

Seasonal characterization and identification of dissolved organic matter (DOM) in the Pearl River, China

Liuchun Zheng^{1,3} · Zhaofeng Song¹ · Peipei Meng² · Zhanqiang Fang^{1,3}

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Abstract Dissolved organic matter (DOM) is considered to be one of active organic carbon components in river water, and its characteristics would affect quality of drinking water if such a river is used for the purpose. DOM in the Pearl River around metropolitan Guangzhou and its six fractions obtained by sequential resins separation and their percentage distribution of total organic carbon (TOC), the UV absorbance at 254 nm (UV₂₅₄), and the specific ultraviolet absorbance (SUVA₂₅₄) were determined. Meanwhile, fluorescence spectroscopy and Fourier transform infrared (FTIR) spectroscopy were used to examine the biodegradable and structural characteristics of DOM. The results showed that the values of TOC, UV₂₅₄, and SUVA₂₅₄ changed with season. Especially, SUVA₂₅₄ was lower than 3 L (mg m)⁻¹, indicating that the hydrophilic fractions were the major components of the DOM. Furthermore, fluorescence spectroscopy revealed the dominant presence of humic-like, fulvic-like, and protein-like fluorophores. Fluorescence index (FI) in four seasons was associated with allochthonous DOM sources and

biological DOM. FTIR spectroscopy suggested the feature of DOM with some specific groups (e.g., carbohydrate C–O, amid C=O).

Keywords Dissolved organic matter · Drinking water source · Fractions · Characterization · The Pearl River

Introduction

Dissolved organic matter (DOM) is considered to be one of the largest numbers of organic constituents in all aquatic ecosystems and includes fulvic acid, humic acid, carbohydrate, and amino acid (He and Wu 2015), and its particle in natural water can pass through a 0.45-mm membrane (Buffle and Leppard 1995). If less affected by anthropogenic activities, DOM can be generally defined as the natural organic matter (NOM), which mainly includes hydrophilic, acidic, and humus substances (Koch et al. 2005), and is released from living and decaying biota (Mopper et al. 1996). In contrast, DOM strongly affected by wastewater has various and uncertain origins (Meng et al. 2013) and increases the solubility and hydrophilicity of organic pollutants, to enhance the environmental risk of organic pollutants (He and Wu 2015). As a result of chlorination in the water treatment processes, DOM is considered to be a precursor in the production of potentially carcinogenic disinfection by-products (DBPs), such as trihalomethanes (THMs), haloacetic acids (HAAs), and haloacetonitriles (HANs) (Panyapinyopul et al. 2005). Especially, THMs negatively affect the liver, the kidney, and the nervous and reproductive systems (Navalon et al. 2008) and induces DNA damage in human-derived hepatoma line to be linked with the increase of cancer risk (Ma et al. 2013; Pifer and Faurey 2012). Therefore,

Responsible editor: Céline Guéguen

✉ Liuchun Zheng
lczhengscnu1@163.com

✉ Zhanqiang Fang
zhqfang@scnu.edu.cn

¹ School of Chemistry and Environment, South China Normal University, Guangzhou 510006, People's Republic of China

² College of Environment, Jinan University, Guangzhou 510632, China

³ Guangdong Technology Research Center for Ecological Management and Remediation of Urban Water System, South China Normal University, Guangzhou 510006, China

DOM imposes adverse impacts on the quality of drinking water and human health (Chen et al. 2013).

The characterizations of DOM in many globally large rivers have already gained increasing concern (Chen et al. 2013). The Pearl River (Zhujiang) is the fourth longest river (ca. 2320 km in length) and the second largest river in terms of water discharge in China. The Pearl River delivers much freshwater and constitutes one of the major drinking water sources of Guangzhou metropolis, where about 3 million cubic meters of potable water is pumped to water plants every day. In recent years, industrial land use in the downstream district of the Pearl River has substantially contributed toward the increase of DOM levels, due to that large amounts of wastewater are discharged to the river. These are proved by the results of anthropogenic input in urbanized rivers (Meng et al. 2013). Fortunately, many efforts have been devoted to understand the roles of DOM in the aquatic environment of the Pearl River, e.g., the distribution of DOM in the estuary (the Pearl River Delta region) (Callahan et al. 2004) and the origin and fate of DOM (from its main tributaries to the estuary) (Meng et al. 2013). Obviously, these researches focus on the larger and various sections of the Pearl River. Moreover, due to the complexity of DOM in the Pearl River, some researches provide information about the molecular weight distribution for each fraction of DOM with different size membranes to study its characteristics (Zhao et al. 2006). But, with resin adsorption, it would be chemically separated into other six organic fractions prior to analysis: hydrophobic acid (HPOA), hydrophobic base (HPOB), hydrophobic neutral (HPON), hydrophilic acid (HPIA), hydrophilic base (HPIB), and hydrophilic neutral (HPIN), of which the hydrophobic fractions were considered to have higher relativities of THM formation than the hydrophilic fractions (Panyapinyopol et al. 2005). To predict DOM fractions, total organic carbon (TOC) is an aggregate parameter and not a direct indicator of the

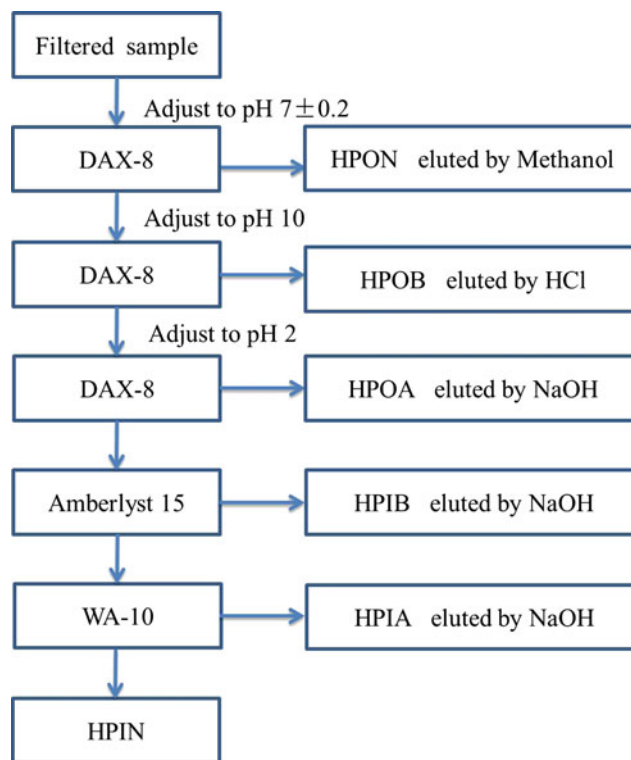


Fig. 2 Fractionation procedure

organic character of the source water (USEPA 1989), and the UV absorbance at 254 nm (UV_{254}) represents the aromatic character of organic matters (Marhaba et al. 2000). Further, specific ultraviolet absorbance ($SUVA_{254}$) is a good surrogate parameter for aromaticity and humic contents of waters (Drews 2010; Wong et al. 2007) and calculated as $SUVA_{254} = UV_{254} / \text{dissolved organic carbon (DOC)}$ (Pifer and Fairey 2012). The three-dimensional excitation emission matrix (EEM) reveals seasonal variations of DOM and identifies the source of water (Callahan et al.

Fig. 1 The location of the sampling site in the Pearl River

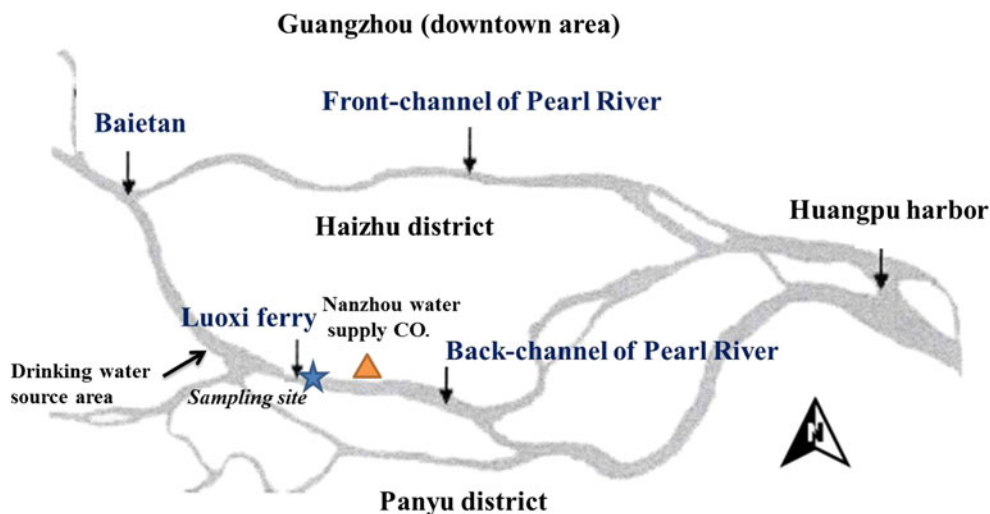
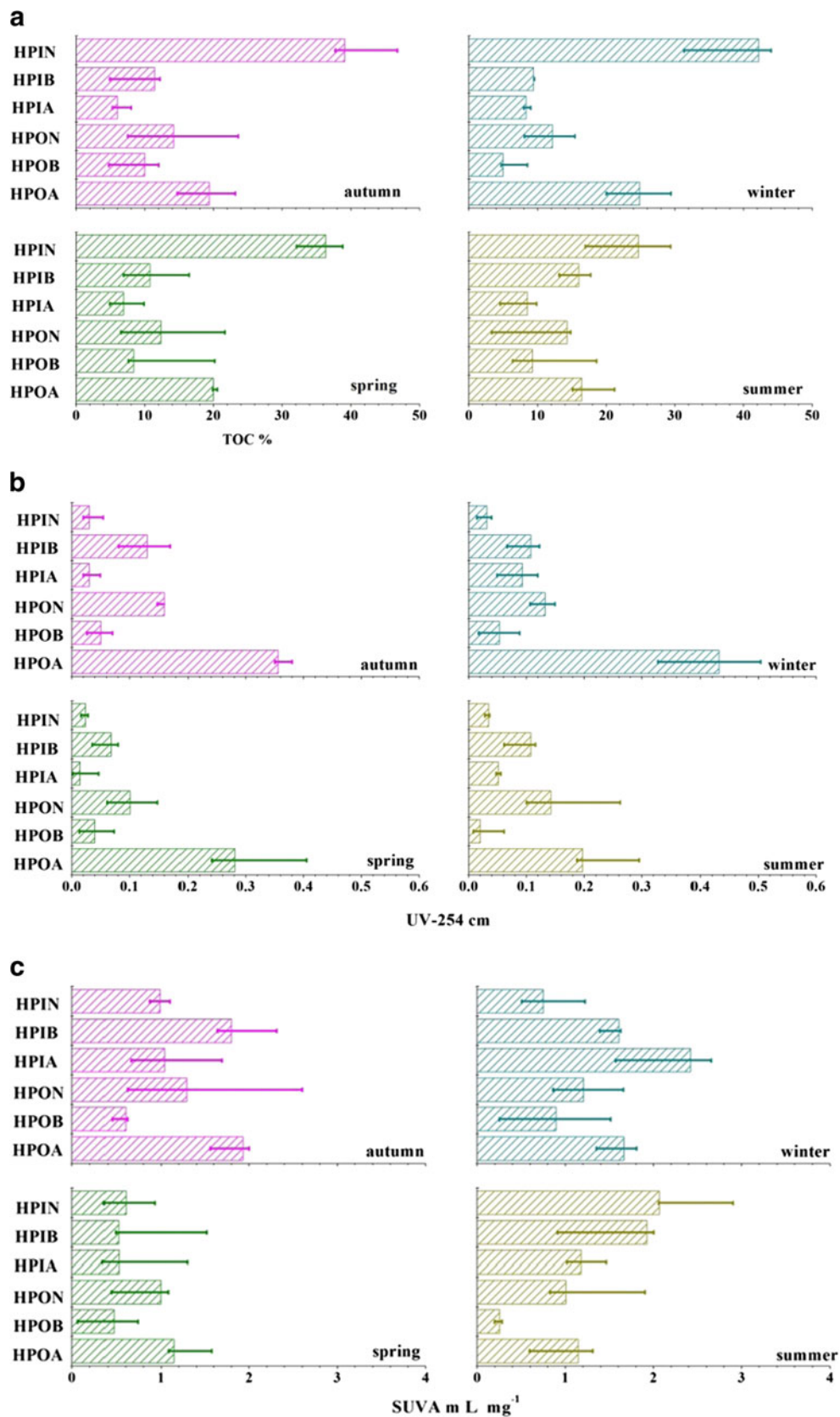


Fig. 3 Distribution percentage of TOC (a) and seasonal variation of UV₂₅₄ (b) and SUVA₂₅₄ (c) for each fraction (sample mean \pm standard deviation; $n=3$, samples collected on three different days of each season)



2004). Fourier transform infrared (FTIR) spectroscopy further provides valuable information on the structural and functional

groups (e.g., the amide, carboxyl, and aliphatic ester) of DOM (Abdulla et al. 2010).

However, these techniques have not used to determine DOM fractions in the Pearl River, especially for the drinking water sources' section of the Guangzhou city. Therefore, the main objectives of the study were to explore the seasonal variations of the DOM characteristics and provide a more detailed description for six organic fractions of DOM in water sample collected from back channel of the Pearl River.

Materials and methods

Sampling and pretreatment

The Pearl River in Guangzhou city is mainly divided into front channel, back channel, and Huangpu channel. Among them, the back channel section (from Baietan to Luoxi ferry) belongs to the drinking water source area. The sampling site was located at Luoxi ferry (between the source area and the populous area) and close to Nanzhou drinking water supply plant, which is one of the most important water services in Guangzhou city (Fig. 1), and sample collections were conducted in spring (March, April, and May), summer (June, July, and August), autumn (September, October, and November), and winter (December, January, and February). The sampling was conducted in three replicates in each season. Samples were collected from the surface of river water (<0.8 m) using glass bottles of 5 L, then filtered immediately through a 0.45-µm cellulose acetate (CA) membrane (acid washed and prerinse with pure water to remove the remaining compounds within the membrane pores prior to use), and stored in the dark at 4 °C before and after fractionation.

Fractionation

The fractionation of DOM was performed through adsorption using three types of resin adsorbents, i.e., nonionic resin (DAX-8), strong cationic resin (Amberlyst 15), and weak anionic resin (WA-10), following the procedure described by Marhaba et al. (2003), and then, DOM was classified into six fractions: HPOA, HPOB, HPON, HPIA, HPIB, and HPIN, respectively. The fractionation procedure is listed in Fig. 2.

Analysis

All fractions were adjusted to a neutral pH prior to the measure of TOC and UV₂₅₄. TOC analysis was conducted by the high-temperature combustion method using Shimadzu V_{CPH} TOC analyzer equipment. And, UV₂₅₄ was measured with a UV-2550 thermo-spectronic (Shimadzu, Japan) with a 1-cm quartz cell.

Water samples were placed in a freezer for freezing about 1.5 h and then in the condition of vacuum freeze for being

Table 1 Assignments and characteristics of EEM components

Characteristics	Raw sample Ex/Em (nm)	HPIA Ex/Em (nm)	HPIB Ex/Em (nm)	HPIN Ex/Em (nm)	HPOA Ex/Em (nm)	HPOB Ex/Em (nm)	HPON Ex/Em (nm)
Microbial humic like	305/376 (Au)	300, 305/376 (Au)	305/376 (Au)	— (Au)	300, 305/376 (Au)	— (Au)	300, 305/376 (Au)
	— (Wi)	305/376 (Wi)	— (Wi)	— (Wi)	305/376 (Wi)	— (Wi)	300, 305/376 (Wi)
	305/376 (Sp)	305/376 (Sp)	305/376 (Sp)	— (Sp)	305/376 (Sp)	— (Sp)	300, 305/376 (Sp)
Terrestrial humic like	300, 305/376 (Su)	300/376 (Su)	305/376 (Su)	305/376 (Su)	305/376 (Su)	— (Su)	300, 305/376 (Su)
	230/380, 340/450 (Au)	260/380 (Au)	350/410 (Au)	350/410 (Au)	260/380, 320/420 (Au)	250/440 (Au)	240/380, 320/380 (Au)
	340/420 (Wi)	360/440 (Wi)	320/400 (Wi)	350/400 (Wi)	320/420 (Wi)	250/400 (Wi)	240/380, 320/390 (Wi)
	230/380, 360/420 (Sp)	260/380, 350/390 (Sp)	230/380, 350/380 (Sp)	230/400, 350/400 (Sp)	240/460, 350/400 (Sp)	240/400 (Sp)	250/360, 320/380 (Sp)
Fulvic like	230/380, 350/400 (Su)	260/460, 350/400 (Su)	230/460, 350/400 (Su)	260/460, 350/400 (Su)	230/360, 350/400 (Su)	350/400 (Su)	350/420 (Su)
	390/509 (Au)	— (Au)	— (Au)	— (Au)	440/509 (Au)	— (Au)	440/509 (Au)
	390/509 (Wi)	— (Wi)	— (Wi)	— (Wi)	440/509 (Wi)	— (Wi)	440/509 (Wi)
	390/509 (Sp)	— (Sp)	— (Sp)	— (Sp)	— (Sp)	— (Sp)	— (Sp)
Protein like	390/509 (Su)	— (Su)	— (Su)	— (Su)	440/509 (Su)	— (Su)	440/509 (Su)
	275/540 (Wi)	220/350, 275/350 (Au)	275/305 (Au)	275/305 (Au)	275/305 (Au)	275/305 (Au)	275/305 (Au)
	220/350, 275/340 (Sp)	275/350 (Wi)	275/305 (Wi)	275/305 (Wi)	275/305 (Wi)	275/305 (Wi)	275/305 (Wi)
	220/350, 275/350 (Su)	275/305 (Su)	275/305 (Su)	275/305 (Su)	275/305 (Su)	275/305 (Su)	275/305 (Su)

Sp spring, Su summer, Au autumn, Wi winter, — none

dried more than 24 h. The samples of 2 mg and dry KBr of 200 mg were mixed and pressed into thin slices under the pressure of 10 t cm^{-2} . The final samples were scanned from 400 to 4000 cm^{-1} by FTIR spectrometer to determine their transmittance.

Fluorescence of the samples was measured at $25 \text{ }^\circ\text{C}$ using spectrofluorometer equipped with two monochromators for both the excitation light source and the emission detector (Hitachi F-2500, Japan), and then, the chosen parameters were as follows: (1) the excitation light source: the 150-W xenon lamps, (2) voltage of 700 V, (3) scanning speed of 3000 nm min^{-1} , (4) crack width: $\lambda_x - \lambda_m$ of 2.5/2.5, (5) the excitation wavelengths (E_x) of 225–525 nm, and (6) the emission wavelengths (E_m) of 240–633 nm. Three-dimensional emission/excitation matrix (EEM) fluorescence was drawn by Origin 8.0 software. In addition, the independent-samples test was used to determine the significance of the measured parameter, and $p < 0.05$ was considered to be statistically significant.

Results and discussion

Seasonal characteristics of total organic carbon, UV absorbance at 254 nm, and specific ultraviolet absorbance

After fractionation, six fractions of DOM were determined as follows: (1) HPOA: carboxylic acid with five to nine carbon atoms, aromatic carboxylic acid with one to two rings, and phenol and tannin with one to two rings; (2) HPOB: protein, aromatic amines with one to two rings, and alkanes; (3) HPON: hydrocarbons, fatty alcohols, alkyl alcohols, esters, ketones, aldehydes, carboxylic acids, and aliphatic amine with >5 carbon atoms, aromatic carboxylic acid with >9 carbon atoms, and aromatic amines ≥ 3 rings; (4) HPIA: fatty acid <5 carbon atoms, hydroxy acids, sugar, alkyl (low molecular weight), monobasic acid, and dibasic acid; (5) HPIB: fatty amine with <9 carbon atoms, amino acids, purines, and pyrimidines; and (6) HPIN: fatty amine, alcohol,

aldehyde, ester, ketone with <5 carbon atoms, and polysaccharide (Kanokkantapong et al. 2006).

As shown in Fig. 3a, HPIN was the major component and followed by HPOA in four seasons. Winter and summer seasons in Guangzhou belong to dry and wet seasons, which these two fractions constituted as much as 70 and 42 % of TOC. These were consistent with previous reports (Marhaba and Van 1999; Bruchet et al. 1987). Last four fractions (HPIA, HPIB, HPON, and HPOB) existed from high to low as follows: HPIB, HPOB, HPON, and HPIA in wet season, whilst HPON, HPIB, HPIA, and HPOB in dry season, respectively. In addition, hydrophilic fractions (HPIA, HPIB, HPIN) were more than the hydrophobic fractions (HPOA, HPOB, HPON) according to the distribution percentages of TOC. Figure 3b displays the seasonal variation of UV_{254} for six fractions. HPOA had the highest values in four seasons and had been followed by HPON and HPIB fractions in order, but HPIN, HPIA, and HPOB still existed in very slight quantity, which indicated that the dissolved aromatic compounds and unsaturated compounds with $\text{C}=\text{C}$ bonds appeared more frequently. On the contrary, the hydrophobic fractions were more than the hydrophilic fractions comparing with TOC results. These were explained that the values of UV_{254} only represent the aromatic character of organic matters and are not considerable relationship with TOC. Figure 3c illustrates the seasonal variation of SUVA_{254} for each fraction. It is generally accepted that the SUVA_{254} corresponds to the nature of organic matter in the water source. Samples with an $\text{SUVA}_{254} \geq 4 \text{ L}(\text{mg m})^{-1}$ have a relatively high content of hydrophobic organic compounds, while samples with an $\text{SUVA}_{254} \leq 3 \text{ L}(\text{mg m})^{-1}$ are largely hydrophilic (Kitis et al. 2001; Chaiket et al. 2002; Karanfil et al. 2002). Obviously, SUVA_{254} was lower than $3 \text{ L}(\text{mg m})^{-1}$ in four seasons, suggesting that the hydrophilic components were the main fraction in the DOM. Actually, SUVA_{254} values for most of the hydrophilic fractions in summer, autumn, and winter were higher, but less than the hydrophobic fractions in spring. Moreover, the higher values for HPOA in autumn and spring, HPIA in winter, and HPON in summer indicated that the DOM of

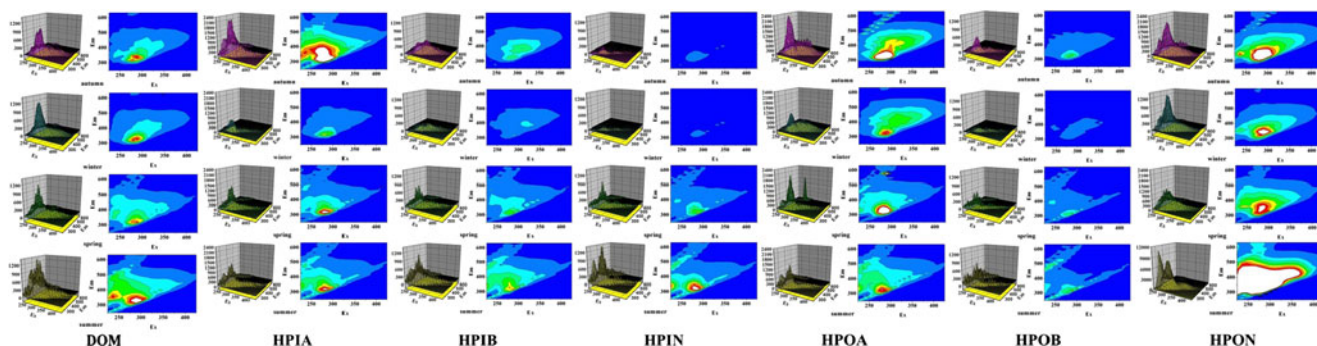


Fig. 4 EEM contour maps of DOM samples, hydrophilic fractions (HPIA, HPIB, HPIN), and hydrophobic fractions (HPOA, HPOB, HPON)

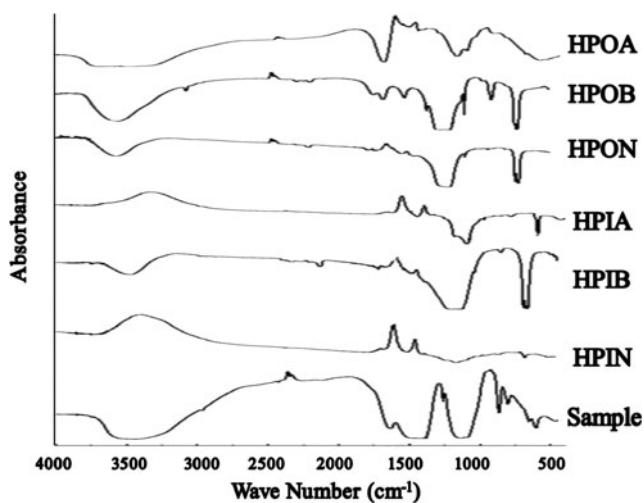


Fig. 5 FTIR spectra of six organic fractions of DOM and raw samples in summer

these samples had higher aromaticity (Mash et al. 2004) and more aromatic organic carbon or organic compounds with conjugated unsaturated double bond.

Characterization of organic composition by excitation emission matrix analysis

Fluorescence properties of DOM could reveal its chemical characteristics and origin (Lombardi and Jardim 1999). Several components, such as humic like, fulvic like, and protein like, have been already associated with DOM in natural waters (Cuss and Guéguen 2013). Actually, there were two types of humic like: microbial and terrestrial humic like. Microbial humic like with maximum fluorescence excitation wavelength was at 300 or 305 nm and emission wavelength approximately at 376 nm, and terrestrial humic-like had two excitation maxima, at ≤ 260 and 360 nm, and one emission ranged between 380 and 460 nm, respectively (Maie et al. 2014). Fulvic-like appeared with an excitation wavelength between 390 and 455 nm and emission wavelength between 509 and 521 nm. Protein like was identified as two excitation maxima at 220 and 275, with other emission peaks at 305 and 350 nm (Baker and Inverarity 2004). The protein-like substances such as a tryptophan-like acid could be observed in terrestrial waters (He and Ohno 2012).

Table 2 FTIR vibration modes for the functional groups identified from six organic fractions of DOM and raw samples in summer

Compounds	FTIR bands	Positions of components						
		Raw sample	HPIA	HPIB	HPIN	HPOA	HPOB	HPON
Carbohydrate (Abdulla et al. 2010)	O–H in-plane bending ($1350 \pm 50 \text{ cm}^{-1}$)	1300	1320	1400	1330	1400	1400	1365
	O–H out-of-plane bending (around 650 cm^{-1})	663	659	619	619	625	630	607
	C–O asymm. stretching ($1100 \pm 100 \text{ cm}^{-1}$)	1116	1105	1116	1105	1129	1105	1116
P compounds (He et al. 2011; He and Ohno 2012)	P–O groups	1116	1105	1116	1105	1129	1105	1116
Amide (Abdulla et al. 2010; Guo et al. 2012)	Amide I (C=O) ($1625 \pm 25 \text{ cm}^{-1}$)	1626	1615	1626	1615	1626	1649	1626
	Amide II (around 1550 cm^{-1})	–	–	–	–	1520	1570	1550
	Amide III ($1260 \pm 40 \text{ cm}^{-1}$)	1280	1276	1300	1278	1250	1255	–
Ester, aliphatic (Abdulla et al. 2010)	N–H vibration of primary amine group and secondary amine group (around 833 and 705 cm^{-1})	833,705	830	830	830	874	811	893
	C=O stretching ($1740 \pm 10 \text{ cm}^{-1}$)	1730	1725	1738	1750	1750	–	1750
	C–C–O stretching ($1185 \pm 25 \text{ cm}^{-1}$)	1160	1174	1190	1174	1172	1174	1160
Carboxylic acid –COOH (Abdulla et al. 2010)	O–C–C stretching ($1065 \pm 35 \text{ cm}^{-1}$)	1020	1018	1030	1032	1070	1010	1023
	C=O stretching ($1710 \pm 15 \text{ cm}^{-1}$)	1700	1710	1710	1710	–	–	–
	C–O stretching ($1265 \pm 55 \text{ cm}^{-1}$)	1280	1276	1300	1278	1250	1255	–
Carboxylic acid –COO [–]	O–H bend in-plane ($1418 \pm 22 \text{ cm}^{-1}$)	1406	1438	1457	1440	1451	1412	1400
	O–H out-of-plane bend ($930 \pm 30 \text{ cm}^{-1}$)	900	950	–	950	900	950	993
	Asymm. stretching ($1600 \pm 40 \text{ cm}^{-1}$)	1626	1615	1640	1620	1626	1649	1626
Lignin (phenol) Ar-OH	Symmetric stretching ($1405 \pm 45 \text{ cm}^{-1}$)	1457	1445	1468	1445	1451	1412	1450
	C–O asymm. stretching ($1230 \pm 30 \text{ cm}^{-1}$)	1220	1250	1250	1230	–	–	–
Lignin (phenol) Ar-(lignin)	Vibration of aromatic ring ($1515 \pm 5 \text{ cm}^{-1}$)	1515	1510	1510	–	1505	1520	1500
Thiols (Guo et al. 2012)	S–H stretch vibration (2680 – 2300 cm^{-1})	2419	2380	2306	2351	2388	2400	2395
Fatty acid, waxes, and aliphatic (Guo et al. 2012)	Aliphatic methyl and methylene groups. Asymmetric and symmetric stretching ($2950 \pm 50 \text{ cm}^{-1}$)	2974	2950	2941	2990	2990	2952	–

– none

The excitation and emission maxima (or ranges) of each component for DOM and its six fractions are listed in Table 1. And then, Fig. 4 presents the identified components from the EEMs of DOM samples. These three fluorescent components were identified in drinking water sources' section of the Pearl River, and the fluorescence intensities of protein-like materials were shown to be strongest, of which seasonal variation was decreased in the order of summer, autumn, winter, and spring. Meanwhile, the fluorescence index (FI) was also calculated as the ratio of the Em intensity ($f_{450/500}$ nm) for the Ex wavelength of 370 nm and then used to differentiate between allochthonous and autochthonous DOM sources (Shafiquzzaman et al. 2014) and also to determine terrigenous DOM (FI 1.4) and biological DOM (FI 1.9) (McKnight et al. 2001). Therefore, FI values of DOM samples were obtained as 2.31 (spring), 1.88 (summer), 2.11 (autumn), and 2.25 (winter), indicating that these FI values were associated with allochthonous DOM sources and biological DOM and attributed to the increase of the amount of wastewater discharged around the back channel section (Haizhu and Panyu districts), which has been become the industrial and residential area. As shown in Fig. 4, protein-like materials were still the major component for both the hydrophilic fractions and the hydrophobic fractions. Among them, the fluorescence intensities of protein-like components for HPIB, HPIN, HPOB, and HPON in summer were higher than those of other seasons, similar as DOM samples, but higher in autumn for HPIA and HPOA. These fractions were mainly composed of humic-like component and dominated by microbial types in summer but less in winter, which explained that the bacteria had better activities in DOM consumption during the summer season. In six fractions, HPOA was deemed to be the greatest precursor for DBPs, particularly THMs (Chang et al. 2001). Thus, it should be paid more attention in water treatment, due to its enrichment in microbial humic-like and protein-like components. However, none of fulvic-like materials exists in the hydrophilic fractions and HPOB.

Fourier transform infrared

Fulvic like and protein like are considered to be associated with the carboxyl group of humic substance structures and DOM in the aromatic ring structure of amino acids, respectively. And, summer is one of the most representative seasons in Guangzhou section. Therefore, the FTIR spectrum of six organic fractions of DOM and raw samples in summer was further analyzed and then is presented in Fig. 5 and Table 2. In Fig. 5, the intensities of several peaks, such as O–H bending, C–O stretching, and N–H vibration groups of the primary amine group, etc., were more significant than some peaks, which included C=O stretching, O–C–C stretching, and N–H vibration groups of secondary amine group, etc. Moreover,

some bands, around 1260 cm^{-1} for instance, were ascribed to the multiple overlapping peaks, implying that it would be corresponded to amide III or C–O stretching of carboxylic acid. And, peaks around 1100 cm^{-1} were mainly C–O stretching and possibly due to P–O groups. Then, these bands were further identified as P compounds after element analysis. These results revealed that DOM samples had relatively higher concentration of amide, ester, carboxylic acid, and thiols owing to their stronger bands and also had a certain contribution from lignin, fatty acid, waxes, and aliphatic (Table 2). In addition, the major materials of hydrophilic and hydrophobic fractions were identical to those of DOM samples and appeared enriched in amide and ester. These were in good agreement with the calculation of SUVA_{254} values and the analysis for fluorescence of fulvic like and protein like.

Conclusions

In this study, DOM and its fractions in the back channel section of the Pearl River were characterized using multiple analytical tools. The values of TOC, UV_{254} , and SUVA_{254} were affected by seasonal changes; the hydrophilic fractions were found to be the main components and enriched with aromatic components. For the spectral features, fluorescence analysis found the fluorophore components present in DOM and its fractions and identified the major presence of microbial and terrestrial humic like, fulvic like, and protein like. FTIR spectra indicated that DOM was more enriched in carbohydrate, amide, carboxylic, and aliphatic compounds.

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