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Compositional variety of dissolved organic matter and its correlation with water quality in peri-urban and urban river watersheds

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ABSTRACT

Urbanization has significant effects to ecosystems in watersheds, but the link between surface water quality and the dissolved organic matter (DOM) composition is poorly understood. We investigated the fluorescent intensities (F_{max}) of DOM components and examined their correlation with the water quality parameters in peri-urban (Zhangxi River) and urban (Lu River) watersheds in Ningbo, East China. DOM quality was measured by fluorescent excitation-emission matrices (EEMs) coupled with parallel factor analysis (PARAFAC). Terrestrial humic-like components (C1 and C2) and protein-like component (C3) were derived by the PARAFAC model. We found more serious water pollution (significantly higher values for most water quality parameters, i.e. chemical oxygen demand (COD), chlorophyll *a* (Chl-a), dissolved organic carbon (DOC), ammonia and total suspended solids (TSS)) in urban than peri-urban watersheds. However, there were no significant differences in the levels of total nitrogen (TN) and total phosphorus (TP) between the urban and peri-urban watersheds. The results showed that the urban watershed had higher terrestrial humic-like C1 (39%) and lower protein-like C3 (30%) than the peri-urban watershed, while the peri-urban watershed showed an inverse trend (33% and 37%, respectively). The results also revealed that the DOM fluorescent indices were significantly different between the peri-urban and the urban watersheds. Redundancy analysis (RDA) was applied to evaluate the correlation between DOM fluorescent indices and water quality parameters (i.e., COD, TN, TP, DOC). It revealed that the pollution sources and water quality correlated to the fluorescent indices and the C1-C3 DOM fluorescent components. A significant linear relationship between COD and C2 was found in both watersheds, suggesting that C2 might be a good COD indicator. Our results suggest that the distinctive DOM composition between the watersheds could be attributed to different human activities at both sites. The correlation between DOM fluorescent components and water quality can be assessed by the EEM-PARAFAC method, indicating considerable potential for the use of this technique to monitor surface water quality.

1. Introduction

Dissolved organic matter (DOM) is ubiquitous in aquatic ecosystems, and plays a fundamental role in several biogeochemical processes (Xu et al., 2017; Williams et al., 2016). For example, DOM provides essential nutrients and energy to aquatic microorganisms, acts as a major pool of dissolved organic carbon (DOC) and is an important global carbon reservoir in aquatic environments (Williams et al., 2016). The quality and quantity of DOM in aquatic ecosystems can be heavily influenced by anthropogenic activities (Williams et al., 2016). Rapid urbanization trends are accompanied by human population growth, resulting in extensive widespread anthropogenic activities in urbanized watersheds. Therefore, towards better health assessment of aquatic ecosystems and to enhance water management practices, it is critically important to understand factors affecting DOM production, its behavior, sources and characteristics.

Urban population has been gradually increasing since the 1950s, with more than 50% of the global population living in urban areas now (Grimm et al, 2008). Increased urbanization leads to changes in water ecosystems and negatively affects water quality (Grimm et al., 2008; Chen et al., 2005; Chen et al., 2016; Mcdonald et al., 2011). Many studies indicate that urbanization is strongly correlated with water

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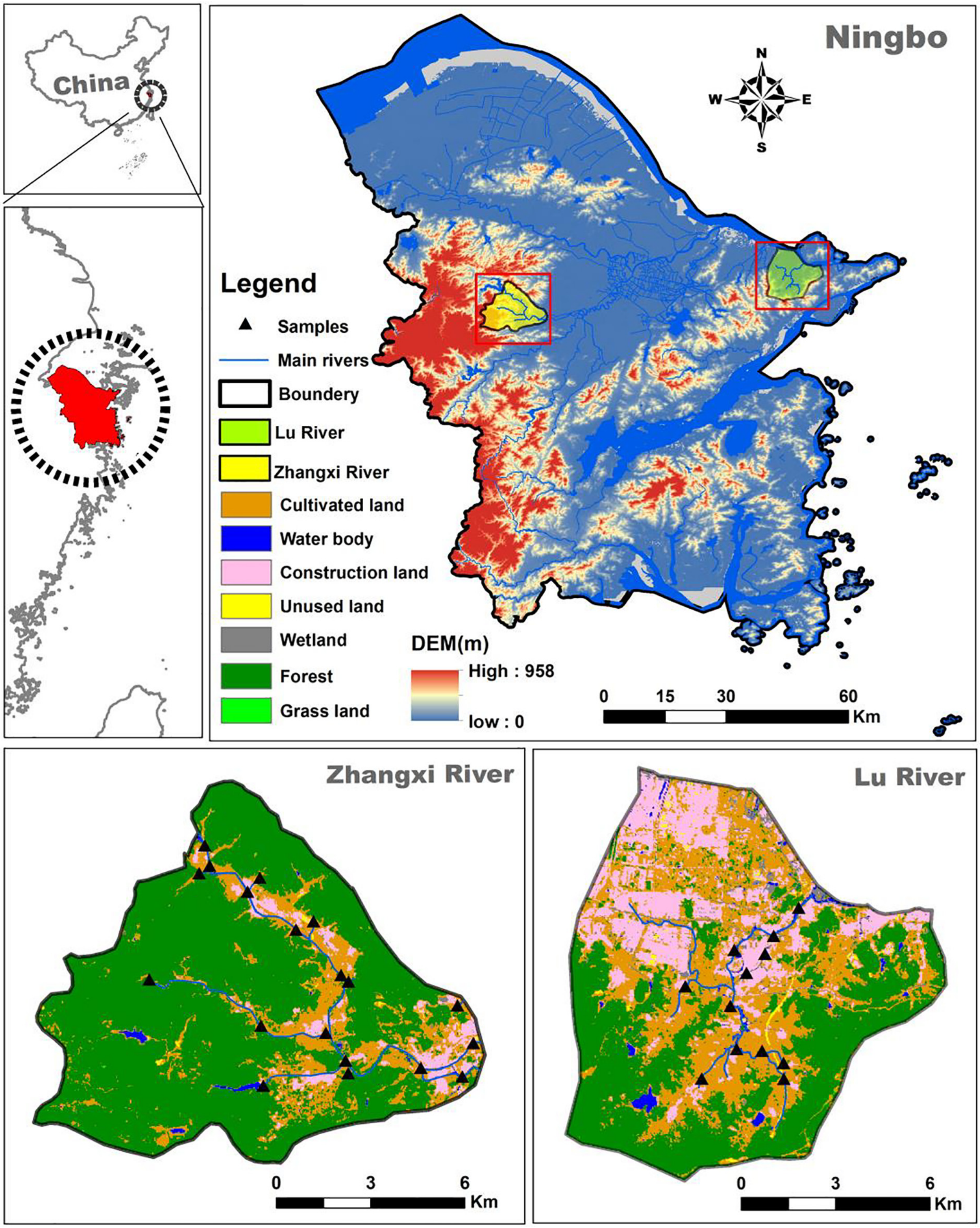

Fig. 1. Location map of the study area and water sampling locations for Zhangxi River and Lu River in East China surrounded by various land use.

quality parameters, including ammonia nitrogen and chemical oxygen demand (COD) (Li et al., 2015; Devilbiss et al., 2016; Zhou et al., 2016; Shi et al., 2017). Human activities are mostly connected to land use, urban development and agricultural activities, which are all positively correlated with water quality parameters (e.g., ammonia, phosphorus, nitrogen) (Yu et al., 2016). Watershed surface water quality can be affected by land use through nonpoint source pollutants, which are the key contaminants of the watershed-coast continuum (Zhou et al., 2016).

Urbanization have a heavy influence on the composition and characteristics of DOM in aquatic ecosystems (Silva et al., 2011; Gücker et al., 2016; Pagano et al., 2014). Such as urbanization increased stream water DOM concentrations (Silva et al., 2011; Gücker et al., 2016) and affected the bioavailability of DOM and its composition (Parr et al., 2015). The natural environmental factors (ie.,pH, metal ions and temperature) within the water body can influence DOM sources (Hudson et al., 2010). The quantity and quality of DOM in rivers are connected to watershed attributes including soil types, agricultural intensity and urban point-source inputs (Shang et al., 2018). It is observed that significant higher humic-like fluorescence were found in agricultural catchments than forested catchments (Graeber et al, 2012). Moreover, DOM in remote water systems is unlikely to be affected by human activities (Zhang et al., 2011), but DOM is strongly affected by human activities such as treated and/or untreated wastewater inputs in urbanized area (Greenwood et al., 2012; Meng et al., 2013). Water pollution due to mixing of anthropogenic and natural organic matter can significantly change the structure and composition of DOM (Guo et al., 2014; Zhao et al., 2017). Human activities can affect aquatic ecosystem DOM exports, and specifically the DOM in watersheds is broadly vitiated, as it is dependent on the unique characteristics of *in situ* DOM production and the terrestrial DOM sources (Stanley et al., 2012).

In addition to many environmental processes in water ecosystems, DOM can benefit tracing of the biogeochemical cycling process and aquatic inputs of DOM (Devilbiss et al., 2016). Optical measurement of DOM sub-fractions can provide useful insights into DOM composition and it has caught attentions in recent years (Devilbiss et al., 2016). Optical tool such as excitation-emission matrix (EEM) spectroscopy is quick and sensitive and has been traditionally used to monitor water quality (Jin et al., 2008). Fluorescent measurements are effective and attractive approaches to monitor water quality (Henderson et al., 2009; Wang et al., 2017). Specifically, EEM spectroscopy is widely used to examine a large-scale of emission and excitation wavelengths within diverse fluorescent components of DOM. Furthermore, parallel factor analysis (PARAFAC) coupled with fluorescent EEMs has become a beneficial tool to identify autochthonous and allochthonous fluorescent DOM components in multiple water ecosystems (Hudson et al., 2010; Devilbiss et al., 2016). Previous studies suggested that EEM-PARAFAC is a promising alternative method to trace water quality linked with DOM composition and water quality in organic sources (Wang et al., 2017). Some studies indicate that the EEM fluorescent composition might be a good indicator for monitoring of lake water quality (Wang et al., 2017; Zhao et al., 2017). However, little is known about the relationship of EEM-PARFAC fluorescence and water quality in peri-urban and urbanized rivers. Additionally, comparison studies examining the correlation between water quality and EEM-PARFAC fluorescence in watersheds with different gradient urbanization are lacking.

Consequently, we hypothesize that: 1) water pollution is more likely in more urbanized watersheds; 2) urbanization affects the aquatic DOM concentration and quality; 3) the characteristics of DOM reflect the water quality in aquatic systems.

2. Materials and methods

2.1. Overview

We conducted our analysis to compare two watersheds with different urbanization gradients. We tested our hypotheses by water sampling in Zhangxi River watershed (a typical peri-urban watershed) and Lu River watershed (a typical urban watershed) in Ningbo City, east China. At each sampling site, a comprehensive panel of water quality parameters was measured, including assessment of DOC concentration and fluorescent characteristics.

2.2. Study area

We studied Zhangxi River watershed and Lu River watershed situated around a sub-provincial city of Ningbo in the Zhejiang Province, located in the Yangtze River Delta in Southeastern China (Fig. 1). This region exhibits a typical subtropical monsoon climate, with dry and wet seasons in each year, an annual mean cumulative precipitation of 1480 mm (Sun et al, 2018). Mean monthly temperature is the highest in July (28.0 °C) and the lowest in January (4.7 °C) (Sun et al, 2018).

Land coverage data are provided by Geospatial Data Cloud site, Computer Network Information Center, Chinese Academy of Sciences (http://www.gscloud.cn). Land use data are from remote sensing image classification based on Landsat 8 software. Land use data were divided into six broad categories: forest, grassland, cultivated land, urban area (construction land), wetland and unused land (Fig. 1). The percentage (%) of each land use category in watersheds (land use composition) was calculated. Land use within the peri-urban (Zhangxi River) watershed is dominated by forest (76.7%) and cultivated land (17.0%), while the urban land (construction land) accounted for only 4.38%. Land use within the urban (Lu River) watershed is dominated by forest (38.4%), cultivated land (35.3%), and construction land (20.6%).

2.3. Water sampling

Water samples were collected during four seasons (December 2016 - September 2017) from 19 locations within the Zhangxi River watershed and from 12 locations within the Lu River watershed. Water samples were collected from the middle of each river into clean plastic bottles and immediately transported (kept in refrigerator) to the laboratory where they stored in the dark at 4 °C. Temperature, DO, salinity, and pH were measured at the time of water sampling by using a portable multi-parameter water quality analyzer (YSI EXO1, USA). All other measurements (see below) were completed within one week following sample collection.

2.4. Water quality measurements

The chemical oxygen demand (COD) was determined according to the methods outlined in Monitoring and Analytical Method of Water and Waste Water (State Environmental Protection Administration of China, 2002). Dissolved organic carbon (DOC) concentrations were quantified using elemental analyzer (Shimazdu, TOC V-CPH, Germany). Nitrogen and phosphorus were measured using standard spectrophotometric methods with a flow injection analysis system. Total phosphorus (TP) and total nitrogen (TN) were determined according to the methods specified in the State Environmental Protection Administration of China (2002). A UV–Vis DR6000 spectrophotometer (Hach) was used to determine chlorophyll *a* (Chl-a) concentration after water samples were extracted with a 90% acetone solution filtered through a 0.45 μm GF/F filter (Whatman).

2.5. UV visible absorption

We used an Analytik Jena UV–visible spectrophotometer (Specord 250 plus, Germany) to measure the ultraviolet (UV) absorbance with a scanning wavelength ranging from 200 to 600 nm. Specific ultraviolet absorbance at 254 nm ($SUVA_{254}$) was measured by taking the absorbance of a DOM sample at 254 nm and dividing it by the DOC concentration, recorded as L mg C^{-1} m^{-1}. Milli-Q water was used as blank and absorption values for the blank were subtracted from each of the analyzed samples. DOM absorption coefficients at wavelength λ (a(λ)) were calculated from the following equation: $a(\lambda) = 2.303D(\lambda)/r$, where D(λ) is the corrected optical density at wavelength λ, and r is the cuvette path length in meters (m). We used values at λ of 350 nm to represent the DOM concentrations.

2.6. Three-dimensional fluorescent measurements and PARAFAC modeling

EEM of DOM was determined according to previously published methods (Tang et al., 2016). Briefly, a fluorescent Cary Eclipse spectrophotometer (Varian Inc., USA) was used to measure EEM using the scan mode. The excitation and emission wavelengths were set to 5 nm, the excitation scan (wavelengths of 240–450 nm) was performed in 5 nm increments, the emission scan (wavelengths of 260–550 nm) was performed in 1 nm increments, the scanning speed was 3200 nm/s, and the integration time was 0.1 s. Milli-Q water was used as blank and

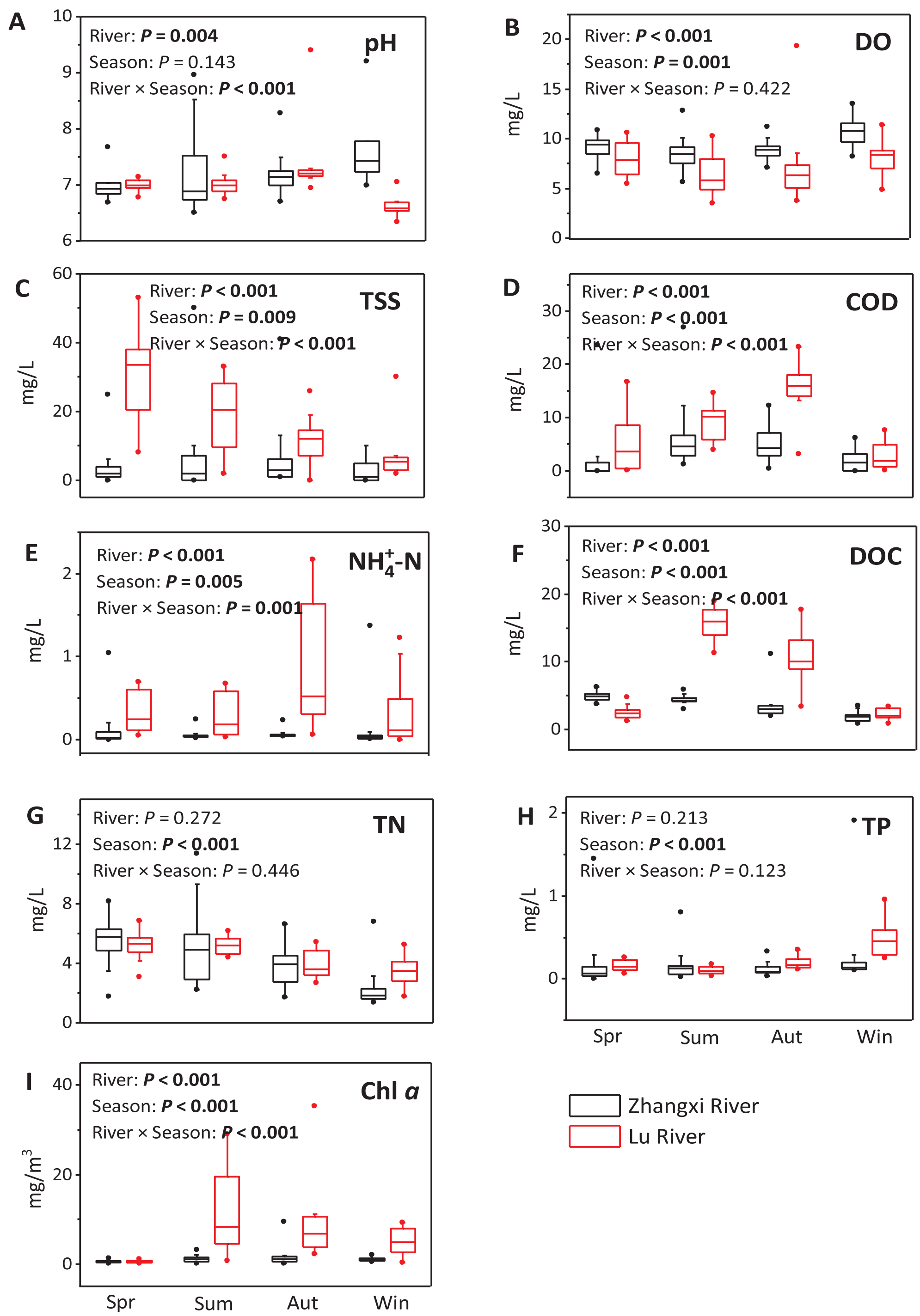

Fig. 2. Values of water quality parameters in Zhangxi River and Lu River. The box represents data between 25th and 75th percentile, the middle band represent the median value (*means significant difference).

Raman scanning was performed at a wavelength interval of 0.5 nm at λ ex = 350 nm. The correction procedure was followed the methods according to Murphy et al (2010): (1) instrument deviation correction with Rhodamine B solution; (2) internal filter effect correction using UV spectroscopy; (3) Samples and blank EEMs are normalized to Raman units by Raman peaks; (4) the blank EEMs were subtracted from the sample EEMs to remove Rayleigh and Raman scattering.

PARAFAC analysis was implemented using the DOMFluor toolbox (Stedmon and Bro, 2008) and MATLAB 2014a software (Mathworks, Natick, MA, USA). This software contains all tools that required to remove Raman and/or Rayleigh scattering and to identify outlier water samples. Using the smoothing function in the drEEM toolbox to remove residual scattering from EEMs (Murphy et al. 2013). This analysis consisted of 128 samples, 3 outliers were removed, and the remaining 125 samples were included for the PARAFAC analysis. Since the excitation wavelength less than 240 nm have high level of noise, these signals were removed from each EEM. Since negative and negative concentrations of fluorescence density are unlikely to occur under chemical conditions, a non-negative constraint was used to the processing parameters to allow only chemical realistic results. A two to eight component for PARAFAC modeling were fitted to the data in order to determine the correct number of components. A three-component model was validated by the four-way split-half analysis procedure according to Stedmon and Bro (2008). This model explains 98.8% of the variance within the dataset. F_{max} values which are the respective excitation and emission maximum fluorescent values of each component, were used to quantify components. The quantitative data were compared with the published data with the online spectral library (the OpenFluor website, http://www.openfluor.org). Similar spectral peak identified in OplenFluor with Tucker congruence θ greater than 0.95 (Murphy et al., 2014).

2.7. Fluorescence spectral index

The r(A/C) values were calculated by the ratio of fluorescence intensity at peaks A and C and represent DOM in the relative composition of humic fractions (Patel-Sorrentino et al., 2002; Wang et al., 2017). Other DOM optical indices and parameters were also calculated, including the Fn (355), the fluorescence index (FI), the biological index (BIX) and the humification index (HIX) (Jiang et al., 2017b). FI is the ratio of fluorescence intensities between emission wavelength 470 and 520 nm and an excitation wavelength of 370 nm. HIX is the area under emission spectra at 435–480 nm divided by the peak area at 300–345 nm. BIX is the ratio of fluorescence intensity between wavelength of 380 nm and 430 nm (emission) and 310 nm (excitation). Fn (355), with excitation at 355 nm, and emission at 440–470 nm, represents fluorescent dissolved organic matter concentration in water samples (Vignudelli et al., 2004).

2.8. Statistical analyses

The data were statistically analyzed using SPSS (version 16.0 for Windows, SPSS Inc., Illinois). One-way analysis of variance (ANOVA) was used to examine differences in water quality parameters and fluorescent indices between the urban and peri-urban watersheds. Statistically significant differences were considered at p-values < 0.05. Principal component analysis (PCA) was used to identify the spatial separation of water quality parameters (pH, COD, DOC, TN, Chl-a, TP and TSS) in the surface water of the two examined watersheds. ANOVA and PCA were performed using SPSS. Redundancy analysis (RDA) performed using Canoco 5 software, which was used to evaluate the relationship between fluorescent indices, DOM composition, and the water quality parameters (water quality parameters were the explanatory variables and the changes in the fluorescent components (C1-C3) and fluorescent index were the response variables).

3. Results and discussion

3.1. Water quality index statistics and analysis

Seasonal change of water quality parameters of pH, DO, TSS, COD, DOC, ammonia, Chl-a, TN and TP were demonstrated in Fig. 2. Water quality varied with seasonal variations. For comparison of the two watersheds, levels of TSS, COD, Chl-a, NH_4^+-N and DOC were significantly higher in the urban (Lu River) compared to the peri-urban (Zhangxi River) watershed (Fig. 2), and significant lower DO were observed in urban watershed, these results were in agreement with our original hypothesis. However, no significant differences were detected in the water quality parameters for TN and TP between the urban and peri-urban watersheds.

The water quality in sampling sites are determined by numerous factors, including land use, hydrological conditions, and anthropogenic activities (Lintern et al., 2018). Agricultural and urban land-use types are closely related to human activities and are positively correlated with water quality parameters (e.g. nitrogen, phosphorus, ammonia), while grasslands and woodlands are less impacted by human activity and exhibit negative correlations with water quality parameters (Chen et al., 2016b). In our analysis, we found that most of the water quality parameters such as COD, Chl-a, DOC, NH_4^+-N and TSS concentrations were significantly higher in Lu river (urban) compared to Zhangxi river (peri-urban) (Fig. 2). Similarly, the land-use types dominated in the urban Lu River are agricultural and urban, while in the peri-urban Zhangxi River the main land-use types are forest. Overall, our results in agree with the previously reported research in other regions (Tu, 2011; Shi et al., 2017). Generally, urban and agricultural lands can contribute most via diffusion pathways to surface water pollution by nitrogen and phosphorus compared to forest and grasslands. So, higher levels of nutrients in particulate and dissolved phase can contribute to pollution (Lintern et al., 2018). Changes in land use towards urbanization and agriculture often involve loading from sewage and fertilizer runoff (Fuss et al., 2017). For example, urban land use was significantly linked with nitrogen pollution in water systems (Tong and Chen, 2002). In the Northwestern U.S., positive correlation between TP concentrations and the proportion of the urbanized land use that was found in 14 river locations (Pratt and Chang, 2012). Interestingly, no significant differences in the TN and TP levels were found between the two rivers examined in the current study. Furthermore, in the peri-urban watershed region farmers use copious amounts of inorganic fertilizer and organic manure with about 100 kg of nitrogen applied per hectare (Sun et al., 2018). Moreover, very high levels of TN (exceeding 2.0 mg/L, the Class IV standard of Chinese standard of surface water environment quality) and TP were found in both rivers, suggesting significant nitrogen and phosphorus pollution in both examined areas. Owing to protection from rain, overland runoff and wind, forested catchments generally show less soil erosion (Lintern et al., 2018). Significantly higher TSS concentration was found in the urban river and it may suggest increasing soil erosion in the urban watershed. Studies report conflicting data in diverse water ecosystems on the effects of land use and DOC concentration in the water stream (Wilson et al., 2008; Graeber et al., 2012). Our analysis revealed significant higher DOC concentration in the urban compared to the peri-urban watershed, similarly to previously reported data suggested that agricultural catchment have significant higher DOC concentration than forested catchment (Graeber et al., 2012).

PCA analysis was performed on water quality parameters from two analyzed rivers (Fig. 3). The first two principal components (PC1, 42.8%; PC2, 20.2%) accounted for 63.0% of the overall data variance.

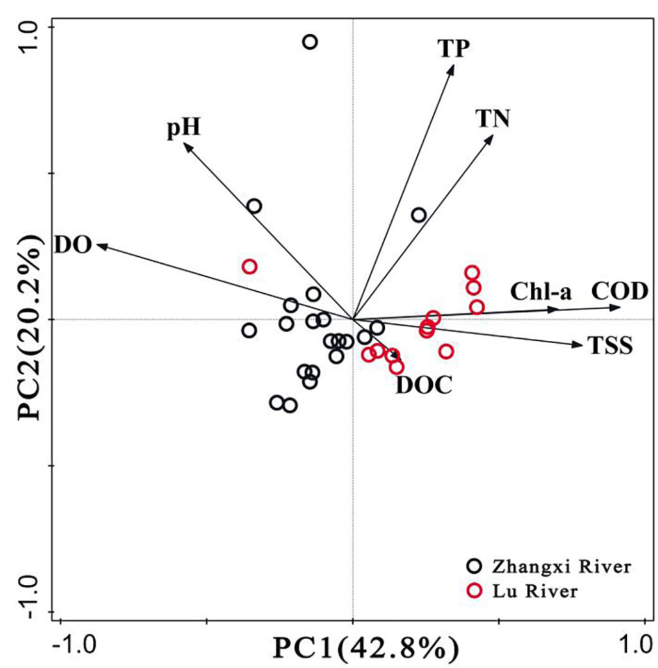

Fig. 3. Principal component analysis (PCA) of the average values of the water quality parameters (TN, TP, Chl-a, TSS, DOC, COD, pH and DO) of Zhangxi peri-urban and Lu River urban watershed.

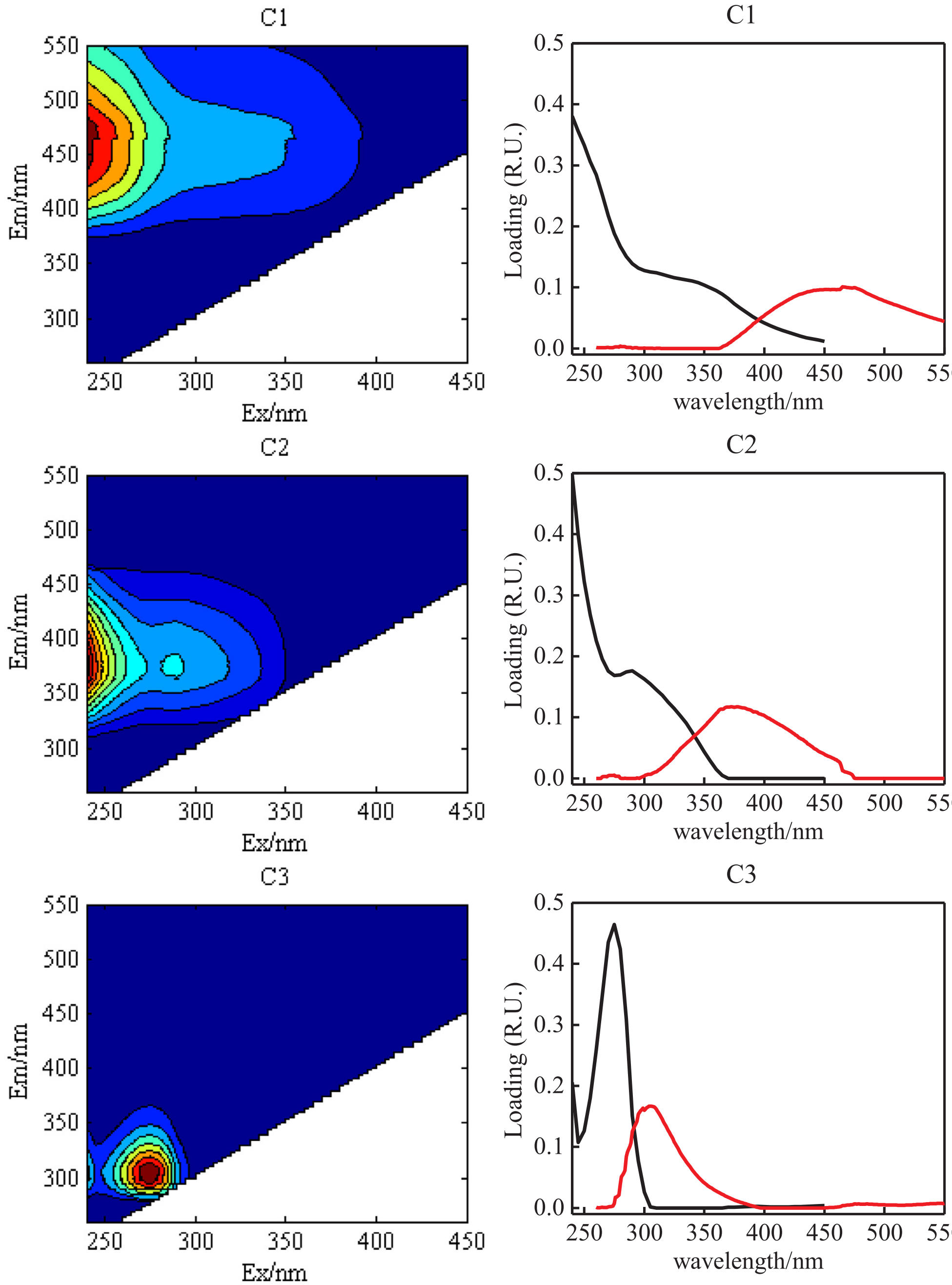

Fig. 4. Contour plots of the three PARAFAC components from water samples of the two studied watersheds.

Table 1
Excitation and emission of PARAFAC components for the water samples.

Component	$\lambda_{excitation}$ (nm)	$\lambda_{emission}$ (nm)	Probable origin	Number of OpenFluor matches[b]
C1	< 240	465	Terrestrial/autochthonous humic-like substances	33
C2	< 240	375	Terrestrial humic-like substances	11
C3	< 240 (275)[a]	305	Protein-like(tryptophan-like) substances	17

[a] Excitation wavelength given in parentheses represent secondary peak.
[b] http:www.openfluor.org conducted September 20, 2018.

The first principal component showed relatively high positive loadings for DOC, TSS, Chl-a and COD, while pH and DO had relatively high negative loadings. All samples (except one) from the urban watershed clustered on the positive side of PC1, with PC2 loading being lower, while most samples from the peri-urban watershed were clustered on the negative side of PC1. The results of PCA analysis indicate that the average values of water quality parameters are different between the peri-urban and urban watersheds. Consequently, different water quality affects the distribution of the fluorescent properties of DOM.

3.2. Comparison of DOM composition and fluorescent indices in the urban and peri-urban watersheds

In this study, three fluorescent compounds including two terrestrial humic-like components and one protein-like components were derived by PARAFAC modeling data of the two studied watersheds, and the corresponding emission and excitation values of the three substances are shown in Fig. 4. Table 1 shows the locations and the matching numbers of each component. In diverse water ecosystems (natural and/or engineered), substances with EEM-PARAFAC emission wavelengths larger than 380 nm are normally considered humic-like, while substances with EEM-PARAFAC emission wavelengths lower than 380 nm are typically considered protein-like (tyrosine or tryptophan-like) (Ishii and Boyer, 2012; Li et al., 2014). Our results were compared with published PARAFAC model data with the OpenFluor online spectral library (Murphy et al., 2014), and the results are good matches with the published PARAFAC results (the derived components with Tucker congruence exceeding 0.95 on Ex and Em spectral) (Table 1). Components C1 and Components C2 were respectively congruent with reported terrestrial humic-like components across a wide rage of environmental matrix including forest streams, agricultural watersheds, storm-water, wastewater (Derrien et al, 2018; Williams et al, 2013; Murphy et al, 2011; Graeber et al, 2012; Fuss et al., 2017). Component C3 were congruent with protein-like (tryptophan-like) substance reported in wastewater, agricultural and forest streams and seawater (Stedmon et al., 2005; Murphy et al, 2011; Graeber et al, 2012; Painter et al, 2018).

The results of EEM-PARAFAC analysis showed that the three derived fluorescent components were distinct between the two studied watersheds and varied specifically in the values of the fluorescent intensity (Fig. 5). Seasonal variation of the three fluorescent components were observed in the two studied watersheds, the values of fluorescence intensity (F_{max}) in autumn were significant higher than other seasons ($p < 0.01$). Obviously, the urban and peri-urban watersheds varied substantially in F_{max} values, significant higher F_{max} values, especially the terrestrial humic-like components (C1 and C2), were found in the urban (Lu River) than the corresponding values in the Zhangxi River (Fig. 5) ($p < 0.01$). Additionally, the percentages of maximum fluorescent intensity for the three components (%F_{max}) were also calculated to compare the differences between the two examined watersheds. In contrast to F_{max} values, much smaller variance was observed in the %F_{max} for each analyzed component (Fig. 5). The composition of DOM in the peri-urban watershed was significantly distinct from that in the urban watershed. Our results demonstrate that urban watershed have significant higher percentage of C1 and lower percentage of C3 than the peri-urban watershed, and no significant of the percentage of C2 were found in the two studied watersheds.

Significant higher percentage of terrestrial humic-like component C1 in urban watershed compared to the peri-urban watershed suggests that DOM from urbanized watershed was likely derived from more humified soil organic matter compared to the peri-urban watershed. DOM composition is sensitive to human activities, although agricultural and urbanized land use can lead to different DOM composition (Gücker et al., 2016). More humic-like DOM composition was more pronounced in the agricultural land use (Graeber et al., 2012; Yang et al., 2018), suggesting that agricultural land use could be an important source that changes the surface water DOM composition towards more humic-like components. Our findings indicate that the humic-like DOM in the urban Lu River watershed is likely released from the humic soil organic matter produced by human activities. Moreover, soil organic matter is the main source of DOM and is supported by its high HIX values (Fellman et al., 2010).

Interestingly, no significant differences for percentage of C2 were observed between the two studied watersheds. Historically, C2 has been connected to point sources like wastewater effluent sites or agricultural fields, and it represents microbial produced anthropogenic humic acids (Hosen et al., 2014). Our results indicate that the peri-urban and urban rivers both receive a large amount of anthropogenic sewage discharge, which was confirmed by examining the r(T/C) values in both rivers.

In this study, a relative high portion (> 30%) of protein-like (tryptophan-like) components (C3) was found in both watersheds, these results can likely be attributed to high temperatures in these river ecosystems, which in turn could accelerate phytoplankton growth and cause an increase in protein-like materials (Liu et al, 2018). Protein-like component are important markers of anthropogenic discharges, such as functioned as an indicator of wastewater discharge (Yang et al, 2018). The peri-urban watershed (Zhangxi River) was found to contain significantly more proportion of protein-like C3 components compared to the urban watershed (Lu River), which is consistent with previous studies examining forested catchment (Graeber et al., 2012; Williams et al., 2016). Typically, relative higher proportion of protein-like materials is found in urban rivers or sewage-polluted rivers (Parr et al., 2015; Liu et al, 2018), and proportions of C3 components are positively correlated with urban land-use (Lintern et al., 2018). The higher proportion of C3 in peri-urban watershed suggests that other factors, such as human activity and land-use changes, can also influence DOM characteristics and composition. Specifically, a significant increase in the proportion of protein-like materials was observed with increasing intensity of human activity in Laurentian Great Lakes region (Hosen et al., 2014; Williams et al., 2016). In the examined peri-urban watershed, where the village is located around the sampling sites, that reflects the agricultural land use and anthropogenic activity is dominated. It is very likely that the significantly higher protein-like DOM found in the peri-urban river was influenced by the anthropogenic intensity. Another reason for such high proportion of C3 may be due to the application of organic fertilizer and pesticide in the examined area (see 3.1 Water quality index statistics and analysis). The residues from these materials can be carried to the river through runoff and erosion and may directly contribute to the protein-like DOM (Osburn et al., 2016) and cause accumulation of high nutrients (TN and TP) in the river, which in turn may increase the proportion of C3 by boosting phytoplankton growth. Moreover, in the study peri-urban area (in scattered villages), the sewage treatment facilities are insufficient, this could induce the peri-urban river receive much wastewater without adequate treatment. This factor may also contribute the higher proportion of protein-like component in the peri-urban watershed.

It is widely accepted to use FI values to distinguish between DOM sources, with FI values larger than 1.9 indicating autochthonous (algal-derived and/or microbial DOM) sources, and FI values < 1.4 indicating allochthonous sources (terrestrially-derived) (Mcknight et al., 2001; Jiang et al., 2017b). In this study, significant difference of FI values were found in spring and summer, and no significant differences were observed in autumn and winter among the two studied watersheds. FI for most of the water samples analyzed in our study was within the range of 1.4–1.8, indicating DOM sources were likely both microbial- and terrestrial-derived. In natural aquatic ecosystems, HIX values usually range from 1.5 to 9.0 with higher values suggesting a higher degree of humification (Chen et al., 2011; Hansen et al., 2016; Jiang et al., 2017a). Significantly higher HIX values were observed in the urban Lu River compared to the peri-urban Zhangxi River (except winter) (Table S1), suggesting that urban river displayed more humified and more aromatic DOM character. Typically, HIX values greater than 10 that convincingly suggest an important terrigenous contribution with strong humic character (Huguet et al., 2009). However, in our study all HIX values were much lower than 10, indicating that the DOM sources were not terrestrial-dominated. BIX is a parameter that characterizes DOM of recently produced microbial contribution (Huguet et al., 2009; Jiang et al., 2017a; Jiang et al., 2017b). BIX values greater than 0.8 indicate DOM with autochthonous sources of recently produced organic matter of bacterial origin or aquatic biology (Huguet et al., 2009). In this study, majority of the water samples had BIX values lower than 0.8, suggesting DOM with less autochthonous sources.

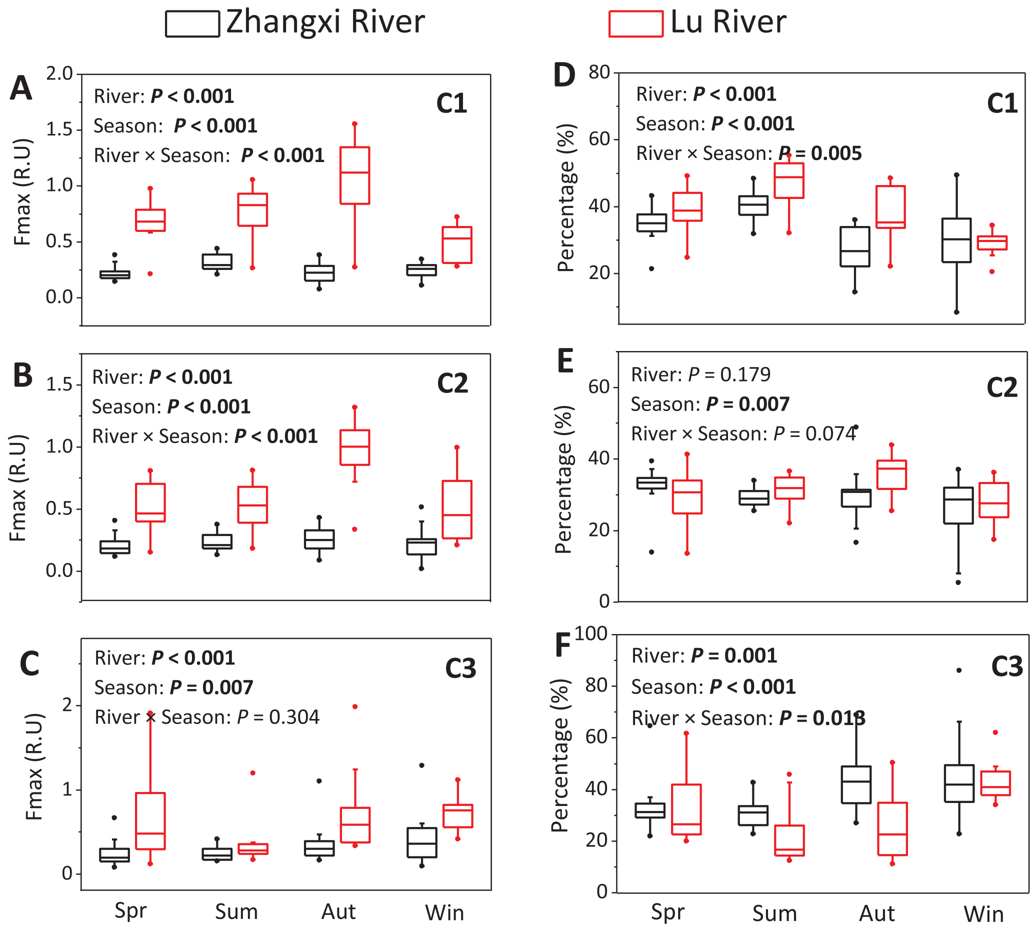

Fig. 5. Box plot comparisons of PARAFAC components among the two watersheds. (a): the PARAFAC abundance and (b): the percentage of each component.

Significant difference between the urban and peri-urban watersheds were observed in summer and autumn, but no significant differences evident were found in spring and winter (Table S1).

To further investigate the sources of DOM in the two studied rivers, r(A/C) and r(T/C) values were calculated according to the corresponding peaks of intensity ratios. As peak C is related to more recalcitrant or older structures, the ratio r(A/C) is a good indicator reflecting the relative humic-like compositions and it distinguishes older and “younger” (relatively less recalcitrant) humic structures (Yan et al., 2015; Jiang et al., 2017b). Significantly higher r(A/C) values were found in the peri-urban Zhangxi River compared to the urban Lu River (Table S1), suggesting that “younger” humic-like DOM components exist in the peri-urban river. Moreover, our analysis suggests that distinct DOM sources were found between the two studied rivers. Human disturbance may shift in composition toward a more “younger” and less “older” DOM (Lambert et al., 2017), and our results were in agreement with the high anthropogenic intensity found in the peri-urban area.

Moreover, we found no significant differences in (T/C) values between the peri-urban Zhangxi River and the urban river Lu River except autumn, suggesting no differences in autochthonous DOM characteristics among the two examined watersheds. In addition, examining the r (T/C) ratio is also of importance when evaluating water pollution. Similar to the use of peak T to track wastewater pollution into natural aquatic ecosystems, r(T/C) is a good predictor of water quality (Baker, 2001; Jiang et al., 2017b). According to the comparison between natural and polluted water (Baker, 2001; Baker, 2002; Carstea et al., 2016), r(T/C) values > 2.0 suggest a significant wastewater discharge and pollution in the analyzed water samples. Our analysis found that r (T/C) values were higher than 2.0 for about 50% of the surface water samples, suggesting that discharged wastewater into that two rivers should not be ignored. A sample from the Zhangxi River showed the highest r (T/C) value of 9.2, indicating the point-pollution sources in the peri-urban river may heavily affects on the water quality. In addition, significant higher r(T/C) values were found in peri-urban watershed in autumn compared the urban watershed, indicating more wastewater discharged to the peri-urban river in autumn.

3.3. Relationship between DOM composition and water quality

Deterioration of water quality has been an important issue in urbanized rivers, where excessive anthropogenic-derived contaminants are rapidly increasing (Wang et al., 2008). Correlation coefficients between PARAFAC components (C1–C3), selected DOM fluorescent indices and water quality parameters (COD, DOC, Chl-a, TN, TP, NH_4^+) were calculated, and relationships were assessed by Pearson’s correlation coefficient (r) (Table 2). Significant correlations were evidently showed among the water quality parameters such as COD, NH_4^+-N and Chl-a and the DOM components C1, C2, C3, suggesting that PARAFAC components might be good indicators of these water quality parameters. The analysis also showed weak correlation between water quality and fluorescent indices. Specifically, Fn(350) exhibited significant correlation with NH_4^+-N and COD, indicating that Fn(350) may be a good indicator for COD and NH_4^+-N in surface waters of aquatic ecosystems. The autochthonous index BIX exhibited a weak negative correlation with DOC, and a positive correlation with NH_4^+-N and TP. HIX index, which is linked to the humification degree of DOM,

Table 2
Pearson's correlation coefficients between selected fluorescence indices and water quality in peri-urban and urban watersheds.

	COD	NH_4^+-N	TP	DOC	TN	Chl-a
C1	0.566**	0.569**	0.043	0.083	0.082	0.501**
C2	0.551**	0.474**	0.057	0.011	−0.015	0.471**
C3	0.140	0.201*	0.112	−0.156*	−0.112	0.159
FI	−0.107	0.214**	0.293**	0.067	−0.015	−0.042
BIX	0.146	0.262**	0.341**	−0.220**	−0.078	0.075
HIX	0.410**	0.166*	−0.059	0.177*	0.155*	0.364**
Fn	0.673**	0.557**	0.129	0.164*	0.245**	0.351**

* Significant levels p values are all lower than 0.05 ($p < 0.05$).
** Significant levels p values are all lower than 0.001 ($p < 0.001$).

was significantly correlated with COD, NH_4^+-N, Chl-a and DOC. Because distinct differences in correlation coefficients were found in our study, it may suggest that alteration processes and variable sources might have obscured any broad relationships between the water quality and DOM composition in diverse water ecosystems (Zhang et al., 2011).

When all water samples in both watersheds were pooled together, C1 and C2 exhibited a positive linear relationship (Fig. 6), suggesting these both humic-like components were likely obtained from a common source. Interestingly, we found that COD was positively correlated with C1 in both rivers, although weaker correlation was found in Zhangxi River (a positive linear relationship was observed) (Fig. 7), which may suggest different contributions of DOM to COD in the different urbanization gradient rivers. In the study examining the lakes of northeast China, TN was positively correlated with the fluorescent component C1 (Zhao et al., 2017). Similar results were also observed in the Ebinur Lake watershed in China (Wang et al., 2017). Interestingly, we did not find a strong correlation between PARAFAC components and TN in this study. This is likely because a single parameter was not enough to reflect the relationship between PARAFAC components and TN, or dissolved inorganic nitrogen and particulate nitrogen contributed a significant portion of TN.

RDA was performed using the measured water quality parameters to account for changes in the fluorescent components (C1–C3) and fluorescent index (Fig. 7). The first two RDA axes accounted for 34.4% of the total variability in fluorescence and fluorescence index (RAD1, 29.3%; RDA2, 5.1%, $p < 0.01$). A significant positive correlation between TSS, COD, Chl-a and fluorescent components (C1–C3 and HIX) was found (Fig. 7). Interestingly, DO was negatively correlated with fluorescent components (C1–C3, FI and HIX). Additionally, pH was negatively correlated with C1-C3, while TN displayed a positive correlation with FI and BIX. DOC was also positively correlated with BIX. Overall, RDA

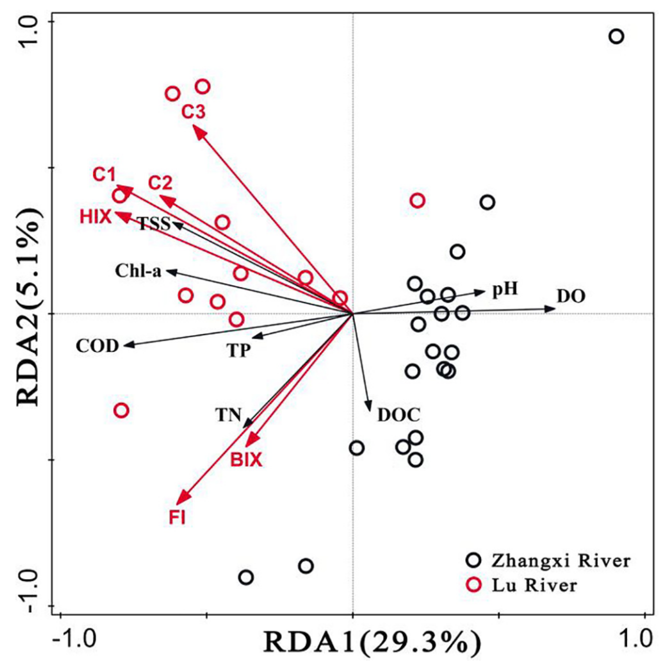

Fig. 7. Redundancy analysis (RDA) of the fluorescent components C1-C3, the fluorescent indices, and the water quality parameters.

analysis suggests that the connection of DOC, TN and fluorescent components is very complicated. Further research is needed to uncover the relationship between DOM and water quality.

4. Conclusions

In this study, a one-year investigation was conducted to investigate the properties of DOM and its links to water quality in the peri-urban and urban rivers. We found higher water pollution in the urban river compared to the peri-urban river, suggesting urbanization has a direct impact on the deterioration of surface water quality.

We used the EEM-PARAFAC method to characterize the fluorescent components. Three fluorescent components C1, C2 and C3 were identified by PARAFAC where C1 and C2 were terrestrial humic-like substances, C3 were protein-like substances, respectively. Fluorescence and DOM composition changed significantly across the peri-urban to urban watershed. Significantly higher percentage of protein-like components and lower percentage of terrestrial humic-like components were found

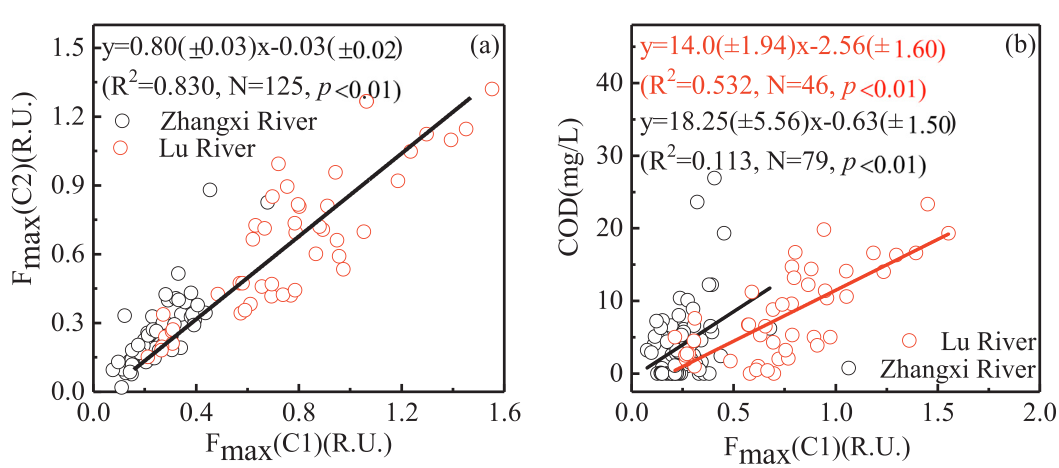

Fig. 6. Correlations between (a) fluorescence intensities of the humic-like F_{max} (C1) and F_{max} (C2); (b) F_{max} (C1) and the water quality parameter chemical oxygen demand (COD).

in the peri-urban river, which suggesting the different land use and/or anthropogenic intensities may play a role in DOM composition. Significantly higher HIX values were found in the urban river, suggesting DOM in the urban river had more of a humified and aromatic character. The results of DOM also confirmed our hypothesis that urbanization could affect the aquatic DOM concentration and quality.

Significant correlations between DOM composition, fluorescent index and various water quality parameters were found in the urban and peri-urban rivers. Moreover, we found COD concentration was positively correlated with humic-like C1 components in the urban and peri-urban rivers, suggesting that humic-like components might be a good predictor for COD, which support our hypothesis of that the characteristics of DOM could reflect the water quality of aquatic systems.

Overall, our hypothesis were accepted by the results and demonstrate that EEM-PARAFAC analysis may be a useful tool for monitoring water quality and characterization of DOM in urban rivers.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.ecolind.2019.05.025.

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