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RESEARCH PAPER

Characterization of Nanming River (southwestern China) sewerage-impacted pollution using an excitation-emission matrix and PARAFAC

Khan M. G. Mostofa · Fengchang Wu · Cong-Qiang Liu · Wang L. Fang · Jie Yuan · Wang L. Ying · Li Wen · Mei Yi

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Abstract Nanming River, the largest urban river in Guizhou Province, southwestern China plateau, has been severely polluted for decades. This study characterizes the organic materials and their sources in the upstream and downstream waters by dissolved organic carbon (DOC), excitation emission matrix (EEM) spectroscopy, parallel factor (PARAFAC) analysis and photo-microbial experiments. DOC concentrations were low (47–120 μM C) upstream and relatively high (146–462 μM C) downstream. The PARAFAC studies on the sample EEM spectra demonstrated that the upstream dissolved organic matter (DOM) was mostly composed of one component that had a fulvic acid-like substance; downstream DOM was composed of two components with mixtures of tryptophan-like and fulvic acid-like substances. From the results of the sewerage drainage samples collected along the bank of the river, it is evident that both household detergent-like and protein-like or tryptophan-like substances are predominantly present, indicating that untreated sewerage effluents are the major sources of organic matter pollution in Nanming River. The degradation experiments conducted on river, sewerage drainage and commercial detergent samples demonstrated that the detergent-like and tryptophan-like substances are both photochemically and microbiologically more decomposable than fulvic acid-like materials under sunlight and dark incubations. These results suggest that the input of the untreated sewerage effluents along the streams is the major pollution source in Nanming River, and the fluorescent DOM was efficiently affected by both photochemical and microbial processes.

Keywords Fulvic acid-like fluorescence · Tryptophan-like fluorescence · Household detergent · Photodegradation · Microbial degradation

K. M. G. Mostofa (✉) · C.-Q. Liu · W. L. Fang · W. L. Ying · L. Wen · M. Yi
State Key Laboratory of Environmental Geochemistry, Institute of Geochemistry, Chinese Academy of Sciences, 550002 Guiyang, People's Republic of China
e-mail: mostofa@vip.gyig.ac.cn

F. Wu
State Environmental Protection Key Laboratory of Lake Pollution Control, Chinese Research Academy of Environmental Sciences, Beijing 100012, People's Republic of China

J. Yuan
State Key Laboratory of Ore Deposit Geochemistry, Institute of Geochemistry, Chinese Academy of Sciences, 550002 Guiyang, People's Republic of China

Introduction

Dissolved organic matter (DOM) in freshwater aquatic environments is a heterogeneous mixture of aromatic and aliphatic organic compounds originating from natural and anthropogenic sources. Naturally occurring DOM comprises a huge variety of organic substances including humic substances (Malcolm 1985; Wu et al. 2005) and other biomolecules, such as carbohydrates, amino acids and fatty acids, in natural waters (Volk et al. 1997; Rosenstock and Simon 2001; Tanoue 2000). Humic substances composed of fulvic and humic acids account for 40–80% in rivers (Mostofa et al. 2009). Fulvic acid is predominantly present in all natural waters due to its universal solubility (soluble at all pHs) (Malcolm 1985). But DOM components in urban rivers include anthropogenic sources, which typically come from agriculture, industries and sewerage effluents in the catchment area

(Baker 2001, 2002a, b; Mostofa et al. 2005a; Hudson et al. 2007). The components of anthropogenic DOM are mostly fluorescent whitening agents (FWAs) or components of detergents (diaminostilbene, DAS1 and distyryl biphenyl, DSBP) (Kramer et al. 1996; Managaki and Takada 2005), persistent organic pollutants including biphenyl, pesticides, polycyclic aromatic hydrocarbons (PAHs), organo-chlorinated compounds and polychlorinated biphenyls (Chau 2006; Luo et al. 2008), and tryptophan (Baker 2001; Mostofa et al. 2007a). DOM components are easily characterized by fluorescence (excitation-emission matrix, EEM) spectroscopy (EEMS) (Stedmon et al. 2003; Coble 1996, 2007; Hudson et al. 2007; Mostofa et al. 2009). Variation of fluorescent components based on several sources can be useful in the understanding of the fluorescent dissolved organic matter (FDOM) in the freshwater and marine environments. Currently, parallel factor (PARAFAC) analysis, a statistical modeling approach, was introduced to the aquatic sciences (Stedmon et al. 2003). The combination of EEMS and PARAFAC has been applied to identify various kinds of FDOM in natural waters (Hall et al. 2005; Cory and McKnight 2005; Borisover et al. 2009) and interactions between trace metals and DOM (Yamashita and Jaffé 2008), as well as during the laboratory-mesocosm experiments (Stedmon and Markager 2005; Stedmon et al. 2007). Therefore, EEMS and PARAFAC can be applied to distinguish the new fluorophore components in FDOM, particularly in the waters of highly polluted rivers.

In Nanming River, the input of organic pollutants frequently occurs in the downstream locations along the river. To deal with the organic matter pollution in the aquatic environment, it is vital to examine the composition of DOM, mainly the DOM sources, and then to identify the components of DOM, which may facilitate developing a removal process. Fluorescence studies of DOM and its role together with Hg(II) in Nanming River have been reported in previous studies (Fu et al. 2007), which did not provide any information about anthropogenic DOM components and their sources, or removal processes for the river waters.

The aim of this study was to investigate the DOM sources, originating from natural forest to urban sewerage and from upstream to downstream locations in the waters of Nanming River using EEMS and PARAFAC analysis. Another key aim of this study was to examine removal processes for various sources of DOM in the downstream waters of Nanming River using photochemical and microbial experiments. Experimental observations were conducted on water samples collected from downstream river water, sewerage and commercial detergents with the aim of examining the solar and microbial effects on degradation of various fluorescent components.

Materials and methods

Sampling

Water samples were collected from upstream to downstream along the Nanming River (16 sites), situated in Guizhou Province, southwestern China plateau, covering an area from 26°11′ to 26°40′N and 106°27′ to 107°03′E, Fig. 1). Nanming River originates from the Baini fields of Linka villiage of PinBa county. It is approximately 118 km long, and its major source is the Wujiang river catchment area, one of the biggest tributaries of the Changjiang River. It flows into Guiyang city from Zhongcao villiage of Huaxi district, then crosses from the southwest to the northeast section of the main zone (Nanming district and Yunyan district) of the city. The river water ultimately flows into Qinshui River by merging with the Dumu River. The waters of Nanming River are largely affected by drainage waters of the two reservoirs (Huaxi and Aha) before entering the river mainstream in Guiyang city. Huaxi reservoir, located in Huaxi town, has a water area of 1.4 km^2 and a storage capacity of approximately 1×10^6 m^3, and Aha reservoir, located on the upper reaches of Xiaoche river, the tributary of Nanming River, has a water area of 20 km^2 and a storage capacity of 54.5×10^6 m^3. Huaxi and Aha reservoirs are surrounded by small mountains, which are mostly covered with growing grass or small plants. Both banks of Nanming River inside Guiyang city

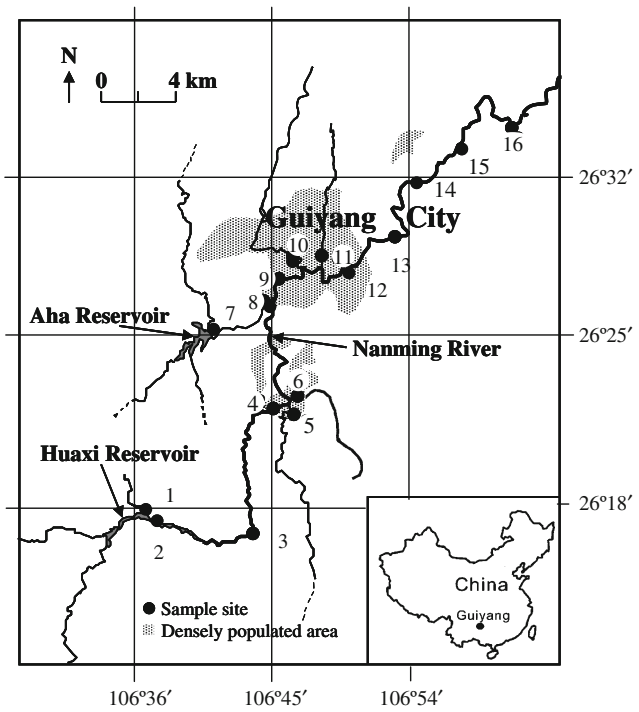

Fig. 1 Nanming River and its watershed from which water samples were collected

are artificially managed using concrete walls to reduce erosion. However, sewerage and other effluents from the city areas are mixed in the channels. A large volume of untreated municipal (~95%) and industrial effluents (~83%) is commonly discharged into the rivers and lakes in China (Wu et al. 1999). Guiyang is the capital city of Guizhou province, an area of 8034 km^2 with a downtown area of 2403 km^2 and an urban population of more than 1.34 million. The downtown area is mostly surrounded by small- and medium-sized mountains (up to 1000 m elevation), which are often covered with verdant forests and a few with coniferous forests. The soil is mainly acidic yellow earth and red earth, covering approximately 39 and 11% of the total area of the province, respectively.

To understand DOM sources downstream, water samples were collected from sewer drainage (7 sites), which is made up of wastewater coming directly from nearby households and factories before flowing into the Nanming River; water also comes from washing machines (1 sample) that use the household detergents examined in this study. Water samples were collected in 1-l polyethylene bottles and returned to the laboratory within 8 h. The samples were filtered with pre-combusted (450°C for 2 h) 0.7-μm fiberglass filters (GF/F, Whatman) and stored at 4°C in the refrigerator until analysis.

Experimental design

The short-term irradiation experiment (180 min) on various river samples was conducted on 24 July 2008 at the Institute of Geochemistry, Guiyang, China. Because of the regular flow of river waters, the effects of natural sunlight on river DOM are typically considered short compared to the surface waters of lakes and oceans. Duplicate pyrex glass beakers were used for each river, drainage and commercial detergent sample. The irradiation experiment was conducted at noon (11:00 a.m. to 2:00 p.m.) for direct irradiation of the samples kept in the pyrex beakers because the penetration of UV light through the pyrex glass did not occur sufficiently. Irradiated samples were collected after 30, 60, 120 and 180 min of irradiation. The other conditions of the experiment were the same as depicted elsewhere (Mostofa et al. 2007b). To examine the biological decomposition, duplicate Pyrex beakers were used and kept in the dark at room temperature. Incubated samples were collected after 1, 3, 6 and 10 days of irradiation for analysis.

Chemicals

To examine the various fluorophores in water samples collected from Nanming River and sewer drainage, we used commercially produced household detergents (two types: Nafine Chemical Industry Group Co. Ltd., China, and Nice Group Co. Ltd., China) in this study.

Analytical methods

DOC concentration was measured using a high-temperature catalytic oxidation method. Potassium hydrogen phthalate was used as a standard. After removing DIC by bubbling with pure air, 200 μl of each sample was injected into a TOC-5000A analyzer (Shimadzu, Kyoto, Japan). System blanks were determined according to the software installed in the TOC-5000A. The fluorescence properties were measured using a fluorescence spectrophotometer (F-4500, Hitachi Ltd., Japan), creating high-resolution fluorescence running with bandpass width slits of 5 nm for both excitation and emission. The scanning ranges were 220–400 nm for excitation and 250–500 nm for emission. Fluorescence readings were collected at intervals of 5-nm excitation with 1-nm emission wavelengths using a scanning speed of 1200 nm min^{-1}. For normalization of fluorescence, we used a quinine sulphate (QS) solution of 4 μg l^{-1} in 0.01 N H_2SO_4. The fluorescence intensities of all samples were calibrated using intensity (1 μg l^{-1} = 1 QS unit, QSU) at the peak (Ex/Em = 350/450 nm) for QS standard.

PARAFAC modeling

The PARAFAC analysis was performed in MATLAB using the N-way Toolbox for MATLAB version 3.1 with methods described in previous studies (Bro 1997; Stedmon et al. 2003). The data EEMs of the samples were modeled with an excitation wavelength ranging from 220 to 380 nm every 5 nm and emission wavelength from 280 to 480 nm every 1 nm. To avoid the mix up of components with a variety of samples, the PARAFAC model was used on sample's EEMs separately, such as upstream ($n = 7$), downstream ($n = 9$), sewerage drainage ($n = 7$), washing water ($n = 2$) and household detergent ($n = 2$) as well as irradiated river water ($n = 2$), sewerage drainage ($n = 2$) and household detergent samples ($n = 2$) after 3 h of sunlight irradiation for these samples, and dark incubated river water ($n = 2$, after 10 days), sewerage drainage ($n = 2$) and household detergent ($n = 2$) samples after 10 days of dark incubation at room temperature. Three steps were followed before running data in the PARAFAC model (Bro 1997; Stedmon et al. 2003). First, the Milli-Q water blank was subtracted from every sample. Second, all values of the Raleigh light scattering were properly eliminated from the data of sample's EEMs to avoid any effect on the component numbers. Third, non-negative constraints were applied in the PARAFAC modeling to avoid the negative values of three decomposing components, such as excitation, emission and concentration (fluorescence intensity) of the respective samples.

We applied bilinear models in this study where it was possible to judge the residuals on the fit (Bro 1999 and references therein). In this model, if systematic variation is left in, the residuals that indicate more components can be extracted. If a plot of the residual sum of squares versus the number of components sharply flattens out for a certain number of components, this indicates the true number of components. To calculate variance-like estimators, give the degrees of freedom

$$\mathrm{dof}(F) = IJK - F(I + J + K - 2)$$

for a trilinear PARAFAC model where I, J and K are the dimensions of the first, second and third mode, respectively, and F is the number of components in the model (Bro 1997 and references therein). Finally, comparison of the external knowledge of the data modeled was also done in this study; it is important to select the true number of components (Bro 1997).

In the PARAFAC model, the number was followed from 1 until the proper components were identified with 'pftest' command for the respective samples, and concurrently, the true number of components were selected on the basis of the residuals, the core consistency (that must be 100%), the number of iterations (which should be near zero) and the findings of the EEM spectra for the respective samples as well as the various standard substances. Finally, the PARAFAC command was used on the selected components to reach the final result, whereas the loadings of the emission and excitation wavelengths were often followed on the positive values as well as used to check the variability of the selected components (Stedmon et al. 2003). The variability explained by the PARAFAC analysis was 84.9% for upstream, 92.7% for downstream and 90.6% for sewerage drainage samples, and ranged from 77.3 to 88.0% for irradiated samples, from 88.2 to 93.8% for microbial dark incubated samples and from 90.8 to 99.6% for the standard substances studied.

Results

DOM and its EEM properties in combination with PARAFAC analysis

DOC concentrations were low upstream (54–120 μM C, sites 1–7) and higher (149–462 μM C, sites 8–16) downstream in Nanming River (Table 1). The rapid increase of DOC concentration downstream is probably caused by the input of untreated sewerage as well as the industrial effluents in the main channel. The pH did not vary much between upstream (7.50–7.90) and downstream (7.67–8.03) in Nanming River (Table 1).

Table 1 The pH and dissolved organic carbon (DOC) concentrations in the waters of Nanming River

	pH	DOC (μM C)
Upstream sites		
Sample 1	7.80	54
Sample 2	7.82	54
Sample 3	7.50	100
Sample 4	7.90	81
Sample 5	7.85	102
Sample 6	7.77	47
Sample 7	7.85	120
Downstream sites		
Sample 8	7.67	149
Sample 9	7.96	146
Sample 10	7.79	155
Sample 11	8.02	147
Sample 12	8.03	188
Sample 13	8.01	154
Sample 14	7.90	147
Sample 15	7.81	217
Sample 16	7.90	462

The various fluorescence peaks detected in EEMs of river and standard samples are presented in Fig. 2. PARAFAC analysis of riverine samples demonstrated that the upstream DOM was composed of one component (Fig. 3a), indicating the occurrence of a fulvic acid-like substance having two fluorophores at Ex/Em = 300–310/423–448 nm (peak M) and 235–240/427–444 nm (peak A) in the original EEM (Table 2). Downstream DOM was characteristically identified with two components (Fig. 3b, c). One component (Fig. 3b) corresponded to the occurrence of a protein-like or tryptophan-like substance with two fluorescence peaks (peak T at Ex/Em = 275–280/337–351 nm and peak T_{UV} at 225–230/340–347 nm, respectively, Table 2). The other component (Fig. 3c) corresponded to a fulvic acid-like substance with two fluorescence peaks (peak M_p at Ex/Em = 300–310/428–447 nm and peak A at 235–255/425–447 nm, respectively, Table 2). PARAFAC analysis of sewerage drainage samples was typically identified with two components, suggesting the protein-like or tryptophan-like component with two fluorescence peaks (peak T at Ex/Em = 280/339–346 nm and peak T_{UV} at 230/338–351 nm, Fig. 3d) and a household detergent-like component with two fluorescence peaks (peak W at Ex/Em = 335–345/432–437 nm and peak $A_{detergent}$ at 240–250/425–443 nm, Fig. 3e) (Table 2). PARAFAC analysis of the washing sample, collected after washing clothes using commercial detergents, showed the two components, suggesting the occurrence of a major detergent-like component including peaks at Ex/Em = 345/437 nm (peak W) and

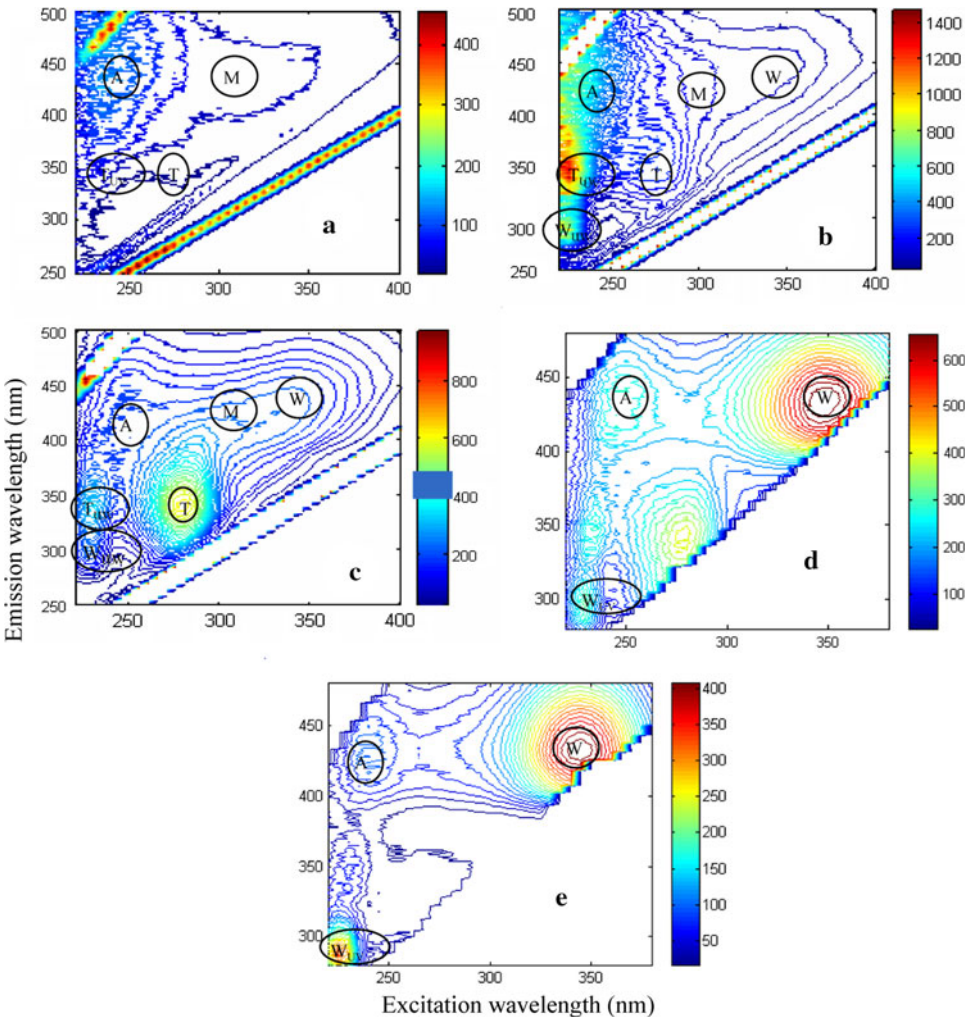

Fig. 2 Examples of the excitation (Ex)-emission (Em) matrix fluorescence of water samples collected in Nanming River watershed and commercial detergents. **a** Upstream water (site 3), **b** downstream water (site 16), **c** sewerage drainage water (sample 3), **d** washing sample (collected after washing of clothes using detergents) and **e** commercial detergent. The Ex/Em wavelengths of various fluorescence peaks in the original EEM spectra are exemplified for depiction of various fluorescent organic substances in this study as well as for standard substances mentioned in Table 2

250/441 nm (peak $A_{detergent}$), and a minor protein-like or tryptophan-like component having peaks at Ex/Em = 280/344 and 235/348 nm.

The fluorescence intensities in downstream DOM are much higher than in upstream DOM (Fig. 4a). The fluorescence intensity of peak T_{UV} was highest in the downstream samples studied. Two key components such as the protein-like (peak T) and detergent-like (peak W) components in sewerage drainage samples were detected using PARAFAC analysis (Fig. 3), but the detergent-like component was not found in downstream DOM. This is likely caused by the dilution effect of sewerage effluents in the mainstream river waters, thereby causing the detergent-like substance to be a minor component that cannot be identified using PARAFAC modeling in the downstream waters of Naming River (Stedmon et al. 2003). Conversely, the fluorescence intensities of peak A and peak T_{UV} in sewerage drainage samples were detected within the same ranges of downstream waters (Fig. 4b). The occurrence of protein-like (peak T) at peak T regions in the samples of sewerage drainages is responsible for the discharge of effluents by human activities in the urban areas.

EEM spectra of commercial detergents showed three fluorophores such as peak W_{Tuv}, peak W and $A_{detergent}$ (Fig. 3e; Table 2); in terms of intensity, the orders of the fluorescence are peak W_{TUV} at Ex/Em = 225/287–289 nm (334 QSU) > peak W at 345/430–435 nm (157 QSU) > peak $A_{detergent}$ at 240/429–433 (45 QSU), respectively (Fig. 2d). PARAFAC analysis of commercial detergents demonstrated two components, indicating the occurrences of a major component having two fluorophores of peak W at peak C region and peak $A_{detergent}$ at peak A region (Fig. 3h), and a minor component with a fluorophore of peak W_{UV} at peak T_{UV} region (Fig. 3i).

Photochemical and microbial changes of riverine DOM

Photodegradation experiments on the river and household detergent samples demonstrated that the fluorescence intensities of various fluorophores were significantly decreased during the irradiation period (180 min) except

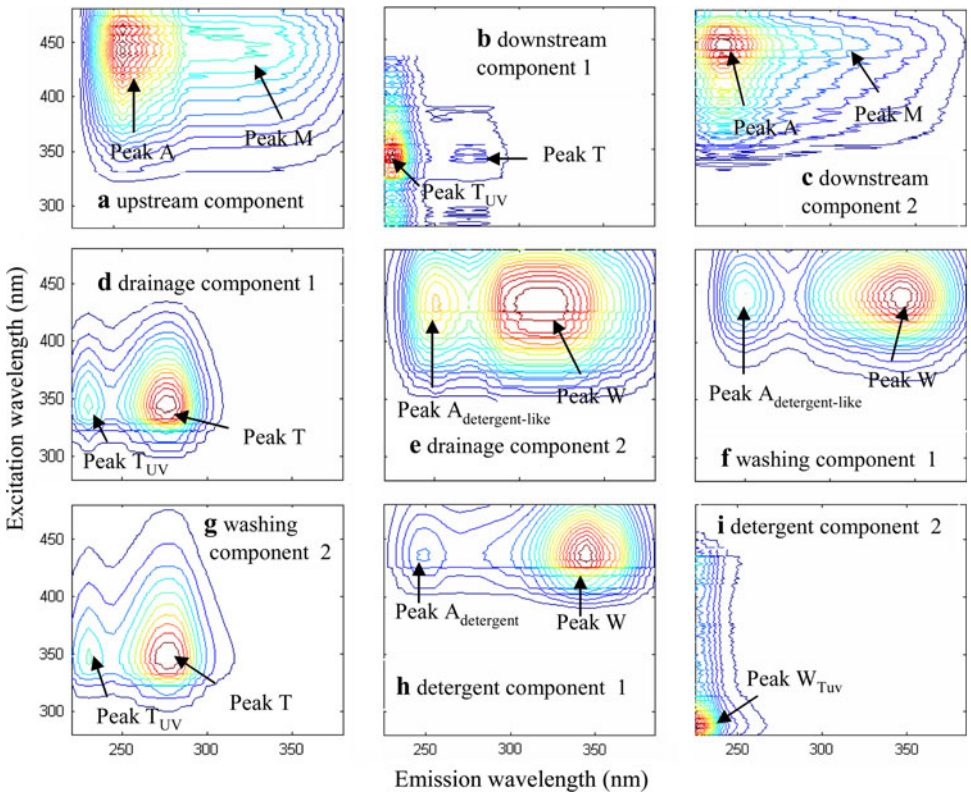

Fig. 3 Various fluorescent components of river samples and aqueous solutions of standard substances identified with the PARAFAC model. The Ex/Em wavelength maxima of the peaks are depicted in Table 2

for the peak W_{UV} where an increase in fluorescence was observed in drainage and detergent samples (Table 3). The decrease in fluorescence of detergent components (peak W) was much higher (34 and 88% in drainage and detergent samples, respectively) compared to those of fulvic acid-like components (peak M; 20 and 27% in river and drainage samples, respectively, and peak A, 21, 18 and 70%, respectively), tryptophan-like components (peak T, 32 and 50%, respectively, and peak T_{UV}, 31 and 36%, respectively; Table 3). An increase in fluorescence of peak W_{UV} was typically detected in drainage (4%) and detergent samples (9%), although their quantities were low. These results suggest that fluorophores at the shorter wavelength were not decomposed or less susceptible to photochemical effects than those of the longer wavelength regions. The PARAFAC analysis on irradiated samples identified one fluorescent component in each sample after sunlight illumination, indicating the occurrence of a photo-bleached fulvic acid-like component (Fig. 5a) in river samples, photo-bleached protein-like or tryptophan-like components (Fig. 5b) in sewerage drainage samples, and unidentified photo-bleached detergent components in detergent samples (Fig. 5c). These results indicate that the commercial detergents are the most susceptible to photodegradation.

From the microbial degradation of the same samples, it was shown that the fluorescence intensity of peaks T, T_{UV} and W_{UV} were greatly decreased, while the fluorescence of peak C or peak W increased during the 10 consecutive days of dark incubation at room temperature (Table 3). The decrease in fluorescence of the peaks T, T_{UV} and W_{UV} were −24, −62 and −84% in river plus detergent samples, and −67, −76 and −90% in sewerage drainage samples, respectively. But the decrease in fluorescence of peak W_{UV} was relatively low (−15%) in commercial detergent samples. This is likely caused as a consequence of the relatively fewer microbial effects on detergent samples because commercial detergents were dissolved in MQ waters. Moreover, the fluorescence intensities of the peaks M, W and A often increased except for the peak A in river plus detergent samples, whereas the fluorescence decreased (−3%), although its quantity was insignificant (Table 3). The PARAFAC model on dark incubated samples (after 10 days) identified one component (fulvic acid-like) in river samples, two components (detergent-like and protein-like or tryptophan-like) in sewerage drainage samples and one component (detergent-like) in detergent samples. These results imply that microbial degradation may typically affect the fluorophores of a component that belongs to a shorter wavelength region.

Discussion

Fluorescent DOM in Nanming River and their sources

The fluorescence peaks M and A, two major fluorophores of fulvic acid-like component identified in the upstream

Table 2 Fluorescence excitation/emission (Ex/Em) wavelengths of standard substances and the subsequent characteristic peaks of the reference components in natural waters

Samples	Fluorescence properties			MQ water				References
Standard substances/ component type	Peak C region			Peak A region	Peak T region	Peak T_{UV} region		
	Peak C Ex/Em (nm)	Peak Mp	Peak W	Peak A/ Peak $A_{detergent}$	Peak T	Peak T_{UV}	Peak W_{UV}	
River waters, upstream locations ($n = 7$)	np	300–310/ 423–448	np	235–240/427–444	280/340–346	230/338–344	np	Riverine samples in this study
River waters, downstream locations ($n = 9$)	np	300–310/ 428–447	335–345/432–437	235–255/425–447	275–280/ 337–351	225–230/ 340–347	225/289–294	
Drain samples ($n = 7$)	np	300–325/ 418–436	335–345/432–437	240–250/425–443	280/339–346	230/338–351	225–230/ 291–296	
Washing samples, collected after washing clothes	np	np	345/437	250/441	280/344	235/348	230/296	
Tap water ($n = 2$)	np	315–320/ 430–450	np	245/429–430	280/333–346	np	np	
Detergents, Nafine Chem. Ind. Ltd., China	np	np	345/430–435	240/429–433	np	225/287–289	np	
Detergents, Nice Group Co. Ltd., China	np	np	345/430	240/427	np	225/287	np	
River waters (unfiltered) + detergents	np	305/417	340/433	240/435	280/343	230/345	225/292	Dissolved in river waters in this study
Naphthalene in landfill leachate	np	np	np	np	np	220–230/ 340–370	nd	Baker and Curry (2004)
Humic-like	330–350/420–480	np	np	np	np	np	nd	Coble (1996), Parlanti et al. (2000)
Marine humic-like	np	310–320/ 380–420	np	np	np	np	nd	
Humic-like	np	np	np	250–260/380–480	np	np	nd	
Tyrosine-like, protein-like	np	np	np	np	270–280/ 300–320	np	nd	
Tryptophan-like, protein-like or phenol-like	np	np	np	np	270–280/ 320–350	np	nd	
Fulvic acid (SJF)	np	310/419	np	np	np	np	nd	Coble (1996, 2007)
Humic acid (EEP2)	np	310/428	np	np	np	np	nd	
Humic acid (EEP2)	np	310/423	np	np	np	np	nd	
Melanoidin	np	363/458	np	np	np	np	nd	
DSBP ($n = 2$)	np	np	355/430–432	np	np	np	nd	Komaki and Yabe (1982)
DAS1 ($n = 2$)	np	np	340–343/430–432	np	np	np	nd	

Table 2 continued

Samples	Fluorescence properties			MQ water				References
Standard substances/ component type	Peak C region			Peak A region	Peak T region	Peak T_{UV} region		
	Peak C Ex/Em (nm)	Peak Mp	Peak W	Peak A/ Peak $A_{detergent}$	Peak T	Peak T_{UV}	Peak W_{UV}	
Tryptophan	np	np	np	np	280/342–346	np	nd	Yamashita and Tanoue (2003)
Tyrosine	np	np	np	np	270–275/ 300–302	np	nd	
Phenylalanine	np	np	np	np	np	255–265/ 284–285	nd	
Soil fulvic acid (extracted)	np	315/437–441	np	np	np	np	nd	
Soil fulvic acid (standard)	np	320/440	np	np	270–280/ 430–440	np	nd	Sugiyama et al. (2005)
River fulvic acid (extracted)	np	300–310/420–430	np	260–270/430–440	np	np	nd	
Lake fulvic acid (extracted)	np	310–320/378–430	np	250/428–446	np	np	nd	
Suwannee River fulvic acid	325/450	np	np	260/460	np	np	nd	Coble et al. (1990)
Tryptophan	np	np	np	np	280/357	227/351	nd	Baker (2005)
Fulvic acids (IHSS standard, $n = 5$)	333 ± 4/452 ± 12	np	np	np	283 ± 3/ 351 ± 2	231 ± 3/ 353 ± 4	nd	
Suwannee River and pine barrens (pH 3–6)	330–340/451–467	np	np	240–260/427–468	np	np	nd	Schwede-Thomas et al. (2005)
Fulvic acid, extracted from lake	np	305/448	np	240/440	np	np	nd	Wang et al. UD
Humic acid, extracted from lake	np	295/464	np	255/462	np	np	nd	
Lake Fryxell and Lake Pony (pH 3–6)	310–330/408–427	np	np	230–240/410–433	np	np	nd	Schwede-Thomas et al. (2005)
Fulvic acids: IHSS standard ($n = 5$)	330–340/456–475	np	np	np	np	np	nd	Mostofa et al. (2005a), UD
	mean = 333 ± 3/469 ± 6	np	np	np	np	np	nd	
Humic acid: IHSS standard ($n = 3$)	320–345/478–498	np	np	np	np	np	nd	
	mean = 330 ± 13/484 ± 13	np	np	np	np	np	nd	
Tryptophan, $n = 3$	np	np	np	np	278 ± 3/354 ± 2	225/343–358	nd	
DAS1: fluorescent whitening agents ($n = 4$)[a]	np	np	335–355/438–449	240–245/434–446	np	np	nd	
	np	np	mean = 345 ± 10/ 443 ± 5	mean = 242 ± 3/441 ± 6	np	np	nd	
DSBP: fluorescent whitening agents ($n = 3$)	np	np	350 ± 0/436 ± 0	235–265/435–445	np	np	nd	

Table 2 continued

Samples	Fluorescence properties			MQ water				References
Standard substances/ component type	Peak C region			Peak A region	Peak T region	Peak T_{UV} region		
	Peak C Ex/Em (nm)	Peak Mp	Peak W	Peak A/ Peak $A_{detergent}$	Peak T	Peak T_{UV}	Peak W_{UV}	
Fluorescent whitening agents (FWAs)	np	np	np	260/430	np	np	nd	Hudson et al. (2007) (reviewed)
Tyrosine	np	np	np	np	270/314	np	nd	Mostofa and Sakugawa UD
Phenol	np	np	np	np	270/297	np	nd	
4-Biphenyl carboxaldehyde	np	305/410	np	np	np	255/315	nd	
o-Cresol	np	np	np	np	275/303	215/304	nd	
p-Cresol	np	np	np	np	280/309	225/309	nd	
p-Hydroxyphenyl acetic acid	np	np	np	np	280/305	230/304	nd	
Salicylic acid	np	300/407	np	235/410	np	np	nd	
Salicylic acid	np	314/410	np	np	np	np	nd	Senesi (1990) and references therein[b]
Methyl salicylate	366/448	302/448	np	np	np	np	nd	
3-Hydroxybenzoic acid	np	314/423	np	np	np	np	nd	
Protocatechuic acid (ionized)	340–370/455	np	np	np	np	np	nd	
3-Hydroxycinnamic acid	np	310/407	np	np	np	np	nd	
Caffeic acid	365/450	np	np	np	np	np	nd	
Ferulic acid	350/440	np	np	np	np	np	nd	
β-Naphthols (ionized)	350/460	np	np	np	np	np	nd	
Xanthone	np	410/456	np	np	np	np	nd	
3-Hydroxyxanthone	343, 365/465	np	np	np	np	np	nd	
3-Hydroxy quinoline	350/450	np	np	np	np	np	nd	

Mp fluorescence Ex/Em maxima of fulvic acid, which is photobleached by photochemical processes or by other natural processes

np no peak identified, *nd* not detected the peak at this regions, *UD* unpublished data

[a] Ranges express the authentic standard at various concentrations (1–5 mg l^{-1}) and mechanical reproducibility

[b] Measurements conducted using two dimensional fluorescence spectophotometer

using PARAFAC analysis (Fig. 3a), are considered to be released from the forest ecosystem in the upstream catchments. The fluorescence peaks T and T_{UV} for the tryptophan-like component are weak upstream (Fig. 2a) where the PARAFAC model did not identify the tryptophan component, suggesting the fewer biological sources of organic components upstream. The tryptophan-like components are typically produced by biological processes in lake and ocean environments (Coble 1996; Mostofa et al. 2005b; Hudson et al. 2007). Less biological production of tryptophan was also reported in previous studies on upstream rivers (Mostofa et al. 2005a, 2007a).

On the other hand, downstream DOM was characteristically different from upstream DOM, with both tryptophan-like or protein-like substances (Fig. 3b) and fulvic acid-like substances (Fig. 3c) detected using the PARAFAC model. The sources of a fulvic acid-like substance downstream were the upstream waters, generally released from the forest ecosystem in the upstream catchment area. The sources of tryptophan-like or protein-like substances are typically input from the urban areas along the bank of downstream locations. This can be judged by the detection of the predominant presence of protein-like or tryptophan-like substances (Fig. 3d) in the sewerage DOM. Another component in sewerage samples was the detergent-like substance (Fig. 3e), although it was not identified in downstream DOM using PARAFAC analysis. The EEM spectra showed the presence of minor fluorescence (peak W_{UV}) in downstream (Fig. 2b) as well as sewerage drainage samples (Fig. 2c; Table 2), which was not detected using PARAFAC analysis, but this fluorophore was confirmed in commercial detergent at Ex/Em = 225/287–289 nm in this study (Fig. 3g). To authenticate whether the peaks W_{UV} and W were characterized in river and sewerage drainage samples, the washing samples were collected immediately after washing clothes using the same commercial detergents (Fig. 2d); the results revealed that the fluorescence intensities were greatly decreased for the fluorophore of peaks W_{UV}, but unaltered for the fluorophore regarding the peak W (Fig. 2d) due to washing processes. This suggests that the washing processes may significantly affect the chemical composition of the fluorophore (peak W_{UV}) in commercial detergents that demonstrated the fluorescence peak in shorter Ex/Em wavelength regions. Such a change in the fluorescence of peak W_{UV} might be responsible for its becoming a minor component in downstream and sewerage samples, thereby resulting in the invisibility of that component in PARAFAC analysis. Experimental results showed that the peak W_{UV} was rapidly mineralized in river plus detergent samples under dark incubation (Table 3). The Ex/Em wavelengths of peak W identified in riverine samples (Fig. 3e) were in agreement with the reported studies of a UK river (344 ± 5.8/433 ± 2.9 nm) in which there was water input from a tissue mill, where components of FWAs were used during the pulp processes (Baker 2002b), and of Japanese rivers (335–350/427–450 nm) where untreated sewerage effluents are directly discharged into the rivers (Mostofa et al. 2005a). The use of household detergents has been largely examined using a chromatographic technique in Swiss rivers and lakes (Kramer et al. 1996; Poiger et al. 1996, 1999; Stoll et al. 1998; Stoll and Giger 1998;) and Japanese rivers and coastal waters (Takada et al. 1992; Hayashi et al. 2002; Managaki and Takada 2005; Hayakawa et al. 2007; Takahashi and Kawamura 2007). Therefore, household detergents or components of FWAs might be important sources of fluorescent organic matter in aquatic environments.

Peak A, a major peak of fulvic or humic acid, was usually detected at Ex/Em = 240−270/430−462 nm in freshwater rivers, at 230−250/410−446 nm in lakes and at 250−260/380−480 nm in marine waters (Table 2). But peak A regions are affected by several other organic substances, such as household detergents (240−245/429−433 nm) or components of FWAs-DAS1 and DSBP (235−265/430−446 nm), and salicylic acid (235/410 nm) (Table 2 and references therein). As PARAFAC did not identify the minor components, the impacts of these compounds on the peak A region in EEM were not revealed using the combination of the EEM and PARAFAC technique.

The fluorescence intensities of peak T are characteristically lower compared to those of peak T_{UV} in downstream waters (Fig. 4a), and both peaks are suggested to be caused by the tryptophan-like component (3b). Standard tryptophan has two fluorescence peaks (T and T_{UV}), whereas peak T_{UV} was approximately two- to three-fold higher than peak T (Mostofa et al. 2009). Although the fluorescence images or peaks (T and T_{UV}) among downstream (Fig. 3b), sewerage drainage (Fig. 3d) and washing samples (Fig. 3g) are similar, fluorescence intensities of peak T in sewerage and washing samples are much higher than those of peak T_{UV}. This is apparently caused by a protein-like component (Coble 1996, 2007) that is likely released from manmade activities into sewerage waters, particularly from urban areas along the bank of Nanming River.

Photochemical effects on anthropogenic DOM in riverine waters

Photodegradation results revealed that the fluorescence regarding peak W of detergent components rapidly decreased in drainage samples (34%) compared to peak M (20 and 27%, respectively) and peak A (21 and 18%, respectively) of fulvic acid-like substances (Table 3). The fluorescence of peak T (32% in river and 50% in drainage

samples) and peak T_{UV} (31 and 36%, respectively) of the tryptophan-like component rapidly decreased compared to household detergents or the fulvic acid-like component (Table 3). Rapid degradation of tryptophan-like fluorescence in this study was inconsistent with previous studies of tryptophan degradation in river waters (Mostofa et al. 2007b), which reported that the tryptophan-like component (peak T) in downstream rivers was less susceptible to photodegradation (59%) than the fulvic acid-like component (80%) during 13 days of sunlight irradiation. The extremely photochemical nature of tryptophan-like fluorescence (peak T and T_{UV} regions) in Nanming River might suggest that fluorophores in the peaks (T and T_{UV}) in the river samples are different from those in Japan's rivers and are more susceptible to photodegradation. This phenomenon is in agreement with the observation of high fluorescence at peak T compared to those of peak T_{UV} in sewerage drainage samples. DOM components in Japanese rivers mostly came from agricultural activities in downstream locations (Mostofa et al. 2005b, 2007b), which is different from the situation for Nanming River, which is affected by sewerage characterized by organic contaminants from the urban areas downstream.

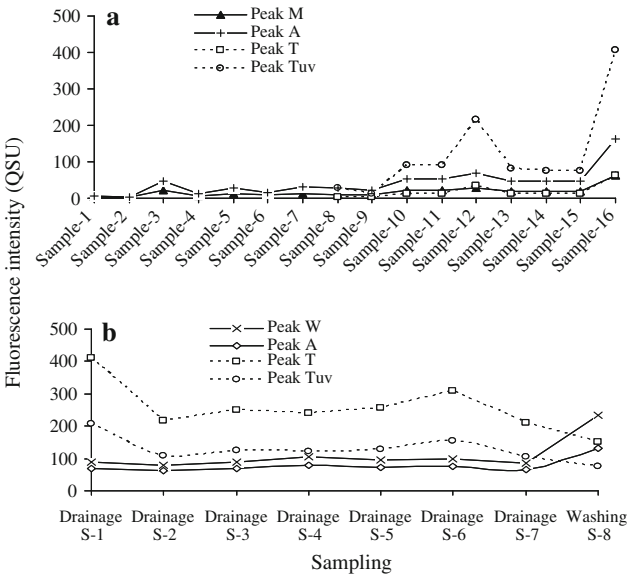

Fig. 4 Variations in the fluorescence intensities of various peaks identified using the PARAFAC modeling on water samples collected from upstream ($n = 7$) and downstream ($n = 9$) in Nanming River (**a**) as well as sewerage drainage samples ($n = 7$) (**b**)

Rapid mineralization of fluorescence regarding peak W and no significant decomposition at peak W_{UV} in sewerage samples are shown by a quick decrease in fluorescence of household detergent samples (88% at peak W, 70% at peak A region and no decomposition at peak W_{UV}) in photo experiments (Table 3). The rapid photochemical changes in fluorescence of household detergents or compositions of FWAs (peak W) are in line with previous studies (Kramer et al. 1996; Mostofa et al. 2005a). A small increase in fluorescence at peak W_{UV} in sewerage drainage (4%) and detergent samples (9%) may be due to solar effects. From the comparison of initial and final photo-bleached components of fulvic acid using PARAFAC analysis, it is estimated that the decrease in fluorescence was highest (28–30%) at longer wavelength regions (Ex/Em = 335–350/430–450 nm) than at peak M (17% at 310/450 nm) and peak A (20% at 250/440 nm) in the downstream river.

This suggests that the fluorophore at the longer Ex/Em wavelength in fulvic acid is primarily susceptible to rapid photochemical degradation in aqueous media. Thus, photodegradation would be useful in the removal of major

Table 3 Changes in the fluorescence intensities of fulvic acid-like (peaks M and A), tryptophan-like or protein-like (peaks T and T_{UV}) and detergent component (peaks W and W_{UV}) in river, sewerage drainage and detergent samples due to photochemical and microbial degradation

Type of samples	Changes in the fluorescence intensities (%)					
	Peak C region		Peak A region	Peak T region	Peak T_{UV} region	
	Peak M	Peak W	Peak A/peak $A_{detergent}$	Peak T	Peak T_{UV}	Peak W_{UV}
Photochemical degradation (180 min)						
River	−20	np	−21	−32	−31	np
Sewerage drainage	−27	−34	−18	−50	−36	(+) 4
Commercial detergent	np	−88	−70	np	np	(+) 9
Microbial degradation (after 10 consecutive days)						
River + detergent	(+) 12	(+) 21	−3	−24	−62	−84
Sewerage drainage	(+) 1	(+) 8	(+) 12	−67	−76	−90
Commercial detergent	np	(+) 14	0	np	np	−15

+ and −: an increase and a decrease in fluorescence intensities of various peaks, respectively

np means 'no peak' identified in the EEM of the respective sample

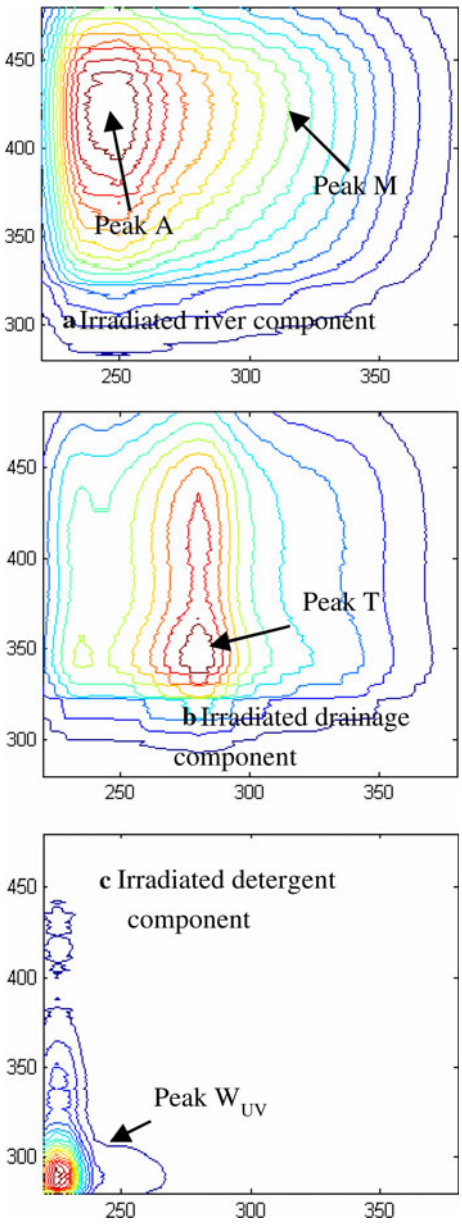

Fig. 5 Photochemical effect changed the fulvic acid-like (**a**), protein-like (**b**) and detergent-like (**c**) components in irradiated river, sewerage drainage and commercial detergent samples, respectively, and these components were identified using PARAFAC modeling individually in the respective samples after 3 h of sunlight irradiation

anthropogenic fluorescent organic contaminants, particularly the fluorophores at the longer Ex/Em wavelengths in rivers.

Microbial effects on removal of anthropogenic DOM

Microbial degradation of samples showed that the fluorescence intensity of peak W in household detergents and river plus detergent samples appeared as a dominant fluorescence at peak C region because of microbial degradation (Table 3). The fluorescence of fluorophores in the detergent component (peak $A_{detergent}$) was often increased in incubated sewerage drainage samples (12%) due to microbial degradation (Table 3). To clarify the microbial degradation of household detergents, they were mixed with unfiltered downstream waters of Nanming River to examine whether the microbes had an effect. The result showed that the fluorophores regarding the peaks (W and A) are microbiologically refractory or recalcitrant to microbial degradation (Table 3). The refractory nature of fulvic and humic acids has already been reported elsewhere (Moran et al. 2000; Coble 2007). The refractory nature to microbial degradation of fulvic acid, humic acid and components of FWAs (DAS1 and DSBP) is hypothesized to be related to the composition of their complex molecular structure composed of a number of aromatic rings having several functional groups in the molecular structure (Aiken et al. 1985; Malcolm 1985). Microbes are not primarily capable of decomposing the fluorescence at the longer wavelength regions, particularly at peak C region in humic substances (fulvic and humic acids) or in detergent components. This is presumably caused by the presence of specific repeating functional groups or units in the carbon matrix in FDOM that may be demonstrated at peak C region (Mostofa et al., 2009).

The decrease in fluorescence of peak W_{UV} of household detergents was much higher in sewerage drainage samples (−90%) and then in river plus detergent samples (−84%) than in commercial detergent samples (−15%) where detergents were dissolved in MQ waters (Table 3). These results suggest that highly polluted waters may rapidly degrade fluorescence of peak W_{UV}-like fluorophores at the peak T_{UV} region. The fluorescence of the tryptophan-like component (peaks T and T_{UV}) was greatly decreased in river plus detergents samples (−24 and −67%, respectively) and in sewerage drainage samples (−62 and −76%, respectively) during the incubation period (Table 3). Microbial degradation of tryptophan-like fluorophores was also reported in previous studies (Baker and Inverarity 2004). Our observations revealed that the fluorescence of peak T_{UV} decreased much more than those at peak T region. On incubated samples, the PARAFAC model identified only one microbiologically altered component of detergent (peaks W and $A_{detergent}$) in river plus detergent samples (Fig. 6a), two components of detergent (Fig. 6b) and protein-like substances (Fig. 6c) in sewerage drainage samples, and one component of detergent (peaks W and $A_{detergent}$) in commercial detergent samples. However, protein-like or tryptophan-like components (peaks T and T_{UV}) and the detergent component regarding the fluorophore of peak W_{UV} in all incubated samples were not identified due to significant losses in their fluorescence intensities as a result of microbial degradation (Table 3).

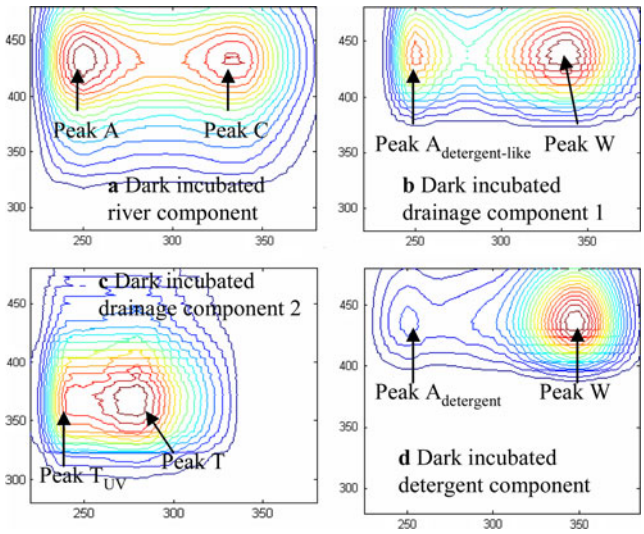

Fig. 6 Microbiologically modified detergent-like component (**a**) in river plus detergent samples, detergent-like (**b**) and protein-like (**c**) components in sewerage drainage samples, and detergent-like component (**d**) in detergent samples. These components were identified using PARAFAC analysis individually in the respective dark-incubated samples after 10 days

This suggests that the microbial degradation has an influence on fluorophores at the shorter Ex/Em wavelengths and is recalcitrant to fluorophores at the longer Ex/Em wavelengths in rivers. Finally, this study may assist in understanding the fluorescence studies of sewerage-impacted organic matter pollution in rivers, which is a great concern as it relates to consequences of anthropogenic fluorescent organic substances in rivers.

Conclusion

This study can be summarized with the following conclusions:

1. The difference in the DOC concentration between upstream and downstream water may be a general concern related to the organic matter pollution in Nanming River. Sewage effluents from densely populated Guiyang city along the river are a major source of organic matter contamination in Nanming River.
2. PARAFAC analysis only identified the fulvic acid-like component (peaks M and A) upstream, both fulvic acid-like and protein-like or tryptophan-like components (peaks T and T_{UV}) downstream, and both protein-like or tryptophan-like and household detergent-like components (peak W) in the sewerage drainage samples. The predominant presence of the peaks T and W in the sewerage drainage samples might be useful as an indicator of anthropogenic activities in Nanming River.
3. Photochemical degradation can decompose the fluorescence of fulvic acid-like (20–27% of peak M and 21–18% of peak A), protein-like or tryptophan-like (32–50% of peak T and 31–36% of peak T_{UV}) and detergent-like components (34–88% of peak W) in rivers, sewerage drainage and household detergent samples, indicating that the fluorophores in the protein-like or tryptophan-like and detergent-like components are susceptible to photochemical degradation in rivers.
4. Microbial degradation can degrade the protein-like or tryptophan-like components (24–67% of peak T and 62–76% of peak T_{UV}) and detergent components (84–90% of peak W_{UV}) in river and sewerage drainage samples, suggesting that the fluorophores at shorter wavelength regions in protein-like or tryptophan-like and detergent-like components are more sensitive to microbial degradation in rivers.
5. Photochemical and microbial processes may decompose most of the fluorophores in various fluorescent components in riverine samples, indicating that these two processes together can be efficiently applied for the removal of sewerage-impacted organic contaminants in rivers.

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References

Aiken GR, McKnight D, Weshaw RL, MacCarthy P (1985) An introduction to humic substances in soil sediment and water. In: Aiken GR, McKnight D, Wershaw RL, MacCarthy P (eds) Humic substances in soil sediment and water. Wiley, New York

Baker A (2001) Fluorescence excitation-emission matrix characterization of some sewage impacted rivers. Environ Sci Technol 35:948–953

Baker A (2002a) Fluorescence excitation-emission matrix characterization of some farm wastes: Implications for water quality monitoring. Water Res 36:189–194

Baker A (2002b) Fluorescence excitation–emission matrix characterization of river waters impacted by tissue mill effluents. Environ Sci Technol 36:1377–1382

Baker A (2005) Thermal fluorescence quenching properties of dissolved organic matter. Water Res 39:4405–4412

Baker A, Curry M (2004) Fluorescence of leachates from three contrasting landfills. Water Res 38:2605–2613

Baker A, Inverarity R (2004) Protein-like fluorescence intensity as a possible tool for determining river water quality. Hydrol Process 18:2927–2945

Borisover M, Laor Y, Parparov A, Bukhanovsky N, Lado M (2009) Spatial and seasonal patterns of fluorescent organic matter in Lake Kinneret (Sea of Galilee) and its catchment basin. Water Res 43:3104–3116

Bro R (1997) PARAFAC Tutorial and applications. Chemom Intell Lab Syst 38:149–171

Bro R (1999) Exploratory study of sugar production using fluorescence spectroscopy and multi-way analysis. Chemom Intell Lab Syst 46:133–147

Chau KW (2006) Persistent organic pollution characterization of sediments in Pearl River estuary. Chemosphere 64:1545–1549

Coble PG (1996) Characterization of marine and terrestrial DOM in sea water using excitation-emission matrix spectroscopy. Mar Chem 52:325–336

Coble PG (2007) Marine optical biogeochemistry: the chemistry of ocean color. Chem Rev 107:402–418

Coble PG, Green SA, Blough NV, Gagosian RB (1990) Characterization of dissolved organic matter in the Black Sea by fluorescence spectroscopy. Nature 348:432–435

Cory RM, McKnight DM (2005) Fluorescence spectroscopy reveals ubiquitous presence of oxidized and reduced quinines in dissolved organic matter. Environ Sci Technol 39:8142–8149

Fu PQ, Wu FC, Liu CQ, Wang F, Li W, Yue L, Guo QJ (2007) Fluorescence characterization of dissolved organic matter in an urban river and its complexation with Hg(II). Appl Geochem 22:1668–1679

Hall GJ, Clow KE, Kenny JE (2005) Estuarial fingerprinting thorough multidimensional fluorescence and multivariate analysis. Environ Sci Technol 39:7560–7567

Hayakawa K, Okumura R, Yamamoto H, Fujiwara M, Yamaji N, Takada H, Kanematsu M, Shimizu Y (2007) Distribution and fluxes of fluorescent whitening agents discharged from domestic wastewater into small rivers with seasonal changes of flow rates. Limnology 8:251–259

Hayashi Y, Managaki S, Takada H (2002) Fluorescent whitening agents in Tokyo Bay and adjacent rivers their application as anthropogenic molecular markers in coastal environments. Environ Sci Technol 36:3556–3563

Hudson N, Baker A, Renolds D (2007) Fluorescence analysis of dissolved organic matter in natural waste and polluted waters—a review. River Res Appl 23:631–649

Komaki M, Yabe A (1982) Fluorometric analysis of fluorescent brightening agents in natural waters. Chem Soc J 5:859–867 (in Japanese)

Kramer JB, Canonica S, Hoigne J, Kaschig J (1996) Degradation of fluorescent whitening agents in sunlit natural waters. Environ Sci Technol 30:2227–2234

Luo X-J, Chen S-J, Mai B-X, Sheng G-Y, Fu J-M, Zeng EY (2008) Distribution source apportionment and transport of PAHs in sediments from the Pearl River delta and the northern south China sea. Arch Environ Contam Toxicol 55:11–20

Malcolm RL (1985) Geochemistry of stream fulvic and humic substances. In: Aike GR, McKnight DM, Wershaw RL, MacCarthy P (eds) Humic substances in soil, sediment, and water: geochemistry, isolation and characterization. Wiley, New York, pp 181–209

Managaki S, Takada H (2005) Fluorescent whitening agents in Tokyo Bay sediments, molecular evidence of lateral transport of land-derived particulate matter. Mar Chem 95:113–127

Moran MA Jr, Sheldon WM, Zepp RG (2000) Carbon loss and optical property changes during long-term photochemical and biological degradation of estuarine dissolved organic matter. Limnol Oceanogr 45:1254–1264

Mostofa KMG, Honda Y, Sakugawa H (2005a) Dynamics and optical nature of fluorescent dissolved organic matter in river waters in Hiroshima prefecture, Japan. Geochem J 39:257–271

Mostofa KMG, Yoshioka T, Konohira E, Tanoue E, Hayakawa K, Takahashi M (2005b) Three-dimensional fluorescence as a tool for investigating the dynamics of dissolved organic matter in the Lake Biwa watershed. Limnology 6:101–115

Mostofa KMG, Yoshioka T, Konohira E, Tanoue E (2007a) Dynamics and characteristics of fluorescent dissolved organic matter in the groundwater, river and lake water. Water Air Soil Pollut 184:157–176

Mostofa KMG, Yoshioka T, Konohira E, Tanoue E (2007b) Photodegradation of fluorescent dissolved organic matters in river waters. Geochem J 41:323–331

Mostofa KMG, Wu FC, Yoshioka T, Sakugawa H, Tanoue E (2009) Dissolved organic matter in the aquatic environments In: Wu FC, Xing B (eds) Natural organic matter and its significance in the environment. Science Press, Beijing, pp 3–66

Parlanti E, Worz K, Geoffroy L, Lamotte M (2000) Dissolved organic matter fluorescence spectroscopy as a tool to estimate biological activity in a coastal zone submitted to anthropogenic inputs. Org Geochem 31:1765–1781

Poiger T, Field FJA, Field TM, Giger W (1996) Occurrence of fluorescent whitening agents in sewage and river water determined by solid-phase extraction and high-performance liquid chromatography. Environ Sci Technol 30:2220–2226

Poiger T, Kari FG, Giger W (1999) Fate of fluorescent whitening agents in the River Glatt. Environ Sci Technol 33:533–539

Rosenstock B, Simon M (2001) Sources and sinks of dissolved free amino acids and protein in a large and deep mesotrophic lake. Limnol Oceanogr 50:90–101

Schwede-Thomas SB, Chin Y, Dria KJ, Hatcher P, Kaiser E, Sulzberger B (2005) Characterizing the properties of dissolved organic matter isolated by XAD and C-18 solid phase extraction and ultrafiltration. Aquat Sci 67:61–71

Senesi N (1990) Molecular and quantitative aspects of the chemistry of fulvic acid and its interactions with metal ions and organic chemicals Part II The fluorescence spectroscopy approach. Anal Chim Acta 232:77–106

Stedmon CA, Markager S (2005) Tracing the production and degradation of autochthonous fractions of dissolved organic matter by fluorescence analysis. Limnol Oceanogr 50:1415–1426

Stedmon CA, Markager S, Bro R (2003) Tracing dissolved organic matter in aquatic environments using a new approach to fluorescence spectroscopy. Mar Chem 82:239–254

Stedmon CA, Thomas DN, Granskog M, Kaartokallio H, Papaditriou S, Kuosa H (2007) Characteristics of dissolved organic matter in Baltic coastal sea ice: allochthonous or autochthonous origins? Environ Sci Technol 41:7273–7279

Stoll J-MA, Giger W (1998) Mass balance for detergent-derived fluorescent whitening agents in surface waters of Switzerland. Water Res 32:2041–4050

Stoll J-MA, Ulrich MM, Giger W (1998) Dynamic behavior of fluorescent whitening agents in Greifensee: field measurements combined with mathematical modeling of sedimentation and photolysis. Environ Sci Technol 32:1875–1881

Sugiyama Y, Anegawa A, Inokuchi H, Kumagai T (2005) Distribution of dissolved organic carbon and dissolved fulvic acid in mesotrophic Lake Biwa, Japan. Limnology 6:161–168

Takada H, Ogura N, Ishiwatarl R (1992) Seasonal variations and modes of riverine input of organic pollutants to the costal zone: 1. Flux of detergent-derived pollutants to Tokyo bay. Environ Sci Technol 26:2517–2523

Takahashi M, Kawamura K (2007) Simple simple measurement of 4, 4′-bis(2-sulfostyryl)-biphenyl in river water by fluorescence analysis and its application as an indicator of domestic wastewater contamination. Water Air Soil Pollut 180:39–49

Tanoue E (2000) Proteins in the sea-synthesis. In: Handa N, Tanoue E, Hama T (eds) Dynamics and characterization of marine organic matter. TERRAPUB/Kluwer, Tokyo, pp 383–463

Volk CJ, Volk CB, Kaplan LA (1997) Chemical composition of biodegradable dissolved organic matter in streamwater. Limnol Oceanogr 42:39–44

Wu CH, Maurer C, Wang Y, Xue SZ, Davies DL (1999) Water pollution and human health in China. Environ Health Perspect 4:251–256

Wu FC, Mills RB, Evans RD, Dillon PJ (2005) Photodegradation-induced changes in dissolved organic matter in acidic waters. Can J Fish Aquat Sci 62:1019–1027

Yamashita Y, Jaffé R (2008) Characterizing the interactions between trace metals and dissolved organic matter using excitation–emission matrix and parallel factor analysis. Environ Sci Technol 42:7374–7379

Yamashita Y, Tanoue E (2003) Chemical characterization of protein-like fluorophores in DOM in relation to aromatic amino acids. Mar Chem 82:255–271