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RESEARCH ARTICLE

Identification of sources, characteristics and photochemical transformations of dissolved organic matter with EEM-PARAFAC in the Wei River of China

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HIGHLIGHTS

- The source of DOM in surface water and sediment is inconsistent.
- The DOC content changes differently in surface water and sediment.
- The content of DOC in the surface water is lower than that in the sediment.
- The DOM in the surface water had higher photodegradation potentials than sediment.

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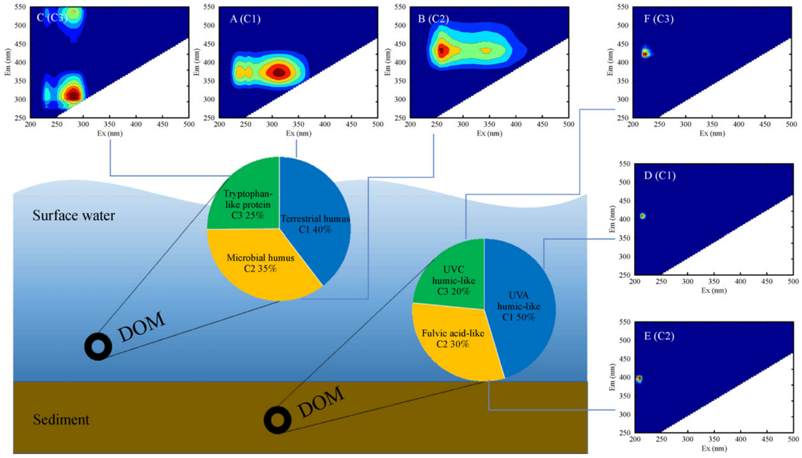
GRAPHIC ABSTRACT



ABSTRACT

Dissolved organic matter (DOM) in rivers is a critical regulator of the cycling and toxicity of pollutants and the behavior of DOM is a key indicator for the health of the environment. We investigated the sources and characteristics of DOM in surface water and sediment samples of the Wei River, China. Dissolved organic carbon (DOC) concentration and ultraviolet absorbance at 254 nm (UV_{254}) increased in the surface water and were decreased in the sediment downstream, indicating that the source of DOM in the water differed from the sediment. Parallel factor (PARAFAC) analysis of the excitation-emission matrices (EEM) revealed the presence of terrestrial humus-like, microbial humus-like and tryptophan-like proteins in the surface water, whereas the sediment contained UVA humic-like, UVC humic-like and fulvic-like in the sediment. The DOM in the surface water and sediment were mainly derived from microbial metabolic activity and the surrounding soil. Surface water DOM displayed greater photodegradation potential than sediment DOM. PARAFAC analysis indicated that the terrestrial humic-like substance in the water and the fulvic-like component in the sediment decomposed more rapidly. These data describe the characteristics of DOM in the Wei River and are crucial to understanding the fluctuations in environmental patterns.

1 Introduction

Dissolved organic matter (DOM) refers to a mixture of natural organic matter that can pass through a 0.45 μm filter membrane (Zhang et al., 2010). DOM mainly includes proteins, humus and other fatty or aromatic

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organic compounds, which originate from both foreign sources such as soil runoff (Elliott et al., 2006) and indigenous sources such as microbial ooze (Yamashita and Jaffé, 2008; Zhang et al., 2009). DOM is central to controlling the spatial distribution, transport, destination and even toxicity of many pollutants in nature via various interactions (Castillo et al., 2010; Huang et al., 2019), and has an important impact on the biogeochemical cycling of pollutants such as heavy metals and persistent organic compounds (Aiken et al., 2011; Hsu-Kim et al., 2013).

Several methods have been developed to investigate the properties of DOM. Among them, fluorescence and absorbance spectroscopies are widely used to elucidate the chemical nature and origin of DOM in aquatic systems (McKnight et al., 2001; Weishaar et al., 2003; Helms et al., 2008). Three-dimensional excitation emission matrices (3D-EEMs) provide more fluorescence than ordinary fluorescence spectra. However, multi-component mixtures such as DOM usually generate complicated and overlapping spectra. Parallel factor analysis (PARAFAC) can be applied to deconvolute overlapping spectral peaks into independent components even with similar fluorophores (Meng et al., 2013). Thus, 3D-EEM combined with PARAFAC has been utilized to characterize and investigate the sources, compositions and spatial trends of DOM in soil (Xian et al., 2018) and surface water, from reservoirs (Awad et al., 2017), rivers (Meng et al., 2013), lakes (Du et al., 2016) and oceans (Stedmon et al., 2007; Xu and Jiang, 2013). Using this method, studies reported that sediment DOM in the subsidence zone of Three Gorges Reservoir in China contains the humus fluorophores A, C, and M and the tryptophanoid fluorophore T (Jie et al., 2015), while the fluorescent components of DOM in the Yangtze river were mainly humus with clear land-derived characteristics (Gan et al., 2013). These studies suggest that land-derived organic components may enter the aquatic environment, and change DOM levels.

Currently, studies on DOM in the surface waters of China mainly concentrate on economically developed regions (Yan et al., 2017), while the north-west region is relatively unexplored. As the largest tributary of the Yellow River, the Wei River flows through the Eastern Gansu and Central Shaanxi provinces in China. There are three distinct areas from upstream to downstream: controlled, agricultural and urban with heavy industrial activity. Thus, the distribution, sources and constituents of DOM in the Wei River likely exhibit large variations from upstream to downstream, which unlike other rivers, is paired with a large amount of sediment in the river bed (Chang et al., 2016; Gao et al., 2019). However, the exchange of compounds between the water and the sediment complicates the identification of the sources and characteristics of DOM in the surface water of the Wei River.

Photochemical transformation is the migration and transformation of DOM in aquatic environments and plays an important role on the environmental behavior of DOM (Meng et al., 2013). Previous studies primarily focused on the influence of different ions and salinity on DOM photochemical transformation (Meng et al., 2013; Zhao et al., 2018) and have demonstrated that the photochemical behavior of amino acids is related to their photoactivity. Relatively stable amino acids accumulate in large quantities during irradiation, while photo-active aromatic amino acids are prone to photodegradation (Du et al., 2016; Zhu et al., 2017). However, few studies exist on the photochemical behavior of sediment-derived DOM. The sediment content in the Wei River is relatively high (Gao et al., 2019), and the influence of sediment on the photochemical transformation of DOM is still unclear.

Therefore this study aimed to: 1) investigate DOM content in the surface water and sediment of the Wei River in Shaanxi; 2) characterize the DOM with fluorescence EEM-PARAFAC, for assessing fluorescent components and determining the potential possible sources of DOM in the surface water and sediment; 3) examine the photochemical transformation of DOM in the two compartments to gain further insights into the destination of DOM in the Wei River.

2 Methods

2.1 Surface water and sediment sampling

Surface water and sediment samples of the Wei River were collected in November 2017 from 15 sampling sites. We collected 43 surface water samples (3 L each), which were taken at three evenly-spaced points across the river from each site. The collected surface water samples were stored in brown glass bottles pre-soaked with 10% nitric acid and rinsed with Milli-Q water. Similarly, 45 sediment samples (1.5 kg each) were collected 0–10 cm from the surface layer using a B-10104 sludge core sampler (Raven Environment Products, USA) and stored in poly-tetrachloroethylene plastic bottles. All samples were stored at –20°C until pretreatment. The longitudes and latitudes of the sampling sites are listed in Table S1.

2.2 Extraction of DOM from water and sediment samples

First, 30 mL water from each sample site was filtered through a pre-combusted Whatman GF/F 0.45 μm glass fiber filter, and stored in brown bottles at 4°C (Han et al., 2016).

Sediment samples were pre-treated as previously reported with minor modifications (Han et al., 2016; Dong et al., 2020). In a centrifuge tube, 10.0 g air-dried and ground sediment was weighed and 100 mL Milli-Q water was added in a 10:1 water-soil ratio. The mixture was oscillated in a shaker for 16 h at 200 r/min in the dark, (THZ-98C, Yiheng Scientific Instruments, China) and centrifuged for 30 min at 4000 r/min (TDZ5-WS, Hunan Xiangyi Laboratory Instrument Development, China). The supernatant was collected and passed through a pre-combusted Whatman GF/F 0.45 μm glass fiber filter and stored in a brown bottle at 4°C.

2.3 Determination of dissolved organic carbon and UV_{254} absorbance

The dissolved organic carbon (DOC) content in the filtrate was measured by a total organic carbon (TOC) analyzer (TOC-L, Shimadzu, Japan) with a detection limit of 4 μg/L. The ultraviolet absorbance at 254 nm (UV_{254}) was determined by a UV spectrophotometer (GENESYS 10S UV-Vis, Thermo Fisher Scientific, USA) with an absorbance range from –0.1 to 3.0 A. Specific UV_{254} absorbance (SUVA) is an index indicating the humus content, which indirectly reflects the aromaticity and hydrophobic/hydrophilic properties of the DOM as well as the relative levels of unsaturated double bonds (Yang et al., 2015). SUVA (L/mg C·m) is determined as the ratio of UV_{254} (AU/cm) to DOC (mg/L) using the following formula: $\mathrm{SUVA} = (UV_{254}/\mathrm{DOC}) \times 100$ (Tang et al., 2009).

2.4 3D-EEM and PARAFAC modeling

The EEM fluorescence data of DOM was obtained by a fluorescence spectrometer (RF-6000, Shimadzu, Japan). The excitation wavelength ranged from 200 to 500 nm in 5 nm intervals and the emission wavelength ranged from 250 to 600 nm in 1 nm intervals. Milli-Q water was used as the blank control. The slits of excitation and emission were 5 nm with a scanning speed of 6000 nm/min. During the test, Raman scatter peaks of water were eliminated by subtracting the EEMs of the blank control. MATLAB 7.1 with DOMFluor Toolbox (Stedmon et al., 2008) was used for PARAFAC modeling. The identified components and their numbers were validated by split-half and residual analyses (Ly and Hur, 2018). The details of PARAFAC modeling are described in the supplementary methods.

3 Results and discussion

3.1 Spatial distribution and characteristics of DOM in surface water and sediment samples of the Wei River

Figure 1 shows the DOC content and the UV_{254} values of

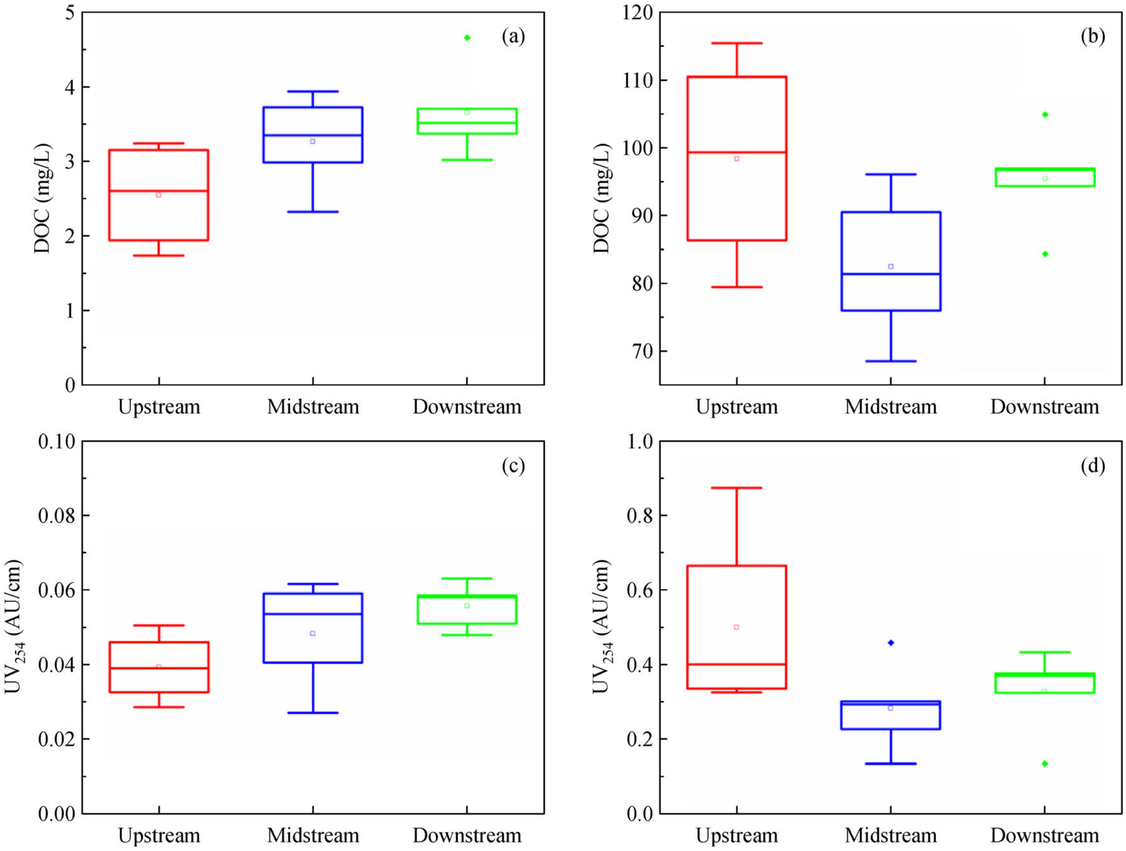

Fig. 1 Levels of DOC content and UV_{254} of the DOM samples collected from the surface water and sediment ((a), (b): DOC content of the surface water and sediment; (c), (d): UV_{254} of the surface water and sediment. Upstream: Sample site 1–5; Midstream: Sample site 6–10; Downstream: Sample site 11–15).

surface water and sediment samples collected from the Wei River. The average DOC levels in the sediment and surface water were 90.78 and 3.45 mg/L, respectively, and the average UV_{254} values were 0.36 and 0.05 AU/cm, respectively. The DOC content in the surface water ranged from 1.73 to 6.96 mg/L, and UV_{254} values ranged from 0.03 to 0.10 AU/cm.

DOC in the surface water displayed an increasing trend from upstream to downstream, which was according to our expectations since the upstream sections of the Wei River are mainly rural and agricultural areas while the urban and industrial areas are located in the downstream regions. These data suggested that the main sources of DOC in the Wei River were foreign and may be attributed to discharge from industrial activity. Liu et al. (2020) correlated soil TOC with gross domestic product (GDP) and reported that the mean GDP and soil TOC increases significantly ($p < 0.05$) with increasing longitude from upstream to downstream. The DOC content at sample site 5 in our study was the highest (6.96 mg/L), which is the intersection of a tributary and is located in an artificial wetland containing a large amount of biomass. Next to this was site 13, where the DOC level was 4.65 mg/L with a high sand content (Fig. S1). DOM may be adsorbed on particulate matters and the soluble fractions are readily released into the water (Xu et al., 2019), resulting in a high DOC content. In contrast, the DOC level at site 7 was comparatively low, which might be due to the low sand content and slow water flow (Fig. S1). The variations of UV_{254} in the surface water corresponded with the DOC content (Table S2 and Fig. 2(a)) and were in agreement with previous literature (Han et al., 2016). The DOC levels and UV_{254} values in the surface water of the Wei River were comparable with those detected in other bodies of water (Meng et al., 2013).

DOC level in the sediment was at a relatively high level and ranged from 68.48 to 115.35 mg/L, while UV_{254} values ranged from 0.13 to 0.87 AU/cm. Similar to the surface water, trends in UV_{254} values paralleled with DOC levels (Table S3 and Fig. 2(b)). This could be explained by the fact that many organic compounds adsorb large particulate matter in water and enter the sediment by gravity sedimentation (Viguri et al., 2002). In addition, some animal and plant residues remain in the sediment, generating DOM during decomposition. In contrast to the surface water, the DOC content in the upstream sediment was higher than in downstream sediment. This discrepancy suggested that the sources of DOM in the surface water differed from the sediment. DOM in the surface water appeared to be greatly influenced by human activity, while DOM in the sediment was less affected. Previous studies have shown that the composition of DOM in an aquatic environment is a combination of material produced by microbial activity within the water itself and material derived from land (Stedmon et al., 2011b). Since sedimentation is a slow kinetic process, DOM in the sediment could also be a snapshot of previous human activity.

SUVA index was used to characterize the aromaticity of DOM. It has been reported that SUVA>4 L/mg C·m generally indicates that the majority of the DOM consists of macromolecules and hydrophobic organics, while SUVA < 4 L/mg C·m suggests hydrophilic organics as the major components (Zhang et al., 2010). As shown in Fig. S2, the average SUVA value in the sediment was 3.89 L/mg C·m, ranging from 1.80–7.57 L/mg C·m. The SUVA value in the sediment was generally higher than in the surface water (average 1.51 L/mg C·m, range 1.16–1.76 L/mg C·m), which indicated that there more aromatic and hydrophobic substances were present in the sediment than in the surface water. All measured SUVA values in the surface water were less than 4 L/mg C·m, suggesting that the major components of the DOM in the surface water were hydrophilic organics (He et al., 2016).

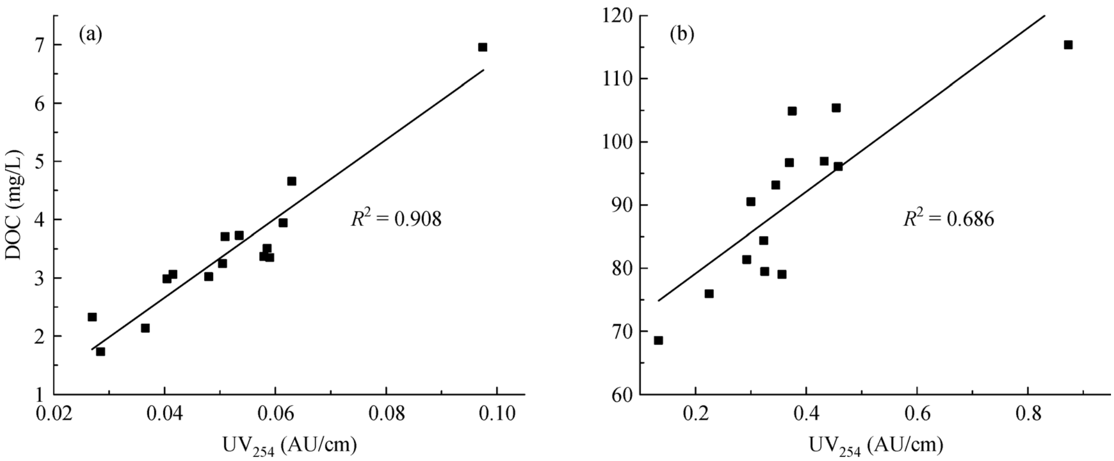

Fig. 2 The correlations of DOC and UV_{254} of the surface water and sediment ((a): the surface water; (b): the sediment).

3.2 Fluorescent components and intensity distribution by PARAFAC

The three-dimensional fluorescence spectrum of each sample is illustrated in Figs. S3 and S4. We noted that the fluorescence index in all sediment samples was higher than in the surface water samples, suggesting higher DOM levels in the sediment, which reflected the DOC level and UV_{254} values described above. PARAFAC is a powerful tool for identifying different fluorescent components from the EEMs of overlapping peaks (Zhou et al., 2017).

Three distinct PARAFAC fluorescent components were extracted from the fluorescence spectra of 43 water samples (across 15 sample sites) by PARAFAC analysis, based on the analysis of residuals and the split-half validation procedure (Fig. 3). Three fluorescent components were identified (Fig. 4). Some of the fluorescent components extracted by PARAFAC indicated the presence of specific organic substances, but could also represent organic compounds with similar fluorescent properties. The EEM measurements were performed at a constant temperature (25°C±1°C) and pH to minimise differences. The maximum fluorescence intensity of each component was obtained and used to illustrate the quantitative and qualitative differences between samples.

DOM in the surface water mainly included humus components (blue fluorescence) and protein components (ultraviolet fluorescence) (Coble, 2013). Of the three distinct fluorescent components in the surface water samples, two were humic acid compounds and one was a protein. Component 1 (W-C1, Fig. 4(a)) displayed two peaks at 240 and 310 nm excitation wavelength and a significant peak at 395 nm emission wavelength. The fluorescence peak at 240/395 nm was similar to that of fulvic-like acid, while the peak at 310/395 nm was comparable to the microbial humic-like acid peak M (Coble, 1996; Bridgeman et al., 2011). The excitation and emission wavelengths of component 2 (W-C2, Fig. 4(b)) were located at 260/468 nm and 345/468 nm, respectively, which were close to the ultraviolet humus fluorescence peak A and visible humus fluorescence peak C (Coble, 1996; Bridgeman et al., 2011). Component 3 (W-C3, Fig. 4 (c)) consisted of two peaks at 230/319 nm and 280/319 nm and was similar to the tryptophan-like peak T (Sheng et al., 2013). Accordingly, W-C1 represented microbial humus, which was primarily observed in the surface water, while W-C2 was a typical humus component with a relatively small molecular weight and was closely related to biological activity (Sheng et al., 2013). However, it is also found in agricultural environments and sewage, which mainly comes from land-derived and microbial organics (Coble et al., 1991; Stedmon et al., 2011a; Guo et al., 2012). W-C3 was an amino acid that was free or bound to proteins, similar to free tryptophan that is widely present in aquatic environments and was an indication of recent biological activity (Zhang et al., 2010; Osburn et al., 2012). Thus, the protein-like component may be associated with refractory DOM (Burdige et al., 2004), and the humus components were mainly derived from the input of terrestrial organisms.

From the 45 sediment samples (across 15 sample sites), we also extracted three fluorescent components by PARAFAC analysis. The excitation wavelengths of all three components were less than 240 nm, and the emission

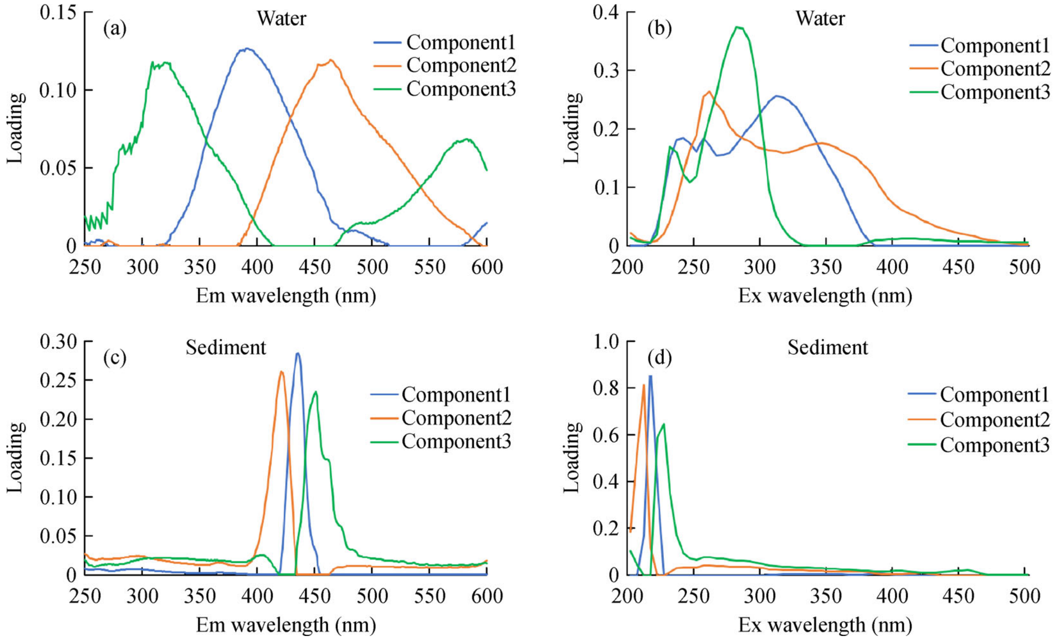

Fig. 3 Emission and excitation loadings of the three fluorescent components obtained by PARAFAC in the surface water and sediment: (a), (c): Em loading of water and sediment; (b), (d): Ex loading of water and sediment.

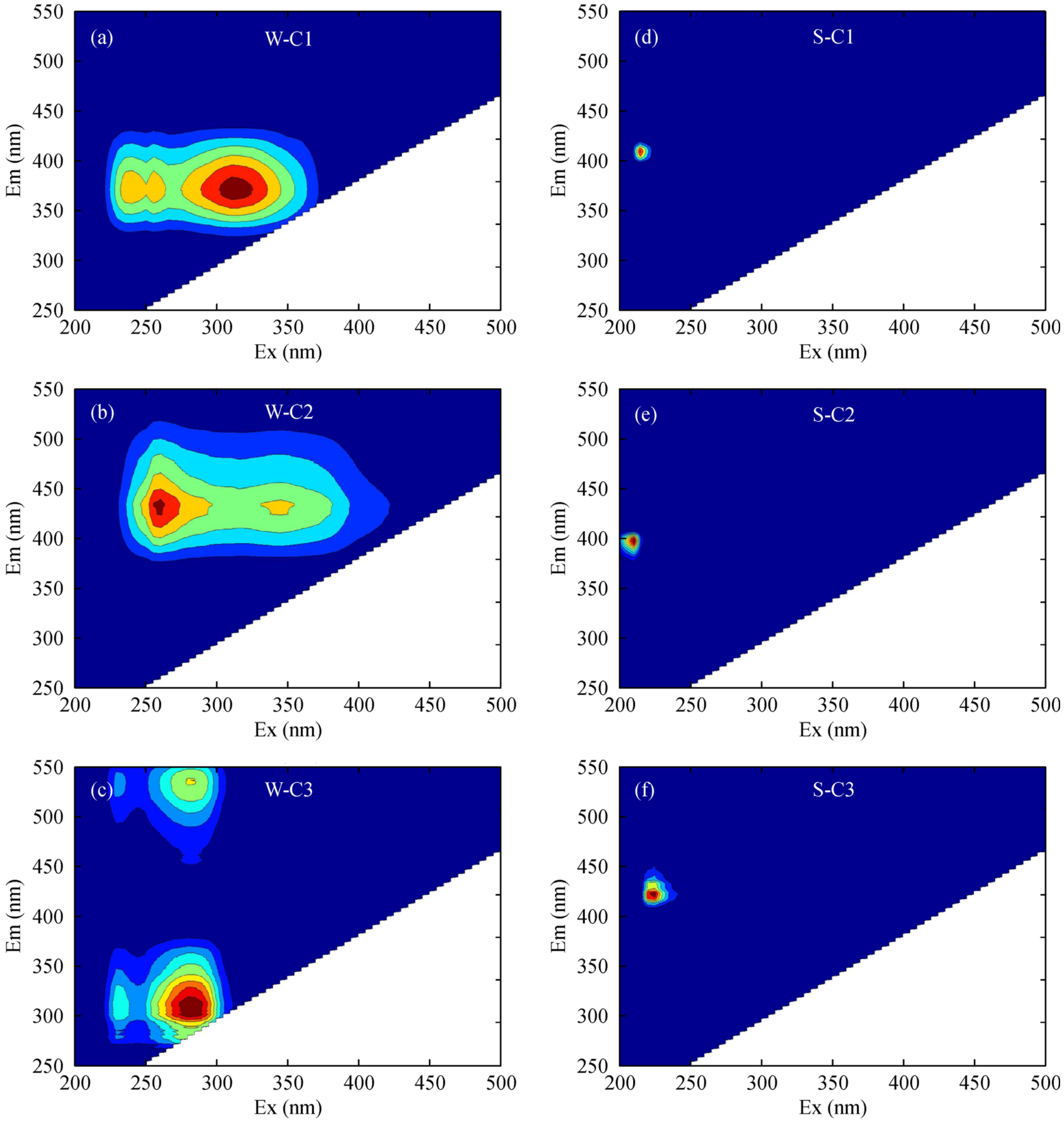

Fig. 4 Contour plots (C1、C2、C3) of the three fluorescent components obtained by PARAFAC in the surface water and sediment (a, b, c: the three components of surface water; d, e, f: the three components of sediment).

wavelengths were between 380 and 540 nm, which matched the fluorescence peaks of ultraviolet fulvic acid (Hao et al., 2012). Component S-C1 (Fig. 4(d)) with a maximum peak at 215/436 nm was identified as a UVA humic-like substance, which is associated with the fluorescence of fulvic-like acid (Cory and Mcknight, 2005; Stedmon and Markager, 2005). Component S-C2 (Fig. 4(e)) with a maximum peak at 210/421 nm was also identified as a fulvic-like acid (Marhuenda-Egea et al., 2007). Component S-C3 (Fig. 4(f)) with a maximum peak at 225/451 nm (Ex/Em) was identified as a UVC humic-like substance related to high-molecular-weight and aromatic humus (Stedmon and Markager, 2005; Murphy et al., 2006).

The fluorescence index (FI) was used to indicate the source of humus components in DOM (Fig. 5 (a)). FI>1.9 indicates a microbial source whereas FI < 1.3 reflects land and soil origins (McKnight et al., 2001; Cory et al., 2010). The FI of more than 87% of the water sample sites was >1.9 suggesting that there was a major contribution of microbes to the DOM in the surface water, which agreed with the W-C1 peak in the PARAFAC analysis outlined above. Since the W-C2 peak indicated terrestrial humus, the results suggested that there were land and soil sources in addition to the microbial source. The FI value was < 1.9 in all sediment samples, indicating that microbial sources had a minor contribution to the DOM found in sediment. The FI values at sampling sites 5 and 10 were < 1.3, indicating that land and soil sources were the primary contributors to the DOM at these sites.

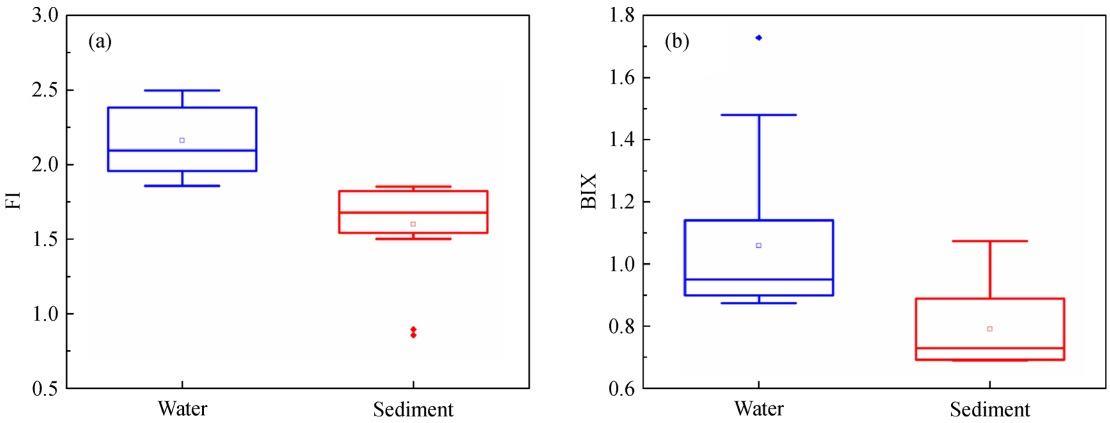

Fig. 5 Box plot of FI and BIX indicator of the surface water and sediment: (a) FI value of the surface water and sediment; (b) BIX value of the surface water and sediment.

To further investigate the source of the DOM, biological source index (BIX) was used as an indicator of DOM traceability. BIX>1 suggests strong microbial activity in the surface water, while a low BIX value (0.6–0.7) indicates a minor contribution (Zhang et al., 2010). As shown in Fig. 5(b), the value of BIX of all surface water samples were higher than 0.8, confirming the FI data that the DOM in the surface water was mainly a result of microbial metabolic activity (Huguet et al., 2009). The BIX of sample site 7 was the highest (1.73), which suggested that there was strong microbial activity at this site and the DOM was mainly composed of microbial humus (Zhai et al., 2017). We observed that 27% of BIX from sediment samples were lower than 0.7, further affirming that microbial sources contributed less to the DOM in sediment.

Figure S5 summarizes the abundance of each PARAFAC component against the total of the three components. The relative abundance of microbial humic-like W-C1 was greater than that a terrestrial humic-like W-C2 in the surface water, while the tryptophan-like component W-C3 contributed the least. In the sediment samples, fulvic-like acid S-C1 was relatively more abundant than high-molecular-weight and aromatic humus S-C3 (Jiang et al., 2017).

3.3 The impact of photodegradation on DOM dynamics

The photodegradation potentials of the fulvic-like acid standard (International Humic Substance Society) and the surface water and sediment samples at sample sites 1 and 10 were investigated using artificial solar light (Fig. S6), which provided a reference to elucidate the impact of light on the migration patterns of DOM in the Wei River. The photodegradation experiments were conducted in 50 mL quartz bottles in a photochemical reaction system equipped with LED lamps (λ = 385 nm, power density = 300 mW/cm^2). The FI_{max} of component 2 (C2) and component 3 (C3) in the surface water from sample site 1 (W1) decreased gradually during light exposure and showed a greater decline than in W10 (Fig. 6). For instance, C2 of W1 and W10 demonstrated a loss of 84.9% and 69.9% respectively, after exposure to artificial sunlight for 7 d. Baker et al. (2004) have reported that tryptophan fluorescence intensity increases with artificial DOM from sources such as sewage and agricultural wastewater. Therefore, tryptophan fluorescence intensity can be used as a reference standard for the determination of water quality. Our study showed that component 3 (C3) representing tryptophan decreased upon light exposure, suggesting that the photochemical reactions may degrade organic pollutants with an aromatic structure in nature, which reduces their harm to the environment.

The FI_{max} of the three components in the light-exposed samples of the surface water declined faster than in the sediment samples. For example, the FI_{max} of C2 in the surface water declined relatively slowly in W10, whereas the FI_{max} of C1 declined more rapidly in S1 (69.9% vs 31.85% loss). The reason for this observation may be that the three sediment components were insensitive to light. In comparison, the FI_{max} of C2 in the fulvic-like acid standard showed a loss of 90.00%, indicating that C2 in fulvic-like acid was more prone to photolysis. The control samples were kept in the dark and the FI_{max} remained stable, suggesting that hydrolysis and biodegradation played insignificant roles in the elimination of fluorophores compared with photodegradation, which further illustrated that photodegradation may be vital for the migration and transformation of DOM in the Wei River.

4 Conclusions

In this study, the content, main composition and photochemical transformation of DOM in the surface water and sediment of the Wei River were studied using EEM-

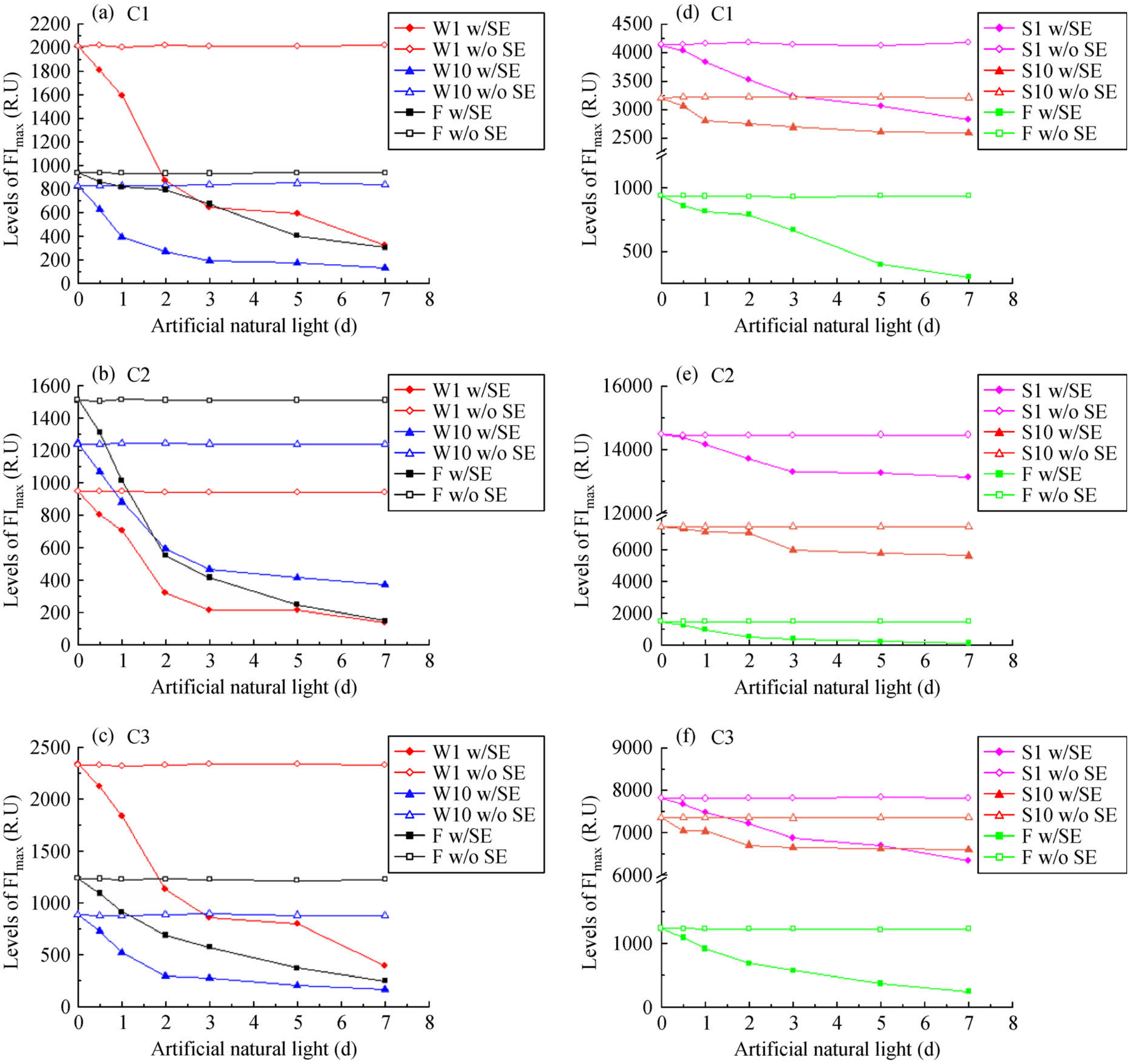

Fig. 6 Variations of the FI_{max} of PARAFAC-components during the photodegradation incubations with (w/) and without (w/o) exposure to artificial natural light (SE): (a–c) FI_{max} of the surface water; (d–f) FI_{max} of the sediment.

PARAFAC and other techniques. The DOC content in the surface water was lower than in the sediment, which may be due to the larger mixing action of water and its impact on precipitation, adsorption, photodegradation and microbial activity. The DOM components in the surface water were terrestrial humus (W-C1), microbial humus (W-C2) and tryptophan-like protein (W-C3) and the DOM components in the sediment were mainly aromatic-like proteins. The DOM in the surface water had higher photodegradation potential compared with the sediment. We provided a reference for further study on the environmental behavior of DOM in the surface water of north-west China.

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