

# Dynamics of dissolved organic matter in a wastewater effluent-impacted Japanese urban stream: characteristics, occurrence and photoreactivity of fluorescent components

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## ABSTRACT

We report the results of using the excitation–emission matrix (EEM) method combined with parallel factor analysis (PARAFAC) to investigate the characteristics and occurrence of dissolved organic matter (DOM) in an urban stream impacted by effluent from a wastewater treatment plant (WWTP). The PARAFAC model divides the bulk EEM spectra into six individual fluorescent components with three humic-like components (C1–C3), two protein-like components (C4 and C5) and a wastewater-derived component (C6). In general, intensities of fluorescent components are abundant in WWTP effluent impacted samples, thus showing that such an effluent is a major source of DOM in urban rivers, but C5 is considered to have autochthonous sources within the stream. In areas where the effluent is released, the fluorescent intensity from components (except C5) gradually decreases as these components are transported downstream. However, concentrations of dissolved organic carbon remain almost constant downstream of the release area. These results would be attributed to degradation and/or modification of fluorophore. Photolysis experiments confirmed that fluorescent intensities can decrease with increase of irradiation times. C6 particularly showed a rapid photodegradation, remaining only 24.1% after 48 h photolysis. These findings would be important when assessing DOM source and water quality in aquatic environments by EEM-PARAFAC.

**Key words** | dissolved organic matter, excitation–emission matrix, photochemical reaction, urban river

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## INTRODUCTION

Dissolved organic matter (DOM) is an important fraction of aqueous organic matter which can pass through filters (generally 0.1–0.7  $\mu\text{m}$  size), and they are ubiquitous in water environments with heterogeneous compositions (Shon *et al.* 2006; Mostofa *et al.* 2013). Since excess anthropogenic DOM input can result in the pollution of the aquatic environments, identifying the source of environmental DOM is essential to maintain better water quality. Conversely, DOM in fresh water and coastal environments are expected to play biogeochemically important key roles, acting as a light inhibitor (Sanchez-Prado *et al.* 2006), chelating agent of toxic heavy metals (De Schampelaere *et al.* 2004) and precursor of OH radicals (Ryan *et al.* 2011). Principally, each type of DOM has distinctive binding affinities to

organic and inorganic chemicals; even organic carbon concentrations levels are similar (De Schampelaere *et al.* 2004; Chen *et al.* 2018). These emphasise the importance of studying chemical composition and environmental behaviour of DOM in aquatic systems.

Owing to its low costs (i.e. low solvent and reagent consumption) and simplicity, the excitation–emission matrix (EEM) method combined with parallel factor analysis (PARAFAC) (EEM-PARAFAC), which decomposes conventional EEM spectra into individual fluorescent components, is becoming a useful tool for characterising DOM (Stubbins *et al.* 2014). Previous studies have applied the EEM-PARAFAC approach to investigate DOM sources, characteristics and dynamics in aquatic environments. DOM

compositions in rural and natural streams are generally dominated by humic-like substances and they are supplied from forest soil and agricultural activities (Suzuki *et al.* 2015). On the other hand, both sources and chemical compositions of DOM in urbanised streams can be distinguished due to different types of land use; Meng *et al.* (2013) found that contents of anthropogenic humic substances and protein-like components increased in Chinese urbanised area. They also hypothesised that the changes in chemical composition of DOM in downstream areas were attributed to the contribution of treated wastewater. To support this, effluent organic matter from wastewater treatment plants (WWTP) are composed of diverse types of DOM including natural organic matter, soluble microbial products and synthetic organic matter (Shon *et al.* 2006). Li *et al.* (2014) investigated the behaviour of DOM in wastewater treatment processes, using EEM-PARAFAC and specific UV absorbance index to suggest that once they have occurred humic substances and protein-like components are not completely eliminated by biological treatment processes. Nevertheless, to the best of our knowledge, the role of WWTP effluent as the key source of DOM in urbanised streams has not been clearly evaluated. This is partially because the DOM discharged into aquatic environments can possibly come from a complex combination of sources in an urbanised area. Even if samples were collected from streams, input of DOM from multiple sources (e.g. runoff discharge) and dilution effects (e.g. river confluence) complicate the interpretation of the results. To resolve this problem, strategic and intensive field surveys are required. Furthermore, riverine DOM would be degraded during transportation toward the river downstream and estuary, receiving environmental processes with certain rates that differ for each particular DOM component. In particular, photochemical reactions would be one of the most important

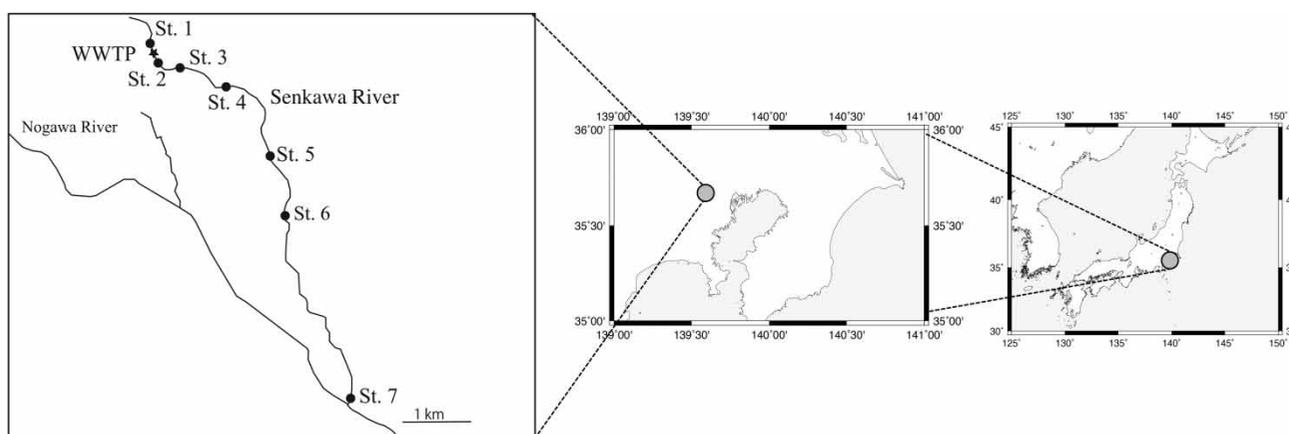
environmental processes for fluorescent DOM components. In order to assess the impacts of WWTP effluent derived DOM on aquatic systems by tracking fluorescent components, the photolytic behaviour of such probes in environments should be examined. However, information on the photochemical degradation of fluorescent components in WWTP effluent is relatively limited (Meng *et al.* 2013; Phong & Hur 2016).

The main purpose in the present study is to clarify DOM dynamics and environmental behaviour in urban streams in a WWTP effluent receiving area using EEM-PARAFAC. Toward this end, we extensively sampled from a small Japanese urban river with water quality that is largely and solely affected by WWTP effluent. Furthermore, to understand the potential photodegradability of the identified fluorescent components derived from the WWTP effluent, we conducted photolysis experiments on a water sample taken from the area into which the WWTP effluent is released.

## MATERIALS AND METHODS

### Samples

Samples of surface river water were taken from the Senkawa River, which runs through a residential area of Tokyo, Japan (Figure 1). The Senkawa River flows through 20.9 km of stream and has 19.8 km<sup>2</sup> of catchment area. This river is a tributary of the Nogawa River, which eventually flows into Tokyo Bay. The Senkawa River receives effluent from an adjacent WWTP that uses activated sludge and sand-filtration systems. The plant serves a population of approximately 99,000 within 7.19 km<sup>2</sup> surrounding the plant, and approximately 24,000 m<sup>3</sup> of treated wastewater



**Figure 1** | Map of sampling sites. Surface river water samples were collected at St.1–St.7 in the Senkawa River.

flows into the stream each day. As a consequence, approximately 50% of the total flow in the Senkawa River consists of WWTP effluent downstream of the plant (Mitaka City 2016). In this study, to examine sources of fluorescent components in the stream, we took samples from both upstream and downstream areas of the effluent. From July 2016 to May 2017, samples were collected monthly (except for January 2017) from seven points (St.1–St.7) in the Senkawa River. The WWTP effluent enters at a point between St.1 and St.2. St.1 is approximately 7.6 km from St.7. Travel time of the river water from St.1 to St.7, estimated based on flow velocity measurements using AEM-1D (JFE Advantech, Japan), was almost 5 h. Notably, no significant interflow is contributed by other rivers until the confluence with the Nogawa River downstream of St.7. No significant rainfall occurred on the sampling days, and samples were collected by using a stainless steel bucket. Samples were collected in pre-rinsed 250 mL polyethylene amber bottles at each site and then transported to the laboratory under cold and dark conditions to avoid DOM degradation.

### Analyses of DOM quality and quantity

Samples were filtered through glass-fibre filters (GS-25, ADVANTEC, Japan. Cut-off size: 0.6  $\mu\text{m}$ ) as pre-treatment. EEM measurements were performed by using an FP-8300 fluorescence spectrophotometer (JASCO, Japan) equipped with an automatic cut filter for higher-order diffraction. The scanning ranges for the EEM were 250–600 nm in 5 nm intervals for excitation and 260–615 nm in 5 nm intervals for emission. The scanning speed was 5,000 nm/min. The fluorescence EEM obtained from each sample were subtracted by the fluorescence EEM of blank solutions (ultrapure water) for Raman scattering correlation. Each sample was analyzed in triplicate using three bottles and mean values were used as reported values of each month.

After EEM measurements, the spectral data set was analysed by using the PARAFAC method, and the Solo chemometrics software (Eigenvector Research Inc., WA, USA) was used to divide the EEM spectra into individual fluorescent components. In this study, PARAFAC modelling was performed without EEM data from the upstream site (St.1) because building a PARAFAC model from water samples with highly variable water quality can lead to inaccurate models (Yu *et al.* 2015a). The fluorescence peaks from St.1 samples are all lower than those from downstream sites (St.2–St.7). The number of data for PARAFAC modelling was 226. We optimised the number of components in the

PARAFAC model on the basis of split-half analysis. To illustrate the composition and relative abundance of each fluorescent component in the samples, we used PARAFAC scores obtained from the PARAFAC model as fluorescent intensity, which is proportional to the amounts of corresponding fluorescent components. Dissolved organic carbon (DOC) in samples was determined by using a TOC-V CPH total organic carbon analyser (SHIMADZU, Japan). The detection and quantification limits for DOC determined based on standard deviations of repeated measurements of blank ultrapure water ( $n = 5$ ) were 0.03 and 0.12  $\text{mg L}^{-1}$ , respectively. To minimise the effects of DOM degradation and transformation, the EEM and DOC were generally acquired within three days of sample collection. Analysis of variance (ANOVA) were conducted by using GraphPad Prism. A significant level was set to  $p < 0.05$ .

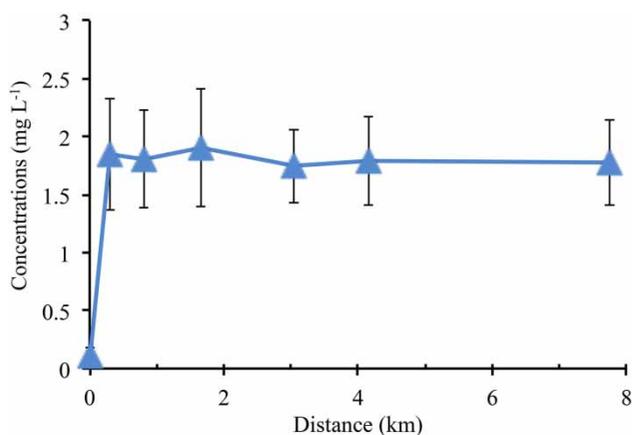
### Photolysis experiment

Fluorescent components are expected to degrade during river transport by sunlight irradiation. Thus we performed additional photolysis experiments to better predict the occurrence of allochthonous fluorescent DOM components in aquatic environments. The sample for the photolysis experiments were collected in July 2018 from St.2, which is located immediately after the WWTP effluent, and showed the highest intensity of fluorescent components (see ‘Occurrence of fluorescent components’). The sample was immediately filtered through a 0.22  $\mu\text{m}$  membrane filter (MF-Millipore) to reliably remove microorganisms. The filtered sample was transferred to sealed quartz cells (12.5 mm  $\times$  12.5 mm  $\times$  58 mm) and irradiated from above with simulated sunlight from a xenon-lamp solar simulator LCS-100 (ORIENTAL INSTRUMENTS, the USA) equipped with an AM 1.5G filter (100  $\text{mW/cm}^2$ ). The samples were analysed by EEM at desired time points (0, 0.5, 1, 2, 4, 6, 8, 12, 18, 24, 36 and 48 h) to determine the temporal change of the fluorescent components. Control samples were kept in the dark at room temperature and also measured at the same time intervals as the exposed group. The experiments were conducted in triplicate ( $n = 3$ ).

## RESULTS AND DISCUSSION

### Concentrations of dissolved organic carbon

DOC concentrations at each site for all sampling periods are summarised in Figure 2. Generally, DOC concentrations in



**Figure 2** | Mean dissolved organic carbon (DOC) concentrations in studied sites as a function as distance from St.1. Error bars represents standard deviations.

the Senkawa River are clearly affected by the WWTP effluent. The lowest concentration of DOC occurs at site St.1 at all seasons with a mean  $\pm$  standard deviation of  $0.35 \pm 0.11 \text{ mg L}^{-1}$ , which gives the background level of the upstream water. This low DOC would be due to the 100% public sewerage coverage of the surrounding area (Bureau of Sewerage Tokyo Metropolitan Government 2013); therefore, no discharge of untreated sewage is expected in the Senkawa River. By contrast, the DOC concentration increases significantly (ANOVA,  $p < 0.0001$ ) at St.2 ( $1.8 \pm 0.53 \text{ mg L}^{-1}$ ) after the input of WWTP effluent. From St.2 to St.7, the distribution of DOC shows little spatial variation, varying from a minimum of  $1.7 \text{ mg L}^{-1}$  at St.5 to a maximum of  $1.8 \text{ mg L}^{-1}$  at St.2. According to ANOVA, no significant variation in DOC concentration occurs from St.2 to St.7 ( $p > 0.05$ ). Therefore, the spatial distribution of the DOC concentration downstream of the effluent-release area is almost uniform. These DOC levels are similar to or slightly less than those previously reported for other urban Japanese rivers and lower than Chinese urban streams (Zushi & Masunaga 2009; Meng *et al.* 2013). These results indicate that WWTP effluent is the important source of DOC in urban rivers.

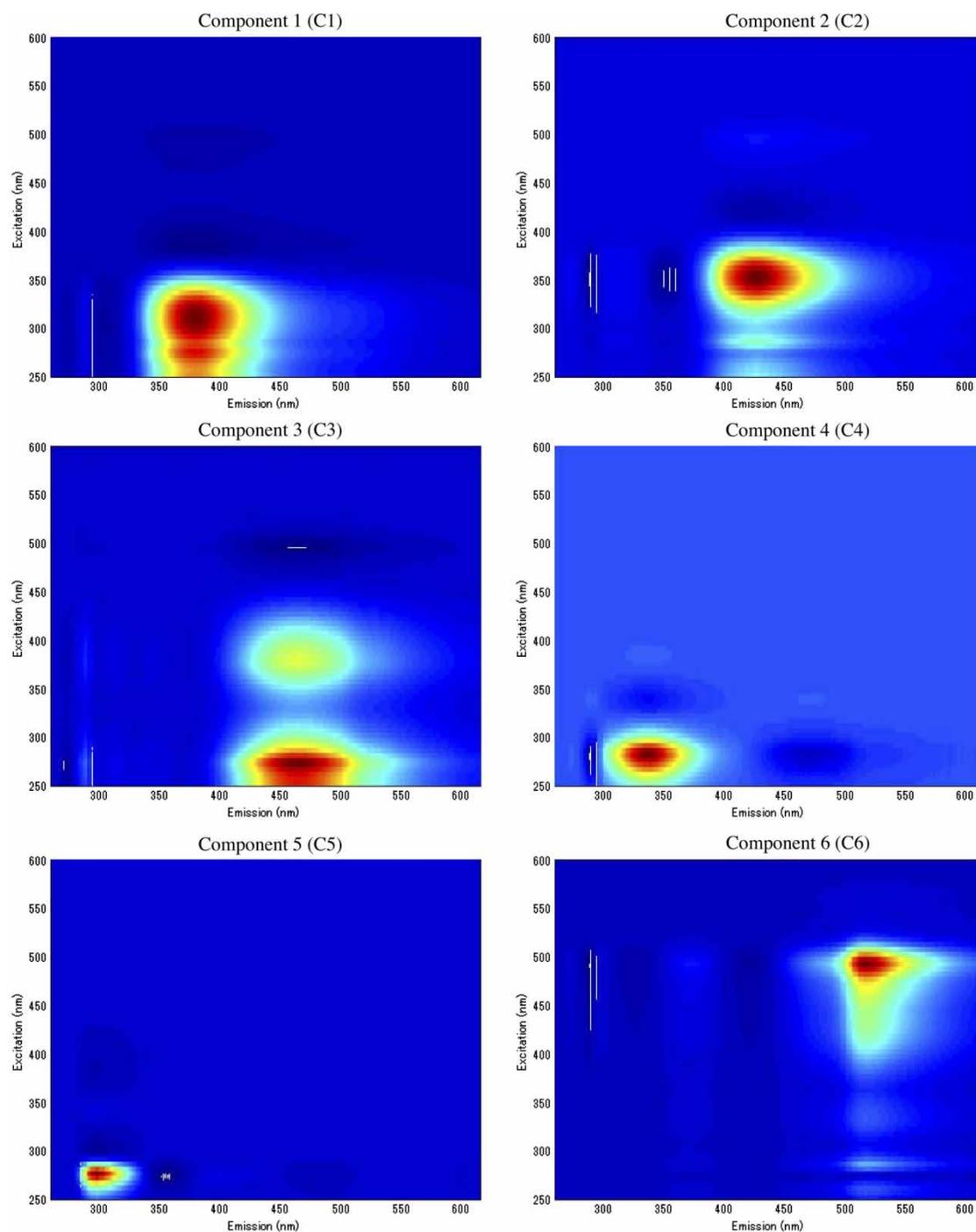
### Fluorescent components

To determine the fluorescence properties, we first determined the optimal number of components in PARAFAC modelling on the basis of split-half analysis. The results show that the bulk EEM spectra in this study should be separated into six individual components with a maximum similarity of 92.9%. Figure 3 shows the typical contour plots of the six

fluorescent components in the downstream area. These fluorescent components are characterised according to previous results (Table 1). For example, component 1 (C1) has an excitation–emission maximum at (ex/em) 320/370 nm, which is similar to a peak reported by Yamashita *et al.* (2008). This component has been traditionally characterised as ‘marine humic-like component’ peak M (Coble 1996). However, sampling sites in this study are sufficiently far from river mouth. Therefore, this component may do not occurred in marine environments in this study. Yamashita *et al.* (2008) state that this component can derive from biological processes involving organic matter. In addition, Yao *et al.* (2011) identified a similar peak in surface water from a Chinese populated lake; this finding is consistent with our results. C2 has a strong excitation–emission peak at 350/430 nm. The emission peak in the visible region is similar to a component previously assigned to a humic-like component that was detected in both river and marine environments (Coble 1996; Yamashita *et al.* 2008). C3 has excitation shoulders at 280 and 380 nm with an emission peak of 460 nm. C3 resembles peaks reported by recent studies using EEM-PARAFAC and can be assigned to another class of humic-like component that appears widely in effluent organic matter, river, lake and marine environments (Yamashita *et al.* 2008; Yao *et al.* 2011; Meng *et al.* 2013; Yang *et al.* 2015; Yu *et al.* 2015b). Murphy *et al.* (2011) also described that this component appears in wastewater-impacted environments. Conversely, C4 and C5 are categorised as protein-like components and are suspected to be tryptophan- or tyrosine-like components (Yamashita *et al.* 2008). Although these components exhibit similar spectral characteristics (C4 peaks at 280/340 nm and C5 peaks at 280/300 nm), tyrosine-like components have emission spectra at shorter wavelengths than tryptophan-like components (Yamashita *et al.* 2008). Thus, we assign C4 to a tryptophan-like component and C5 to a tyrosine-like component. The final component, C6, has characteristic EEM spectra with peaks in the long-wavelength region (500/520 nm). This component is also similar to previously reported peaks which can be attributed to a specific component in treated wastewater (Galapate *et al.* 1998; Komatsu *et al.* 2008). The excitation spectrum at longer wavelength indicates that this component consists of larger conjugated systems.

### Occurrence of fluorescent components

Figure 4 presents the fluorescent intensity based on PARAFAC score values of each component in samples collected from sites St.1–St.7 in the Senkawa River.



**Figure 3** | EEM contours of the six fluorescent components characterised by PARAFAC model.

Generally, for all components, the fluorescent intensities from the upstream water (St.1) are less than those from the water downstream of the effluent-release point. The intensity of all components increases at St.2, where the WWTP effluent is released (Figure 4). These results are consistent with the results for DOC. In addition, relative distribution of

fluorescent components are shown in Figure 5. Although simply comparisons of fluorescent intensities among different components cannot be correlated with their quantities, the changes in distribution of fluorescent intensity between upstream and downstream are shown: C5 (tyrosine-like) exhibited relatively higher intensities than other components

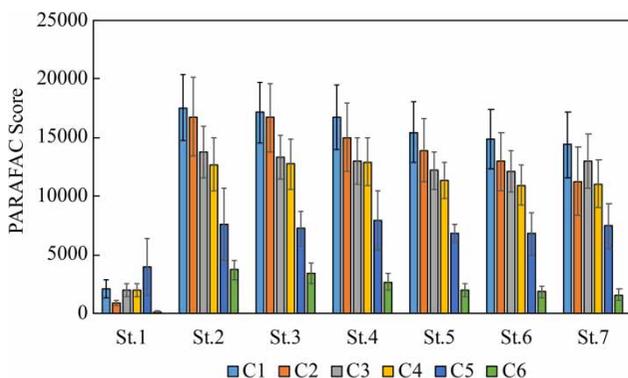
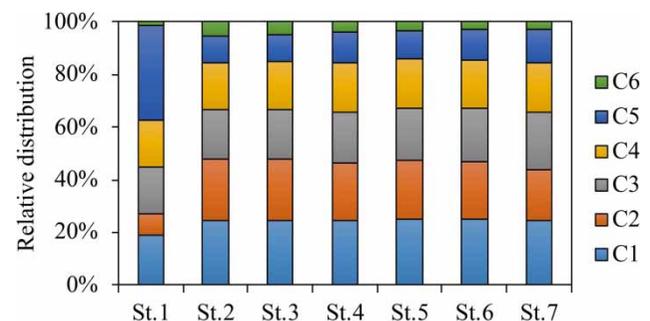
**Table 1** | Excitation emission matrix (EEM) spectral features of the identified fluorescent components and comparison with other studies

Component	Excitation (nm)	Emission (nm)	Comparison with other reports	
			Identified name and peak position (Ex/Em)	Assignment
1	320	370	Component 6: 325 (<260)/385 <i>Yamashita et al. (2008)</i>	Marine humic-like component
			Peak M: 312/380–420 <i>Coble (1996)</i>	Marine humic-like peak
			Component 2: 235 (355)/461 <i>Yao et al. (2011)</i>	Humic-like component
2	350	430	Component 2: 345/333 <i>Yamashita et al. (2008)</i>	Terrestrial humic-like component
			Peak C: 350/420–480 <i>Coble (1996)</i>	Humic-like peak
3	280 (380)	460	Component 3: 390 (275)/479 <i>Yamashita et al. (2008)</i>	Terrestrial humic-like component, biogeochemical processes of particulate organic matter
			C3: 250 (355)/461 <i>Yao et al. (2011)</i>	Terrestrial humic-like component
			Component 1: 265 (360)/447.5 <i>Yang et al. (2015)</i>	Terrestrial humic-like component
			Component 4: 260 (365)/444 <i>Yu et al. (2015b)</i>	Humic-like component
4	280	340	Component 4: 280/318 <i>Yamashita et al. (2008)</i>	Tryptophan-like component
5	280	300	Component 7: 270–299 <i>Yamashita et al. (2008)</i>	Tyrosine-like component
6	500	520	Peak 5: 490–495/515–520 <i>Komatsu et al. (2008)</i>	Fluorescent component specific to WWTP effluent

in the upstream point (St.1) but humic-like and tryptophan-like components become more important in the downstream areas of WWTP effluent. Therefore, the WWTP effluent is the dominant important source of anthropogenic fluorescent components in urban streams as suggested by *Meng et al. (2013)*.

Interestingly, the intensity of fluorescent components increased at St.2 and thereafter gradually decreased upon

moving downstream (i.e. with increasing transport time). Such decrease trends were observed in components except C5. In particular, C2 and C6 were significantly decreased at St.7 compared to St.2 ( $p < 0.05$ ) (ANOVA followed by Tukey's test). The intensity from C6 in samples from St.7 was reduced to 42% of those from St.2. The decreases in fluorescent intensities are attributed to factors such as dilution effects and component degradation. Although no significant tributaries flow into the Senkawa River in the area under study, leaving the WWTP effluent as the only major

**Figure 4** | Spatial changes of PARAFAC scores for each component in studied sites.**Figure 5** | Relative intensities of fluorescent component in the Senkawa River.

contribution in this area, dilution may be caused by unrecognised runoff water and/or groundwater. However, such simple dilution effects cannot alone explain the constant level of bulk DOC in the downstream sites, which suggests that the fluorophores may also degrade during transportation downstream (see Figure 2). Previous studies have indicated that fluorescent DOM can degrade in the environment. For example, photolysis reduces the abundance of PARAFAC components (Meng *et al.* 2013; Yang *et al.* 2014; Du *et al.* 2016). Other reports suggest that microbial activity may contribute to the degradation of fluorophores, but humic-like components are generally considered to have relatively low bioavailability (Coble *et al.* 2014). Mostofa *et al.* (2005) reported that fluorescent intensity from fluorescent whitening agents in river water varies diurnally, with lower values in daytime, thus suggesting that photodegradation is important for fluorescent components. Although in this study we did not determine any fluorescing pollutants in samples, fluorescent DOM might be degraded in the stream. An exception was found in a protein-like component C5 (tyrosine-like component), which showed a more characteristic distribution than the other components. It is detected at St.1 with comparable abundances to those in downstream sites. Note that a detailed discussion of the distribution of C5 is hindered by its large variability, which may be attributed to the spectrum of the xenon lamp used to excite the samples in EEM measurements (Maie 2009);

this lamp is generally characterised by low intensity in the short-wavelength region. Nevertheless, the presence of C5 with relatively higher intensity in St.1 samples might be indicative of a relatively large contribution of an autochthonous (plankton-derived) tyrosine-like component produced in the upstream ecosystem, as suggested previously (Yao *et al.* 2011). In addition, downstream of St.2, C5 intensity does not systematically decrease in contrast to other components. When seasonal variations were examined, only C5 showed higher amounts in the summer (July–September) season than winter (December, February and March) (Figure 6). These results may also be a consequence of autochthonous production of a tyrosine-like component in the downstream water promoted in summer. Therefore, the tyrosine-like component is considered to have significant autochthonous sources.

### Effects of photolysis

We also irradiated environmental samples collected from St.2 with simulated sunlight to rationalise the occurrence of fluorescent components that showed decreasing trends in the downstream area (C1, C2, C3, C4 and C6). As we expected, the abundance of fluorescent DOM in the irradiated samples decreased with time while those in the control groups did not show such trends (Figure 7), which shows degradation of components. Component C6 was the

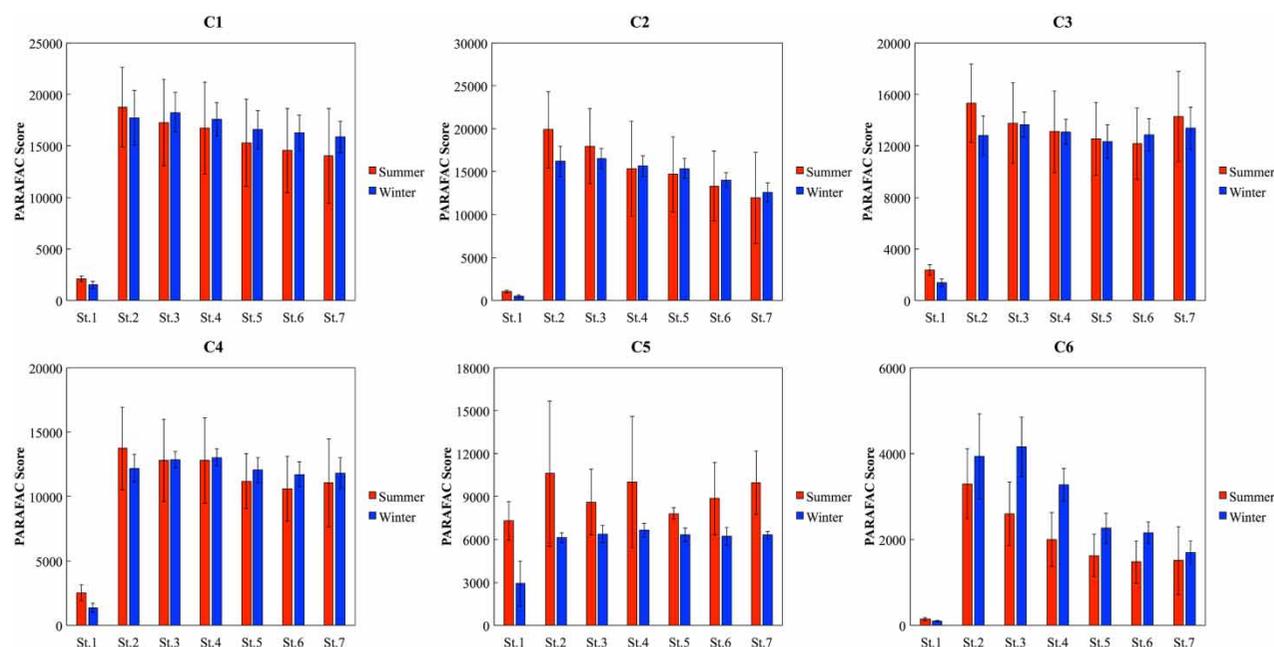
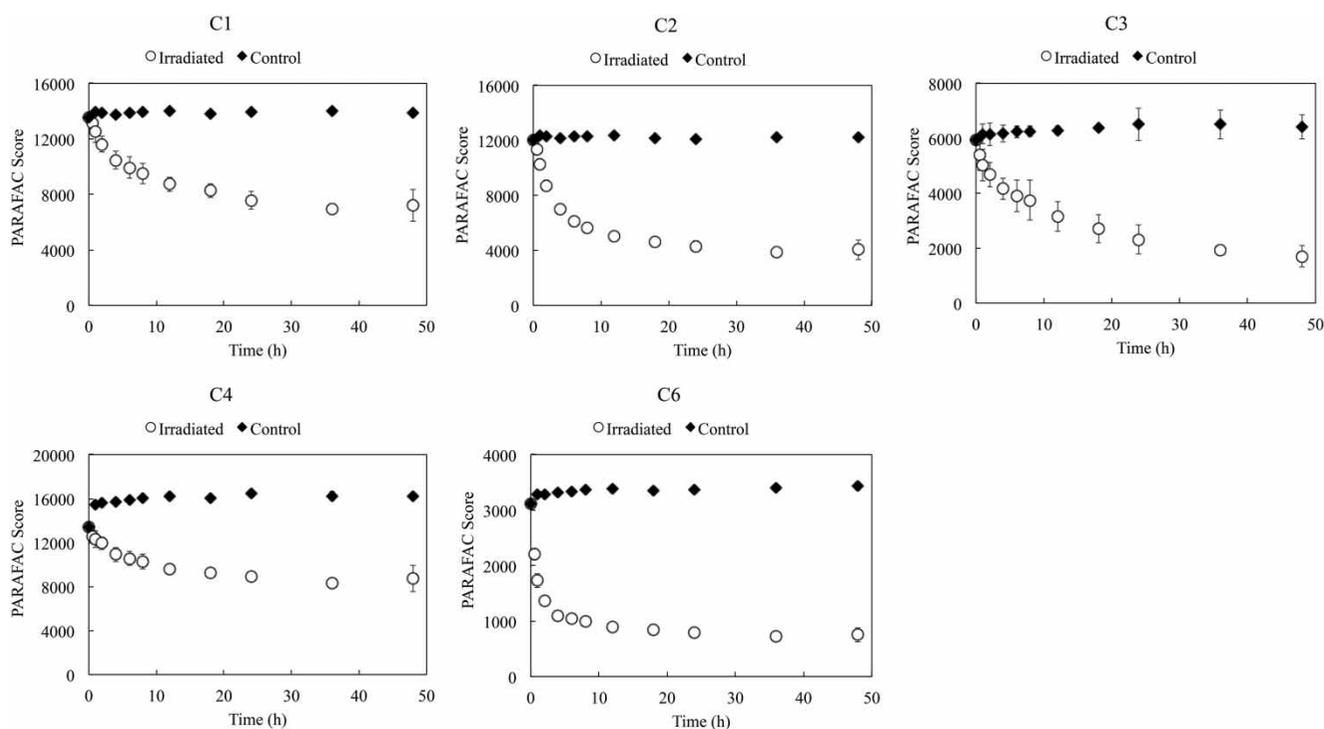


Figure 6 | Seasonal changes of fluorescent components.



**Figure 7** | Temporal changes of PARAFAC components during photolysis experiments. Results of C5 are not shown due to repeatability. Data at 36 h in the exposed groups are based on duplicate experiments ( $n = 2$ ).

most susceptible to photolysis and rapidly photodegraded, with only 33.3% remaining after the first 6 h photolysis. After 48 h of irradiation, the intensity of C1, C2, C3, C4 and C6 decreased to 53.1%, 33.63%, 28.5%, 65% and 24.1% of the initial values, respectively. The photolability of C6 might be attributed to the absorption band at the longer wavelengths region, as suggested from its excitation spectrum (Ishii & Boyer 2012).

We note that it is difficult to directly extrapolate these experimental results to the Senkawa River, even if the photodegradation rate constants of components were determined, because irradiating conditions are not exactly the same between the photolysis experiment and the river environments. Due to this limitation, in the present study we cannot conclude that decreases of fluorescent intensity within the stream are solely consequences of sunlight irradiation. Nevertheless, the result may at least partially explain the environmental occurrence of fluorescent components in the downstream. For example, the rapid degradation of fluorescent intensity from C6 during light exposure would support rapid decrease trends of this component within the stream. In addition, C2 and C4 showed similar levels of fluorescent intensities at the initial time of the experiments, but C2 decreased faster with irradiation

time than C4. Harmonious trends are observed in the downstream area of the effluent (Figure 4). Since humic acid generally hardly receives biological degradation (Coble *et al.* 2014), sunlight exposure is a potential key factor to control the occurrence of WWTP-derived anthropogenic DOM.

## CONCLUSION

This study is part of an effort to track the behaviour of DOM in urbanised streams by using EEM-PARAFAC. Field research revealed that humic-like components and the tryptophan-like component are mainly allochthonous (anthropogenic), originating from treated effluent, while the tyrosine-like component has autochthonous sources within the river. In water downstream of where the effluent is released, the DOC concentration remains almost uniform (Figure 2), but the intensities of anthropogenic components significantly decreased. These results suggest that DOM receives partial degradation and/or modification while amounts of organic carbon are unchanged. In addition, the photolysis experiments using simulated sunlight showed that it is likely that photochemical reactions are

an important factor to control distribution of the anthropogenic DOM components in rivers downstream and lakes. The EEM-PARAFAC method allows us to trace these processes by which DOM is modified, which cannot be done by simple DOC monitoring. These findings would be important when assess DOM sources and their fates in urbanised aquatic environments. Further studies on the degradation mechanisms of each fluorescent component and their environmental implications should be conducted.

## ACKNOWLEDGEMENTS

This study was supported by the River Fund of the River Foundation, Japan (20175311006). The authors also thank Saeka Ishikawa and Hibiki Moroi (Graduate School of Science and Engineering, Saitama University) for their contribution in the sampling campaign and for constructive discussions.

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First received 7 September 2018; accepted in revised form 26 October 2018. Available online 9 November 2018