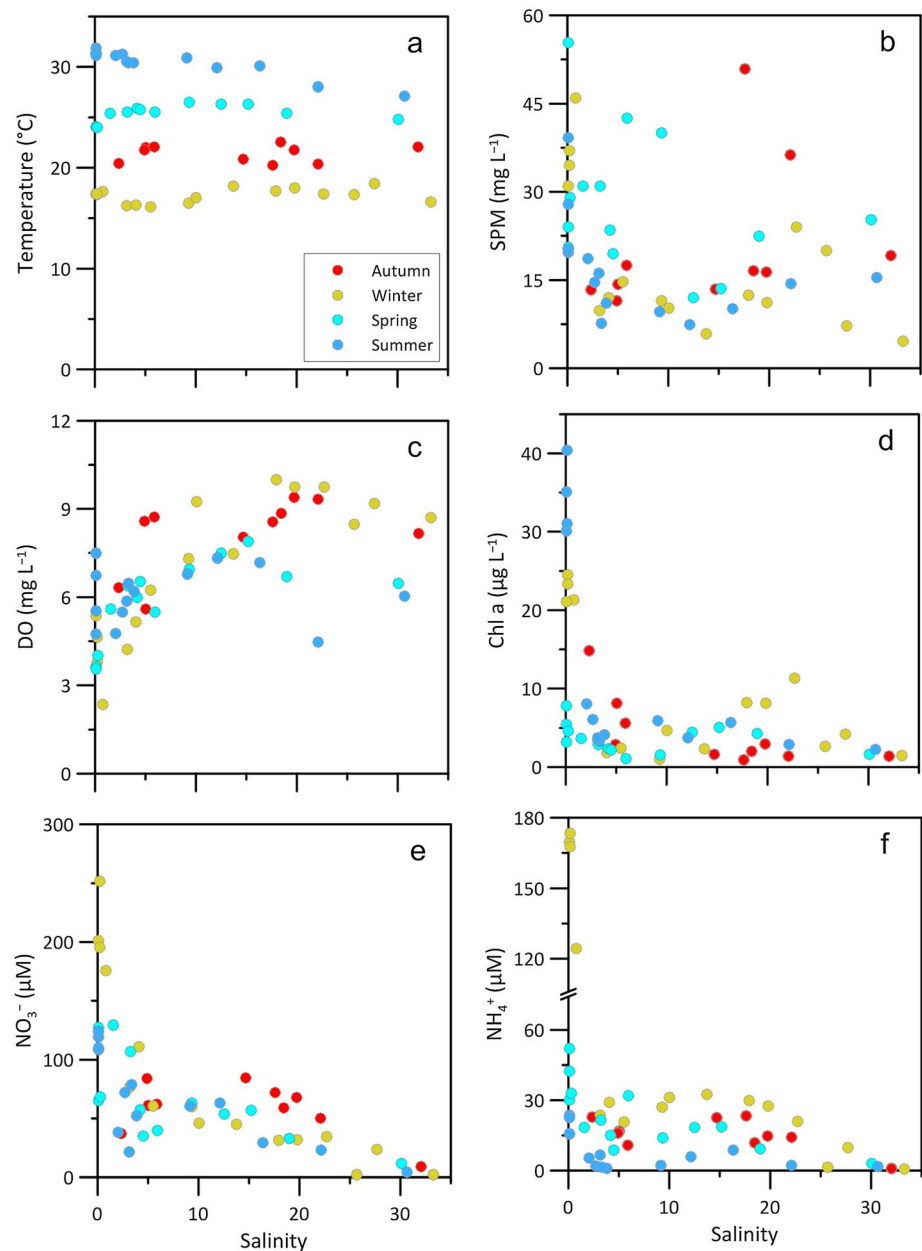


Figure 2. Distributions of (a) temperature, (b) SPM, (c) *Chl a*, (d) DO, (e) nitrate, and (f) ammonium concentrations along the salinity gradient in the Pearl River estuary. Note that SPM, *Chl a*, and some of the nitrate and ammonium data are from Guo et al. (2015) and Ye et al. (2016).

3.3. Isotopic Data

Throughout the entire salinity gradient covered here (from ~ 0 to >30), the stable carbon isotope ratio of DOM ($\delta^{13}\text{C}_{\text{DOC}}$) ranged from -26.9‰ to -22.9‰ and its seasonal variations were subtle (Figure 4). In general, DOM collected from brackish waters (with higher salinities) has heavier $\delta^{13}\text{C}$ signatures than that in rivers. Our data are comparable to previous measurements in other estuaries and coastal systems around the world and are indicative of a shift from terrestrial sources (-25‰ to -32.4‰) to marine phytoplankton (-21‰ to -22‰) dominating the DOM (Coffin & Cifuentes, 1999; Raymond & Bauer, 2001; X.-C. Wang et al., 2004).

The stable nitrogen isotope values of DOM ($\delta^{15}\text{N}_{\text{DON}}$) ranged from -4.9‰ to 4.0‰ in the PRE across all seasons, but their distributions differed among the seasons. In general, the $\delta^{15}\text{N}_{\text{DON}}$ values of samples with high salinities were significantly isotopically enriched relative to those of low-salinity waters during all seasons

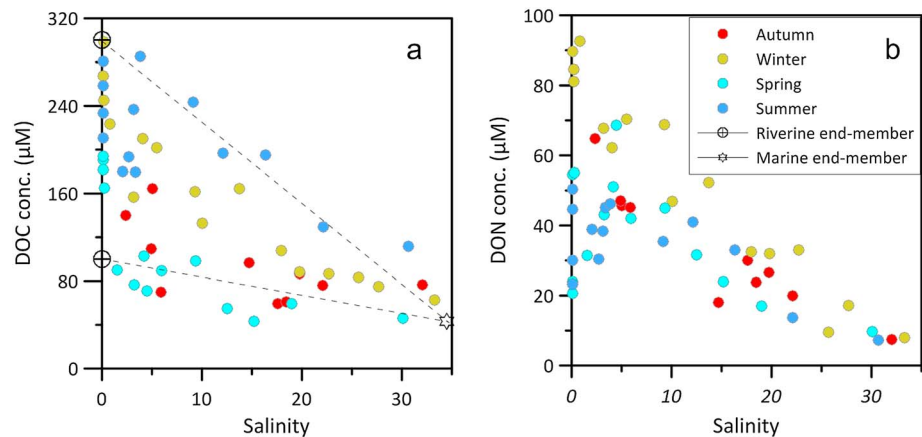


Figure 3. Distributions of (a) dissolved organic carbon (DOC) and (b) dissolved organic nitrogen (DON) concentrations along the salinity gradient in the Pearl River estuary.

except spring, when isotopically more depleted but relatively constant values (around -4.0‰) were found in waters with salinity of >5.0 . In addition, both riverine and marine waters showed distinct seasonality. These observations are consistent with previous measurements that found no systematic variations in the $\delta^{15}\text{N}$ of HMW-DON or $\text{DON}+\text{NH}_4^+$ (L. Guo et al., 2003; Schlarbaum et al., 2010; X.-C. Wang et al., 2004). Estuarine $\delta^{15}\text{DON}$ was greatest in summer and lowest in spring, with autumn and winter showing intermediate values.

To identify correlations among the measured parameters (DOC, DON, their isotopic values, and those of other N species), we analyzed data for each season separately (Table 1). $\delta^{13}\text{DOC}$ negatively correlated with DOC concentrations in all seasons sampled, whereas no consistent correlation was found between $\delta^{13}\text{DOC}$ and $\delta^{15}\text{DON}$ in different seasons. In winter, $\delta^{15}\text{DON}$ and $\delta^{15}\text{PN}$ varied similarly and are strongly correlated, indicating a close relationship between the dissolved and particulate matter fractions. In contrast, there is a lack of correlation between these N isotopes in spring. In autumn and summer, they are inversely correlated along the salinity gradient. Moreover, we found slightly lower $\delta^{15}\text{DON}$ than $\delta^{15}\text{PN}$ in middle- and high-salinity waters during summer.

4. Discussion

Clear seasonal differences in the concentration and the stable isotope composition of DOM were observed during the observation period (Figures 3 and 4). In contrast to DOC, the seasonal dynamics of DON appear to be more differentiated and can therefore be separated into several phases. In the following subsections,

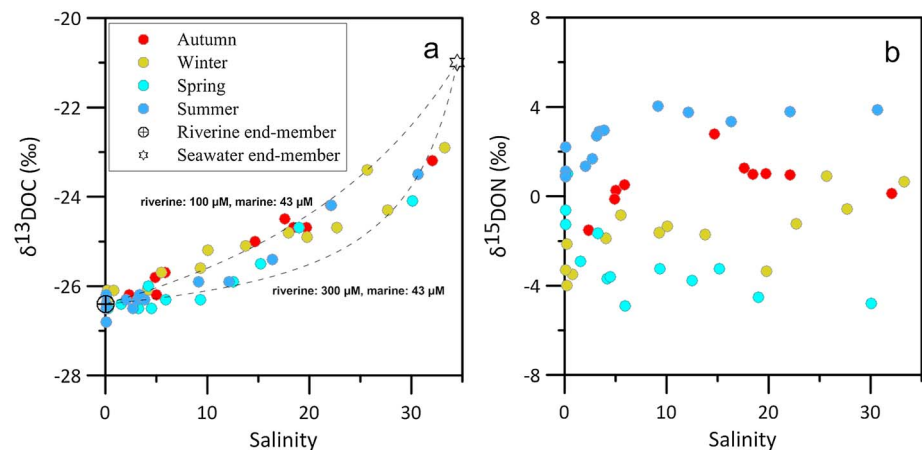


Figure 4. Distributions of (a) $\delta^{13}\text{C}$ and (b) $\delta^{15}\text{N}$ of dissolved organic matter along the salinity gradient in the Pearl River estuary. For $\delta^{13}\text{C}$, the conservative mixing lines are calculated by assuming riverine and marine end-members of -26.4‰ and -21‰ , respectively.

Table 1
Correlation Coefficients (*r*) of Variables for All Stations Sampled

	Autumn	<i>n</i>	Winter	<i>n</i>	Spring	<i>n</i>	Summer	<i>n</i>
$\delta^{13}\text{C}/\text{DOC}$	-0.70	10	-0.83	14	-0.65	14	-0.79	14
$\delta^{13}\text{C}/\text{DON}$	-0.46	10	-0.69	14	0.83	14	-0.35	14
$\delta^{15}\text{N}/\text{DOC}$	-0.89	10	-0.72	14	0.14	14	0.48	14
$\delta^{15}\text{N}/\text{DON}$	-0.33	10	-0.34	14	-0.39	14	-0.67	14
$\delta^{15}\text{N}/\text{PN}$	-0.83	10	-0.28	14	-0.34	14	0.73	14
$\delta^{15}\text{N}/\text{NH}_4^+$								

Note. Significant values ($p < 0.05$) are in bold.

we evaluate the possible DOC and DON sources within the PRE and elucidate the most plausible transformations based on a combination of both C and N isotopic signatures, with emphasis on the turnover processes of DON.

4.1. Seasonality of Riverine DOC and DON Sources

4.1.1. Riverine DOC Sources

Concentrations of DOC in freshwater end-members were higher in winter and summer than in autumn and spring (Figure 3), which could be attributed to seasonal differences in terrestrial OC sources (e.g., soil-derived OM, sewage OM, and algal production) and/or loadings (Gao et al., 2002; He et al., 2010). Moreover, there is a lack of correlation between DOC concentration and phytoplankton biomass (*Chl a* content) in all seasons (data not shown), thus indicating that external sources rather than in situ algal production dominated the DOC distribution within the PRE. In contrast to

DOC concentration, the spatial (salinity) distribution of $\delta^{13}\text{C}$ values shows only minor seasonal variations (Figure 4), which is indicative of little seasonality in DOC sources and turnover processes. For the riverine end-member ($S < 1.0$, not truly riverine as they also reflect the influence of saline waters to some extent), DOM had a lighter $\delta^{13}\text{C}$, with relatively constant values of -26.9‰ to -26.1‰ in all seasons. These are within the typical range reported for other rivers (-25‰ to -32.4‰) that discharge into estuaries or coastal oceans (Kaldy et al., 2005, and references therein).

Among the numerous sources, DOC originating from freshwater phytoplankton and sewage treatment plant effluents, in general, has depleted $\delta^{13}\text{C}$ values. For example, riverine DOC derived from in situ algal production is expected to have an average $\delta^{13}\text{C}$ value of -30‰ to -31‰ (W. Guo et al., 2015; Raymond & Bauer, 2001), whereas the $\delta^{13}\text{C}$ of sewage-derived DOC is reported to encompass a wide range of values ($< -30.0\text{‰}$ to -22.7‰), with more depleted $\delta^{13}\text{C}$ values ($< -30.0\text{‰}$ to -25.9‰) are suggested for treated sewage (Bridgeman et al., 2014; X.-C. Wang et al., 2004). Considering that the majority of sewage effluents ($>80\%$) have been treated over the Pearl River Delta region (www.gdepd.gov.cn), local sewage inputs could also contribute OM with depleted $\delta^{13}\text{C}$ values. Even if DOC from raw sewage inputs cannot be neglected and have much more enriched $\delta^{13}\text{C}$ values (i.e., -22.7‰ to -23.9‰), the dominance of sewage inputs over other sources is unlikely because the most contribution of sewage-derived should be in the dry period when freshwater dilution is low and much heavier $\delta^{13}\text{C}$ values are expected (He et al., 2010). This is inconsistent with the pattern observed in the freshwater. Therefore, we can exclude algal production and sewage effluents as the major sources carried by the Pearl River. As compared with other OC sources, particulate organic carbon (POC) originating from terrestrial soil organic matter is characterized with more positive $\delta^{13}\text{C}$ value. For example, a mean $\delta^{13}\text{C}$ of -24.0‰ was reported for soil-derived OM in the Pearl River Delta region (Wei et al., 2008; Yu et al., 2010). In addition, some previous studies (Gregorich et al., 2000; Tu et al., 2011) have shown similar $\delta^{13}\text{C}$ values of DOC and POC in terrestrial soils. As a consequence, we infer that highly degraded soils may be the most important terrestrial source of DOC to the PRE, even though the contribution of DOC from other sources cannot be excluded. Similar findings have also been reported in the York River estuary and the Mississippi River estuary (Raymond & Bauer, 2001; X.-C. Wang et al., 2004).

A mixing model with three end-members was used to assess the relative proportions of freshwater DOC from different terrestrial sources to the PRE in each season. The model is quite similar to a widely used isotopic mixing model (Bauer & Bianchi, 2011; Hu et al., 2006). We assumed that each sample is a mixture of soil-derived OM (f_{soil}), sewage OM inputs (f_{sew}), and freshwater phytoplankton (f_{phyto}). From this, we can adopt the following equations:

$$f_{\text{soil}} + f_{\text{sew}} + f_{\text{phyto}} = 1 \quad (1)$$

$$f_{\text{soil}} * \sigma_{\text{soil}} + f_{\text{sew}} * \sigma_{\text{sew}} + f_{\text{phyto}} * \sigma_{\text{phyto}} = \sigma_{\text{obs}} \quad (2)$$

where σ_{soil} , σ_{sew} , and σ_{phyto} represent the $\delta^{13}\text{C}$ of DOC for the three end-members of soil, sewage, and freshwater phytoplankton OM, respectively. The σ_{obs} value is the $\delta^{13}\text{C}$ of DOC observed in freshwater ($S < 1.0$) during each season. The model *Iso-Source* (Phillips & Gregg, 2001, 2003) is used to calculate the relative

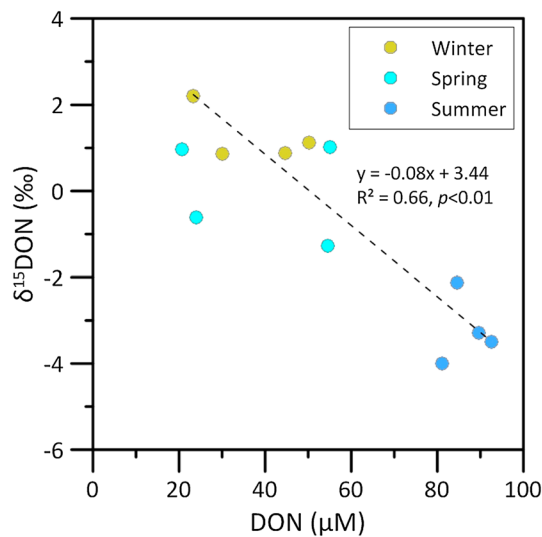


Figure 5. Relationship between DON concentrations and $\delta^{15}\text{DON}$ at low salinities for all seasons. DON = dissolved organic nitrogen.

three seasons (winter, spring, and summer) when near-freshwater samples ($S < 1.0$) were collected. This further indicates that riverine DOC loading is strongly influenced by terrestrial soil OM. Moreover, domestic wastewater effluents were important sources of DOC in the PRE, and the contribution is stable and low relative to that (32–54%) estimated by a previous study in the Guangzhou Channel during April 2007 (He et al., 2010). The discrepancy could be associated with the distinct sampling stations and hydrological conditions (i.e., a low flow rate of $5,240 \text{ m}^3/\text{s}$ in April 2007). The relative contribution from freshwater phytoplankton was also significant. We note there are large uncertainties in the quantification discussed above, and further research of specified DOC sources is needed to better constraint the relative importance of different sources. As a whole, however, the riverine DOC inputs into the PRE are dominated by terrestrial OC transported by the Pearl River.

4.1.2. Possible Riverine DON Inputs

The DON concentrations measured here were generally within the range for estuaries worldwide summarized by Berman and Bronk (2003). Along the salinity gradient, DON concentrations were generally lower in the wet season than in the dry season (especially winter), presumably in response to larger freshwater dilution and/or variability in DON sources/inputs. However, in comparison with previous studies (e.g., L. Guo et al., 2003; Schlarbaum et al., 2010; X.-C. Wang et al., 2004), our study region showed relatively depleted $\delta^{15}\text{DON}$ values, possibly due to the consumption and/or sorption of DON before its discharge from the forest and anthropogenic sources (Koba et al., 2012; Rastetter et al., 2005). Note that low $\delta^{15}\text{DON}$ values (average $-2.5 \pm 7.7\text{‰}$, with a range of -19.9‰ to $+10.7\text{‰}$) have been reported in the stream water of an N-saturated subtropical forest in the Pearl River delta (Koba et al., 2012).

The near-fresh waters ($S < 1.0$) showed high DON concentrations coupling with depleted $\delta^{15}\text{N}$ values in winter, and vice versa (Figure 5). This may also be related to the differences in terrestrial OM sources contributing to the estuary, each of which had distinct concentration and $\delta^{15}\text{N}$ ranges. The upper reaches of the PRE (i.e., the upstream Humen) are located in a highly populated and industrialized area and thus are expected to have elevated concentrations of DON ($>200 \text{ μmol/L}$) owing to input from domestic sewage treatment plants, particularly during the dry period when flow is low (Harrison et al., 2008; Lin et al., 2004). These sewage effluents generally contain large amounts of heterotrophic and nitrifying bacteria (Aissa-Grouz et al., 2015; Cébron et al., 2003). As a result, the DON pool in sewage effluents includes inert DON in the raw sewage, biodegradable DON that was not completely removed, and soluble microbial products (exudates) released by microorganisms during biological processes such as breakdown of bacterial cell walls. Many studies have reported a wide range of DON originating from soluble microbial products, ranging from approximately $35 \pm 16\%$ to 85% of the DON pool in the effluent (Nam & Amy, 2008; Namkung & Rittmann, 1986).

contributions of DOC from each source, although this does not provide a unique solution as there are three variables in two equations. It gives a range of feasible source contributions. For graphical representation of the data, the mean (50th percentile) value of the feasible contributions from each source was taken for every sample. Measurement error of $\pm 0.15\text{‰}$ in $\delta^{13}\text{C}$ analysis of water sample and each end-members was included in the calculation of most feasible source contributions by setting the mass balance tolerance of 0.1‰ in the model. In this study, mean values of soil-derived OM (-24‰ ; Yu et al., 2010; Y. Zhang et al., 2014) and in situ freshwater phytoplankton (-30.5‰ ; W. Guo et al., 2015) from the Pearl River delta and estuary were taken as soil and algal phytoplankton end-members, respectively. The mean $\delta^{13}\text{C}$ value of treated effluent DOC ($-28 \pm 1.0\text{‰}$) (Bridgeman et al., 2014) was taken as the sewage end-member. A major advantage of the isotopic mixing model is that it does not rely on the concentrations of DOC for the soil and phytoplankton end-members, which are generally difficult to determine and vary with time (Gao et al., 2002; He et al., 2010).

Our results suggest that the most likely relative contributions of riverine DOC from soil, sewage, and newly produced freshwater plankton were in the (mean) ranges of 46–55%, 27–33%, and 17–21%, respectively, in all

Based on three lines of evidence, we argue that the more negative $\delta^{15}\text{DON}$ values seen here at low salinities in winter (i.e., at the upstream of Humen) reflect a strong influence of sewage-derived DON. First, two additional samples collected near sewage treatment plants upstream at Guangzhou and downstream at Macau showed depleted $\delta^{15}\text{DON}$ values (-2.5‰ and -0.9‰). Second, nitrifying bacteria are known to produce soluble microbial products during the biological processing of domestic sewage, contributing large amounts of newly produced DON to the DON pool in the effluent (Eom et al., 2017; Ni et al., 2011), which would therefore add isotopically depleted DON to the estuary. In fact, recent work employing stable and radiogenic isotopic techniques has also shown that the final treated effluents are depleted in $\delta^{13}\text{DOC}$ (-29‰ to -27.9‰) relative to raw sewage (-22.7‰ to -23.6‰), which was attributed to the new sources of OC added during the treatment processes (Bridgeman et al., 2014). Third, analysis of the fatty acid composition of the SPM in the PRE provides further supporting evidence for the strong influence of bacteria-derived OM in low-salinity waters during the dry season (W. Guo et al., 2018). Heterotrophic bacteria are extremely depleted in ^{15}N compared with their N sources, as indicated by $\delta^{15}\text{N-DNA}$ analysis in the open ocean (Meador et al., 2007). Overall, the much-depleted $\delta^{15}\text{DON}$ in the upstream of Humen during the dry season can be attributed mainly to high inputs of DON from domestic sewage. However, further investigations of the formation pathways of effluent DON and its influence on estuarine N cycling are needed, with particular emphasis on processes associated with nitrification.

In contrast, terrestrial soil OM could be the most significant contributor of DON to the upper estuary during the wet season. In the soil profile of forest, grassland, and agricultural systems, $\delta^{15}\text{N}$ values of OM increase with profile depth, due mainly to the preferential uptake of ^{14}N during microbial decomposition (Chabbi et al., 2008; Natelhoffer & Fry, 1988). Moreover, the $\delta^{15}\text{N}$ values of fresh plant litter (e.g., leaf and root) and forest floor are lower than those of bulk soil, with a typical range of -4.7‰ to 0.2‰ for the former (Chabbi et al., 2008; Gioacchini et al., 2006; Natelhoffer & Fry, 1988). In the Pearl River catchment, the wet season can be further subdivided into the early flood period (April to June) and the late flood period (July to September; Luo et al., 2008). During the early flood period, rainfall and runoff increase abruptly in the Pearl River watershed due to frontal precipitation, which washes out the terrestrial OM from surface soils (including leaf litter accumulates) into the river and subsequently into the PRE (Belnap et al., 2005; W. Guo et al., 2015). Moreover, it is important to note that the consumption and/or sorption of DON before its discharge from the soil could significantly lower the $\delta^{15}\text{DON}$ of stream water relative to that of bulk soil. There is more severe soil loss and erosion from the watershed in the late flood period, which is characterized by more enriched $\delta^{15}\text{N}$ values of OM than the early flood period as a consequence of microbial decomposition (Natelhoffer & Fry, 1988). Furthermore, the high temperature ($>30\text{ °C}$) and strong sunlight in summer may together stimulate phytoplankton growth and microbial activity in rivers; and therefore, in-stream DON production following assimilation of inorganic N could also be a substantial source of DON in estuarine ecosystems (Johnson et al., 2013).

The above discussion confirmed that the riverine DON inputs may have been altered by biotic and/or abiotic processes prior to entering the PRE, further complicating the potential of $\delta^{15}\text{DON}$ as a direct tracer of DON sources. As a consequence, we are not able to quantitatively evaluate the relative importance of different sources to riverine DON inputs.

4.2. Estuarine Dynamics of DOC and DON

4.2.1. Main DOC Processing Within the Estuary

During the early mixing stage ($S = 1-2$, near the Humen), the concentration of DOC decreased sharply with increasing salinity, whereas $\delta^{13}\text{DOC}$ values were relatively unchanged in all seasons (Figures 3 and 4). Note that this decline was much steeper than that observed in middle- and high-salinity waters, which was clearly caused by dilution by seawater (with low DOM). Indeed, a similar distribution pattern has also been reported in previous studies (Callahan et al., 2004; He et al., 2010). Three possible mechanisms may explain the sharp decrease. One is dilution of highly polluted freshwater from the upstream Humen by other local but less polluted rivers (e.g., $117-125\text{ }\mu\text{mol/L}$ in the Jiaomen and Hengmen vs. $175\text{ }\mu\text{mol/L}$ in the Humen outlet; Ni et al., 2008). Another is flocculation, aggregation, and/or adsorption onto suspended sediments in the mixing zone with the increase in ionic strength at the land-sea interface and elevated SPM concentrations. The third is microbial degradation of DOC, which is reflected by the low DO contents in our study (Figure 2) and high DOC consumption rates found in an earlier study (He et al., 2010). Among these, the relative contribution of

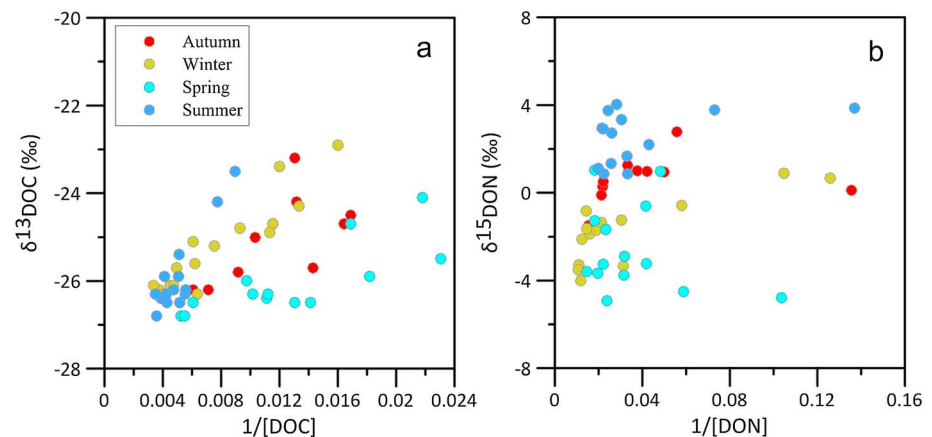


Figure 6. Relationships between (a) $\delta^{13}\text{C-DOC}$ and $1/[\text{DOC}]$, and (b) $\delta^{15}\text{DON}$ and $1/[\text{DON}]$. DOC = dissolved organic carbon; DON = dissolved organic nitrogen.

dilution should be much more important than the other two processes that would be accompanied by detectable C isotope fractionation due to preferential utilization and/or adsorption (Bauer & Bianchi, 2011; Pérez et al., 2011). However, we were not able to quantify the relative importance of each process during this initial mixing, as there are multiple end-members in this complex estuarine system.

Further downstream at middle and high salinities, mixing of freshwater and seawater may be largely responsible for the distribution of DOC in all seasons, as evidenced by the near conservative mixing for DOC concentration and its isotopic values along the salinity gradient, as well as the significant linear relationships between the $\delta^{13}\text{C}$ value and the inverse of DOC concentration (Figure 6a). During estuarine mixing, the $\delta^{13}\text{C}$ values increased gradually with increasing salinity, indicating a shift in the sources of DOC from terrigenous material in the upstream Humen to predominantly plankton in the lower estuary. The $\delta^{13}\text{C}$ values of the marine end-member are consistent with reported values (-22‰ to -20‰) in other estuarine and coastal systems (Bauer & Bianchi, 2011). However, it is important to note that both the concentration and $\delta^{13}\text{C}$ values of DOC showed substantial deviations from the conservative mixing, that is, nonconservative mixing in the salinity range of 5 to 22 in all seasons (Figures 3 and 4). This phenomenon could be closely related to microbial degradation of DOC in the PRE, while photochemical degradation and phytoplankton assimilation are not significant because of the high turbidity within the estuarine mixing zone (Z. Chen, Li, & Pan, 2004; Harrison et al., 2008). Indeed, lighter carbon isotope is preferentially utilized during the bacterial degradation of DOC, and the residual DOC pool has much more enriched $\delta^{13}\text{C}$ values. Our results are in good agreement with He et al. (2010), in which they observed pronounced removal of DOC in waters with salinity <20 during a dry period (April) in the PRE. They attributed the removal to bacterial degradation of major compounds such as carbohydrates and amino acids. It should be noted that even though our data are seasonal based, we did not find seasonal variations in the main DOC processing during estuarine mixing.

4.2.2. Possible Biogeochemical Processes Influencing DON Dynamics

Unlike DOC, estuarine DON is highly dynamic along the salinity gradient of the PRE. Its distribution pattern varied each season, clearly indicating that DON and DOC were uncoupled, a likely result of their distinct sources and/or a more rapid turnover of DON compared with DOC (Seitzinger et al., 2002; Wiegner et al., 2006). In fact, several studies have reported that DON is more bioavailable than DOC (Hopkinson et al., 1997, 2002). Mixing of riverine (with higher DON concentration) and marine (with lower DON concentration) end-members may play a significant role in the DON decrease (Figure 3). However, there were apparent anomalies in $\delta^{15}\text{DON}$ along the salinity gradient (Figure 4), such as in the low- and middle-salinity waters. Moreover, the $\delta^{15}\text{DON}$ values were not correlated with the inverse of DON concentration in most seasons (Figure 6b). These characteristics suggest that other major processes and/or external sources must be influencing the pattern of DON in the water column.

Photochemical release of biologically labile N from DOM could be an important sink for DON in estuaries (Bushaw et al., 1996; Moran & Zepp, 1997). However, the fractional conversion rate of DON has been

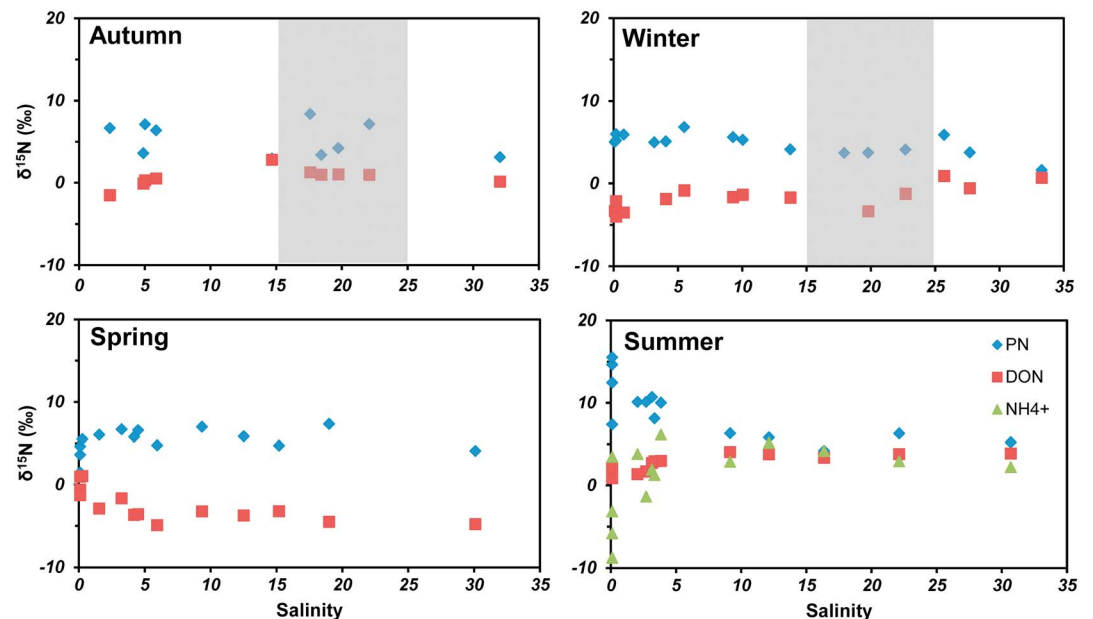


Figure 7. Relationships between the N isotopic values of DON, PN, and NH_4^+ (vs salinity) in the Pearl River estuary. Gray background represents the medium-salinity zones with relatively high SPM concentrations in the dry period. Note that some of the PN and NH_4^+ isotopic data are from Ye et al. (2016). DON = dissolved organic nitrogen; PN = particulate nitrogen; SPM = suspended particulate matter.

reported to be in the range of 0.0025 to 0.0097 hr^{-1} in aquatic systems (Bushaw et al., 1996), suggesting that complete conversion would take more than 100 days, which is far longer than the residence time in the PRE. Similar to that of DOC, we can also rule out photochemical alteration as the main sink for DON in our study region, even though the conversion of DON to other N forms (e.g., NH_4^+) cannot be excluded in coastal waters (Callahan et al., 2004; J. Chen, Li, Yin, & Jin, 2004). In fact, Badr et al. (2008) arrived at the same conclusion from DON data of the Yealm and Plym estuaries in England. In addition to photochemical reactions, heterotrophic bacteria and phytoplankton N uptakes could be the potential sinks for DON. However, in estuaries where P limitation occurs (as in the PRE), direct uptake of DON by phytoplankton is considered to be minor (Korth et al., 2012; Middelburg & Nieuwenhuize, 2000).

In winter, the release of DON from PN might occur or these species experience similar N sources/processes, as inferred from the parallel progression of PN and DON isotopes along the salinity gradient (Figure 7). In fact, during the dry season when wind-driven mixing is strong, sediment resuspension and subsequent processes (e.g., adsorption/desorption) may play an important role in the biogeochemical behavior of DON in coastal waters, particularly in shallow waters (Lomstein et al., 1998; Suratman et al., 2008). In addition, it has been demonstrated that sediment-water interaction and sediment resuspension constitute an important source of inorganic N (predominantly NH_4^+) in the water column of the PRE (Ye et al., 2016; L. Zhang et al., 2013). To our knowledge, there have been no measurements of the efflux of DON from sediments in the PRE. However, the notably high SPM and PN concentrations at middle to high salinities (i.e., the lower estuary) during the dry season can be interpreted as evidence of active resuspension of bottom sediments. In the regions studied here, the $\delta^{15}\text{N}$ of surface sediments has a narrow range, from 3.9‰ to 6.4‰ (Hu et al., 2006). Bacterial remineralization of OM occurs without substantial N isotope fractionation ($\epsilon < 2.0\text{‰}$) (Möbius, 2013); therefore, we expect DON to be produced with a similar $\delta^{15}\text{N}$ to that of the sediment N from which it is derived. However, given that the DON input from sediment resuspension had a much higher $\delta^{15}\text{N}$ value than sewage-derived DON, the DON input from resuspension of sediments and its subsequent processes appear to have an important effect on DON dynamics during the dry period, at least for the relatively high $\delta^{15}\text{N}$ -DON values observed in mid-salinity waters.

In addition, DON can be adsorbed onto suspended particles in estuarine particle-rich turbidity zones, and thus be removed from the dissolved phase. During the adsorption, the ^{15}N -enriched fraction might be

preferentially removed from the water column (Koba et al., 2012; Schlarbaum et al., 2010). Sorption can be quick (i.e., a few hours), indicating that steady state partitioning is possible in estuaries with relatively short residence times such as in the present study (Arnarson & Keil, 2000; Badr et al., 2008). Intriguingly, $\delta^{15}\text{N}$ DON and DON concentration decreased in parallel at intermediate salinities (~ 20.0), coincident with the high-turbidity zone in the dry period (Figure 4). Moreover, they both increased again farther seaward. It therefore seems that selective adsorption/desorption of ^{15}N -enriched moieties onto particle surfaces can explain some of the DON isotope anomalies. However, we cannot separate this influence from the anomalies attributable to efflux from the sediment.

After a peak in winter, DON concentrations decreased in springtime, and there was no clear relationship between DON and phytoplankton biomass (*Chl a*), which indicates that the contribution of algal DON production to the total DON pool is low in comparison with the terrestrial inputs. In fact, the first phase of precipitation occurring during spring over the Pearl River catchment washes out large amounts of terrestrial OM from the forest floor and surface soils into the river and estuary. High levels of SPM and an apparent isotopic difference between POC and in situ phytoplankton (W. Guo et al., 2015) in low-salinity waters were taken as evidence of the predominance of soil-derived DOM during this period. These terrestrial OM inputs are generally depleted in $\delta^{15}\text{N}$ (Natlhoffer & Fry, 1988). For example, $\delta^{15}\text{N}$ values of -7.6‰ to -1.8‰ for the forest floor and 0.4‰ to 2.8‰ for soils have been reported in 14 forest ecosystems in the Pearl River delta (Fang et al., 2011). With respect to DON, a low DON/TDN ratio (13% on average) and a depleted $\delta^{15}\text{N}$ (average $-2.5 \pm 7.7\text{‰}$) have been reported in the stream water of an N-saturated subtropical forest in the Pearl River delta, possibly related in part to the consumption and/or adsorption of DON before its discharge from the forest (Koba et al., 2012). The low DON concentrations may also be due to freshwater dilution by higher discharge at this time of year.

In the low-salinity areas of the PRE ($S < 5.0$, i.e., the upper estuary), $\delta^{15}\text{N}$ DON decreased significantly seaward (Figure 4). This, in conjunction with an increase in DON concentrations, suggests additional sources with isotopically light N. Adsorption/desorption processes cannot be primarily responsible for the observed isotope depletion, because $\delta^{15}\text{N}$ -enriched DON moieties are suggested to be selectively adsorbed/desorbed onto suspended particles (Schlarbaum et al., 2010). Farther seaward within the estuary (with increasing salinity), $\delta^{15}\text{N}$ DON values remained relatively constant, possibly due to two factors. First, the uptake of the bioavailable DON fraction is complete to the point that there is no apparent isotope effect, whereas the recalcitrant DON fraction is resistant to further biological processing (Schlarbaum et al., 2011); indeed, DON from natural regions (i.e., forests) is generally considered to be less bioavailable than DON originating from agricultural and urban sources (Seitzinger et al., 2002). Second, the DON experiences relatively little processing due to the short residence time of water during this high-discharge period. We cannot separate the two influences in the present study, and further studies are required to verify this issue.

As typhoon-induced rainfall continues through summer, the pool of N available to be transported to the river is mainly from deeper organic and mineral soils (W. Guo et al., 2015). These DON inputs are enriched in ^{15}N compared with surface soil because of the preferential loss of ^{14}N during microbial decomposition (Koba et al., 2012; Natlhoffer & Fry, 1988). Most importantly, high water temperature and strong sunshine in summer may promote the breakdown and/or microbial degradation of particulate OM (to DON and NH_4^+), which comprises mainly in situ algal products and has $\delta^{15}\text{N}$ values of 4.2‰ to 15.5‰ but much higher $\delta^{15}\text{N}$ values in low-salinity waters (W. Guo et al., 2015; Ye et al., 2016). DOM from the above-mentioned processes is expected to be more ^{15}N -enriched than that in the upstream river water because of the limited N isotope fractionation during particulate organic matter remineralization. Consequently, the N isotope value of DON peaked in summer. Another noteworthy point during this season is that at middle and high salinity (> 15), DON is much more depleted in $\delta^{15}\text{N}$ than PN but more enriched in $\delta^{15}\text{N}$ NH_4^+ (Figure 7). Regarding their concentrations, DON was inversely correlated to both PN and NH_4^+ along the salinity gradient at this time (data not shown). This is, therefore, best explained by a close coupling of DON production and consumption. Our hypothesis is further supported by the following three observations. First, a large fraction of PN is likely mineralized and recycled during summer, and the distribution of water column NH_4^+ in summer was controlled mainly by OM remineralization, as evidenced by the close relationship between PN and NH_4^+ concentrations (Ye et al., 2016). Second, DON production from PN occurs with limited or no isotopic fractionation, whereas DON destruction has substantial fractionation ($1.0\text{--}6.0\text{‰}$; Knapp et al., 2012). Third, the susceptibility of DON

to bacterial mineralization increases as it is transported from fresh water to more saline environments, which could be due in part to the elevated percentage of DON relative to the total N pool (J. Chen, Li, Yin, & Jin, 2004; Stepanauskas et al., 1999). Researchers have suggested that bacteria are able to directly transport LMW compounds through their cell membranes via permeases, whereas HMW compounds may also be utilized by bacteria after hydrolysis to LMW compounds via hydrolytic enzymes. Moreover, bacterial DON utilization and mineralization will also be high in summer due to the increased water column temperature (Berman & Bronk, 2003; Veuger et al., 2004). In fact, J. Chen, Li, Yin, and Jin (2004) suggested that phytoplankton and bacteria might use dissolved amino acids as their main N source in the lower estuary of the PRE.

5. Conclusion

This study has shown that stable isotopic compositions can be used to improve our understanding of the complexity of DOM dynamics in large perturbed subtropical estuaries like the PRE in south China. Riverine DOM input is primarily derived from terrestrial-derived materials. Intensive physical mixing between fresh and saltwater was dominant in controlling the distributions of DOC and DON in most seasons, particularly during dry periods. However, our isotopic data indicated that DOC undergoes substantial removal in the salinity range of 5 to 22 and exhibits no clear seasonality, which could be attributed to bacterial degradation of DOC. Different from DOC, the seasonal biogeochemical cycle of DON is more complex, indicating a decoupling of DON and DOC dynamics. The $\delta^{15}\text{N}$ values of DON and other associated N species provided strong evidence for active biotic and/or abiotic processing of DON along the salinity gradient of the estuary, but with distinct N turnover processes in different seasons. More importantly, our data reinforce the conclusion that DOM is an active participant in C and N cycling in river-dominated estuaries.

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