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Characterization of dissolved organic matter under contrasting hydrologic regimes in a subtropical watershed using PARAFAC model

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Abstract Dissolved organic matter (DOM) was characterized during five basin-scale investigations (either after storms or in droughts) in Jiulong River, China that is affected by the Asian Monsoon, tropical storms and anthropogenic activities. Dissolved organic carbon concentration, DOM absorption and fluorescence (excitation-emission matrix spectra, EEMs) were measured. Parallel factor analysis (PARAFAC) of EEMs identified three humic-like and two protein-like fluorescent components. DOM concentration was highest at two polluted stations in droughts while lowest in pristine headwaters (station N1). DOM concentration increased most evidently after storms in May, 2009, indicating effective flushing of DOM from land to the river close to the onset of flood season. The protein-like fraction in PARAFAC results decreased after storms in May and June, 2009, highlighting changes in DOM composition and thus its environmental role. Dam constructions likely increased the residence time of DOM in river, making the inflow of DOM during storms have more implications for the riverine (in comparison with estuarine) biogeochemical processes. The effect of storm in August, 2008 after intense DOM flushing during several preceding storms, was not evident. A severe dinoflagellate algal bloom occurred during the extreme drought in the lower watershed, which increased DOM concentration and the protein-like fraction at impacted stations. Different DOM compositions during and after algal bloom were discriminated using the two protein-like components. This study demonstrates the importance of hydrologic regimes and anthropogenic activities on freshwater DOM and its environmental role, which has implications for a number of other rivers that share similar characteristics.

Keywords DOM · Fluorescence · PARAFAC · Storm · Drought · Algal bloom

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Introduction

The fluvial discharge of dissolved organic matter (DOM) from land to ocean links terrestrial and marine ecosystems and biogeochemical processes (Jaffé et al. 2008; Hood et al. 2009). Abundant carbon, nitrogen and trace metals are transported in DOM, significant portions of which are bioavailable and can affect downstream aquatic heterotrophic production (Bushaw et al. 1996; Raymond and Bauer 2000; Wiegner et al. 2009). Additionally, chromophoric DOM (CDOM) is a determinant of aquatic optical property, affecting the attenuation of photosynthetically active radiation and harmful ultraviolet radiation with ecological significance (Hansell and Carlson 2002; Coble 2007). The degradation of DOM is also an important process releasing nutrients, low molecular weight organic compounds and trace gases such as CO_2 and CO (Bushaw et al. 1996; Moran and Zepp 1997; Stedmon et al. 2007; Stubbins et al. 2008). Chemical and biochemical oxygen demand (COD and BOD) are also correlated with the fluorescent DOM (FDOM) parameters in some rivers (e.g., Baker and Inverarity 2004; Holbrook et al. 2006).

The quantity and quality, including the composition and bioavailability, of freshwater DOM are dependent on its source, land cover, land use, hydrology as well as microbial and photochemical transformations (Jaffé et al. 2008; Huang and Chen 2009; Fellman et al. 2009a, b; Spencer et al. 2009). Freshwater DOM is derived from various allochthonous and autochthonous sources such as soils, plant detritus, anthropogenic activities and phytoplankton degradation, and is characterized by abundant humic-like materials in natural systems while intensified protein-like signals are found in polluted waters (Baker 2001; Holbrook et al. 2006; Hudson et al. 2007; Balcarczyk et al. 2009; Guo et al. 2010). Hydrology is another important determinant of DOM quantity and composition. In particular, storms are responsible for delivering a large portion of DOM to coastal waters (Wiegner et al. 2009; Fellman et al. 2009b) and it is important to characterize the influence of storms on DOM composition and reactivity (Vidon et al. 2008; Spencer et al. 2010). Finally, photodegradation can both remove aquatic DOM and change its biochemical composition (Spencer et al. 2009; Stubbins et al. 2010).

Due to the important roles of DOM in biogeochemical processes and its dynamic nature as a result of variable dependent factors, it is essential to characterize the spatial and temporal variability of DOM in watersheds and reveal the underlying controlling factors. While recent DOM studies focused disproportionately in temperate and northern high-latitude rivers (Spencer et al. 2010), Jiulong River in this study is a typical subtropical river with a substantial seasonal variability of precipitation (i.e., wet summer and dry winter), which is dominated by the Asian Monsoon system and affected by tropical storms. The freshwater discharge of Jiulong River is concentrated in the flood season (from April to September), a feature similar to a number of other largest rivers of the world such as the Changjiang River and Pearl River that are affected by the Asian Monsoon. Furthermore, many rivers in this region are affected by rapid economic development with increased sewage discharge, dam construction and land use change. However, there is still limited information about the dynamics of DOM in the rivers of this region, although freshwater discharge is an important source of DOM to the estuaries as evidenced by the decrease of DOM levels with salinity (Hong et al. 2005; Guo et al. 2007, 2011). As a part of a project to better understand the biogeochemical linkages in typical river-estuary-coastal ocean systems, this study examined the variability of DOM in the Jiulong River under the impacts of contrasting hydrologic regimes (after storms vs. during extreme droughts) and intense human activities (sewage discharge and dam constructions).

Materials and methods

Study area

The Jiulong River is a medium-sized subtropical river in southeastern China with a drainage area of 14,741 km^2 and consists of three major tributaries (North Stream, West Stream and South Stream, Fig. 1). The North Stream is the main tributary which is 274 km long and converges with the West Stream at the head of the Jiulong Estuary, while the South Stream is a small tributary entering into the middle estuary directly. The watershed land cover is 21% hills and plains and 79% middle and low mountains, comprising 67% forest, 17.5% arable land and 3% residential land, etc. (Chen et al. 2008). Affected by the Asian Monsoon, the mean annual temperature and precipitation are 19.9–21.1°C and 1400–1800 mm respectively. Approximately 75% of the precipitation occurs from April to September, partly due to the influence of tropical storms (typhoons). The combined mean annual runoff of North Stream and West Stream is 123×10^8 m^3, $\sim$74% of which is discharged from April to September. The watershed, with a mean population density >200 persons per km^2, is affected intensively by human activities, receiving a large amount of sewages from cities (e.g., Longyan and Zhangzhou) and animal feed areas (e.g., around

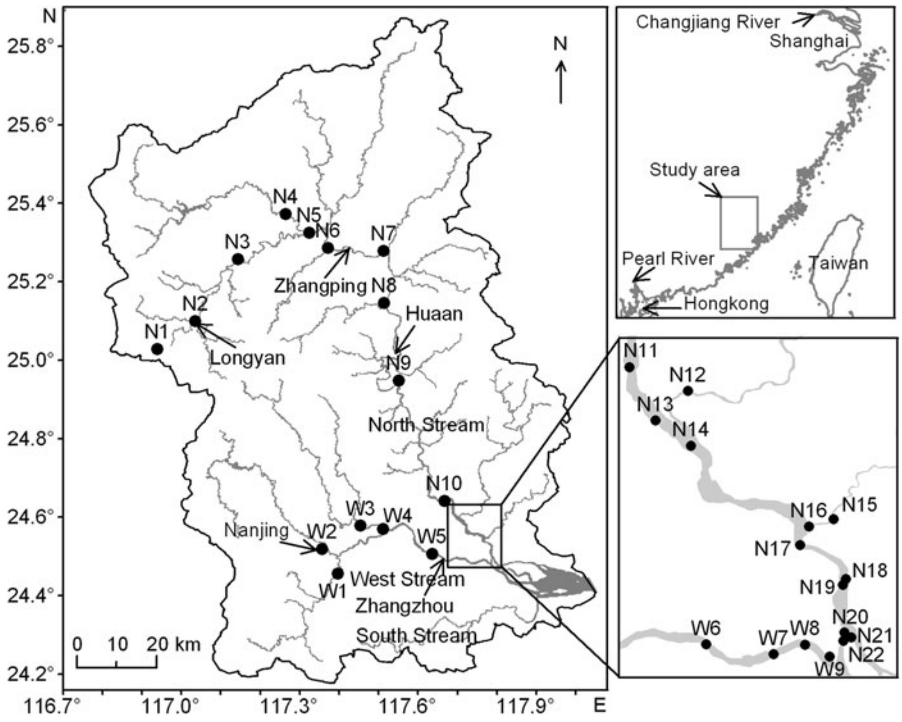

Fig. 1 Study area and sampling stations (stations N(13–18) and N21 were only sampled in the algal bloom monitoring). The location of three cities (Longyan, Zhangping and Zhangzhou) and two counties (Huaan and Nanjing) were indicated with arrows; dense animal cultivation are around Longyan and from N10 and W4 downstream; there are many dams between N2 and N9, N20 and N22, W6 and W7

Longyan City and from N10 and W4 downstream, Fig. 1). Furthermore, there are a number of dams in the watershed (such as those between N2 and N9, N20 and N22 as well as W6 and W7), affecting the discharge, evaporation and residence time of water.

Field sampling

140 surface water grab samples were collected during five sampling campaigns from North Stream and West Stream (Fig. 1). Three investigations were carried out in the flood season after storms (August 3rd–4th, 2008, May 21st and June 24th, 2009). There were heavy precipitations during both July 28th–31st, 2008 and June 20th–23rd, 2009, which were associated with typhoons "Fung Wong" and "Linfa" (Fujian Meteorological Bureau and Fujian Climate Center 2009, 2010). The mean precipitation was 45 mm (maximum: 156 mm) during May 17th–19th, 2009 (Fujian Meteorological Bureau unpublished data). The other two were carried out in the drought months (November 20th–21st, 2008 and February 3rd, 2009) and in most regions, no evident precipitation occurred from middle October, 2008 to early March, 2009 (Fujian Meteorological Bureau and Fujian Climate Center 2010). The drought and accumulation of pollution in the river led to water quality degradation and North Stream was additionally sampled at selected stations (N(13–18) and N21) from February 2nd to 26th, 2009, since a severe dinoflagellate (*Peridiniopsis* elpatiewski) algal bloom occurred between N14 and N21 ($\sim$15 km long) from January 29th to February 13th. The chlorophyll concentration and the algal abundance (up to several million cells l^{-1} at some stations) peaked intermittently during this period, turning the water color into a deep brown (N.W. Chen and B.Q., Huang, unpublished data). N13 was considered as a reference station (i.e., upstream non-bloom impacted site) while the other stations were impacted by the algal bloom. Additionally, 26 samples collected from the outlets of 15 sub-watersheds throughout the whole Jiulong River watershed in August 2009 were also included in parallel factor analysis (PARAFAC) and correlation analysis.

Samples were filtered through GF/F filters that had been precombusted (500°C for 5 h) and then acidified with HCl for dissolved organic carbon (DOC) measurement. Samples for absorption and fluorescence measurements were filtered through acid-rinsed 0.2 μm Millipore polycarbonate filters and stored in cold (4°C) and in the dark before analysis.

DOC and absorption measurements

DOC concentration was measured via high temperature catalytic oxidation after removal of inorganic carbon by oxygen purging, using a Multi N/C 3100 TOC-TN analyzer (Analytik Jena, Germany). The measurements were performed in triplicate and the analytical precisions were within 4% (mostly < 2%). A six-point calibration was carried out using solutions of potassium hydrogen phthalate as standards. The accuracy of the measurement was verified daily with Low Carbon Water and Deep Sea Water (from D. A. Hansell, University of Miami). The measured DOC concentration of Deep Sea Water (45.6 ± 1.9 μmol l^{-1}) was in good agreement with the recommended values (44–46 μmol l^{-1}).

Absorption spectra of DOM were scanned using a Techcomp 2300 UV–Vis spectrometer at the wavelengths of 200–800 nm (every 1 nm) with Milli-Q water as the blank (Guo et al. 2007). Absorbance measurements at each wavelength (A) were baseline corrected by subtracting the mean absorbance from 700 to 800 nm, and then converted to absorption coefficient (a) as $a_\lambda = 2.303\ A_\lambda/l$, where λ is the wavelength and the l is the path length (0.1 m). a_{280} is presented in this study, and can be converted to previously widely used a_{350} by multiplying a factor of 0.31, based on the tight correlation between them (r = 0.986, $p < 0.01$).

Fluorescence measurements and PARAFAC

Excitation-emission matrix (EEM) fluorescence spectra of DOM were measured using a Cary Eclipse fluorescence spectrophotometer (Varian, Australia), scanning emission spectra from 230 to 600 nm (every 2 nm) at excitation wavelengths of 200–450 nm (every 5 nm). The fluorescence spectra were corrected for instrument specific bias according to the manufacturer's correction files. High concentration samples were diluted to a point where A350 at 1 cm path length was within 0.02 to minimize inner-filter effects (Kowalczuk et al. 2009). The EEM of each sample was Raman calibrated (Lawaetz and Stedmon 2009) and subtracted from a Raman normalized Milli-Q water EEM which was scanned on the same day.

A total of 162 EEMs were subject to the multivariate modeling technique PARAFAC, using MATLAB 7.5 with "the N-way toolbox for MATLAB" (Andersson and Bro 2000; Stedmon and Bro 2008). The fluorescence data at excitation wavelengths <250 nm and emission wavelengths <300 nm were not used to avoid the interference of noise signals (Stedmon and Markager 2005). The number of components was determined with split-half validation (Stedmon and Bro 2008). Four EEMs (samples from N1 and N10 at August and N1 and W1 at November), were identified as outliers during PARAFAC modeling following the protocols of Stedmon and Bro (2008) and were therefore excluded from the PARAFAC model. PARAFAC analysis decomposed the EEMs into individual components and the fluorescence intensity of each component was represented by the maximum fluorescence F_{max} (R.U., i.e., Raman units) (Stedmon and Markager 2005; Kowalczuk et al. 2009). The protein-like fraction was calculated as the ratio of F_{max} sum of protein-like components to F_{max} sum of all components (Fellman et al. 2009a, b; Kowalczuk et al. 2009).

Results

DOC and a_{280}

DOC concentration varied from 0.4 to 13.1 mg l^{-1} and was mostly within the range of 1.0–4.0 mg l^{-1} throughout the sampling period (Fig. 2a, b). The highest value was found during the algal bloom (see following results). Samples with DOC < 1.0 mg l^{-1} were only found at N1 (mean: 0.6 mg l^{-1}), while DOC yielded relatively high values at stations N2 and N3, especially in the drought months (3.5 ± 0.6 mg l^{-1}). Most stations in North Stream had highest DOC in May. In West Stream, DOC concentration decreased in the order of May > June > November ≈ August, with the exception of four highest DOC concentrations >4.0 mg l^{-1} at stations within the village (W1) or Zhangzhou City (W6 and W7).

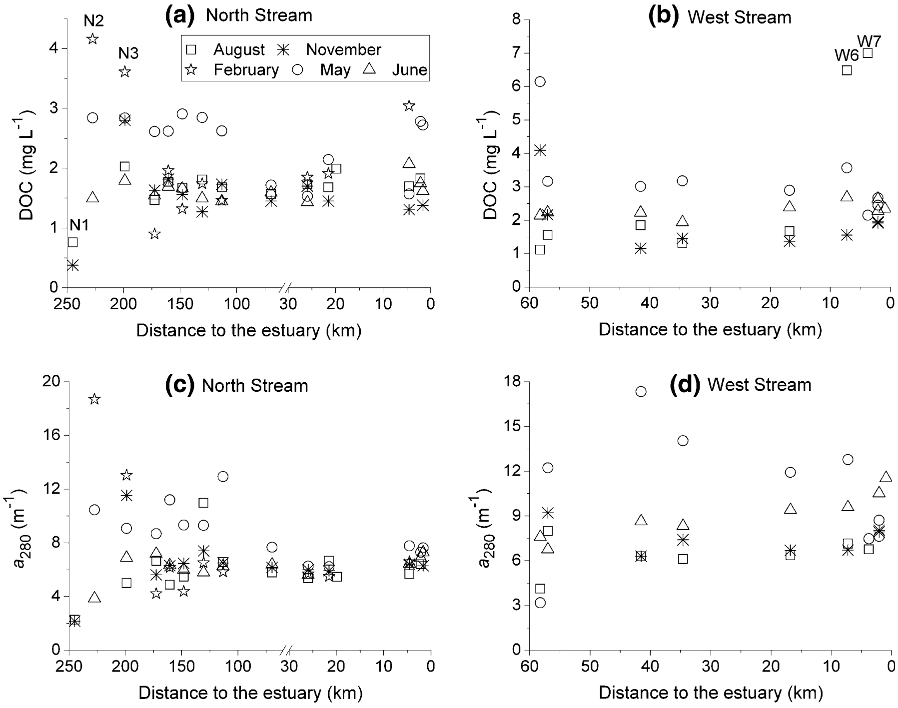

Fig. 2 Spatial and temporal distribution of DOC (mg l^{-1}) and a_{280} (m^{-1}), sampling stations were N(1–12), N(19–20), N22 in North Stream and W(1–9) in West Stream. Three sampling campaigns were after storm events (August, 2008, May and June, 2009) while the other two (November, 2008 and February, 2009) were in drought months

The absorption coefficient a_{280}, as an indicator of CDOM concentration, varied within 2.2–18.7 m^{-1} and was mostly within the range of 4.0–13.0 m^{-1}. a_{280} was correlated with DOC significantly (r = 0.78, $p < 0.01$) and had an overall similar variation pattern as DOC (Fig. 2c, d).

PARAFAC results

Five fluorescent components were identified using PARAFAC (Fig. 3) and could be grouped into two categories based on spectral characteristics and intercorrelations of F_{max} (Tables 1, 2): humic-like components (C1, C2 and C3) and protein-like components (C4 and C5). C1 and C3 both resembled a combination of traditionally defined peak A and peak C while C2 resembled a combination of peaks A and M (Coble et al. 1998; Coble 2007, Table 1). C1, C2 and C3 were tightly correlated with each other and were likely derived mainly from terrestrial humic-like substances. C4 was a tryptophan-like component which could originate from both autochthonous production and sewage (Hudson et al. 2007; Coble 2007). C5 was correlated with C4 most closely and was likely a protein-like component in this study. Additionally, all the components were correlated significantly with both DOC and a_{280}, especially the humic-like components (Table 2). These five components modeled the measured EEMs well (e.g., Online Resource 1).

F_{max} sum of humic-like components ranged from 0.24 to 1.22 R.U. (mean: 0.47 R.U.), while that of protein-like components varied within 0.09–0.96 R.U. (mean: 0.27 R.U.). Humic-like components were more abundant in May and June in both tributaries, although higher levels were found in the dry season at sites N2 and N3 (Fig. 4a, b). Protein-like components were generally most depleted in June in North Stream and in August in West Stream (Fig. 4c, d). Additionally, there was an overall increase of both humic-like and protein-like components downstream in West Stream, especially from station W4 downward. The protein-like fraction (C4 and C5) varied within 17.7–52.8% (i.e., 36.8 ± 7.0%) and was higher in the drought months than in the flood season (41.3 ± 3.3% vs. 31.6 ± 6.5%) in both tributaries, although that in August was higher at some stations in North Stream (Fig. 5a, b).

Results of algal bloom event

The monitoring results of the dinoflagellate bloom occurred between N14 and N21 intermittently from

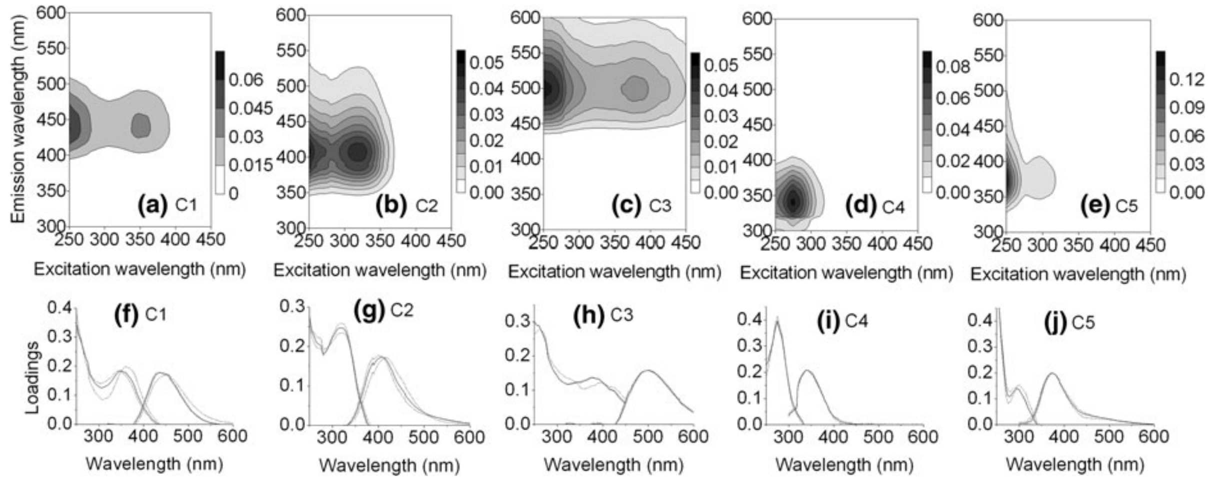

Fig. 3 EEM contours (graphs (**a–e**) and the excitation and emission loadings (graphs (**f–j**)) of the five fluorescent components identified by PARAFAC. The dashed line shows the similarity of two independent, five-component PARAFAC models on two random halves of the whole data, while the solid line represents the results of PARAFAC model on the complete data in graphs (**f–j**)

Table 1 Excitation/emission maxima (nm) of the five fluorescent components identified by PARAFAC model in this study, with secondary excitation maxima in parentheses and compared with previous studies

Components in this study	EEM peaks (Coble et al. 1998)	Components in previous studies	Description
C1: ≤250 (350)/436	A and C	C4 (Stedmon and Markager 2005); C1 (Balcarczyk et al. 2009)	Humic-like
C2: ≤250 (320)/406	A and M	C4 (Stedmon et al. 2003); C3 (Stedmon and Markager 2005); C3 (Kowalczuk et al. 2009)	Humic-like
C3: ≤250 (375)/500	A and C	C3 (Stedmon et al. 2003); C2 (Stedmon and Markager 2005); C4 (Kowalczuk et al. 2009)	Humic-like
C4: 275/340	T	C7 (Stedmon and Markager 2005); C8 (Fellman et al. 2009a)	Tryptophan-like
C5: ≤250 (295)/374	N	C5 (Stedmon et al. 2003); C6 (Kowalczuk et al. 2009)	Unknown or protein-like

Table 2 Correlations of fluorescent components, DOC and a_{280}

	C1	C2	C3	C4	C5	a_{280}
C2	0.93					
C3	0.96	0.88				
C4	0.62	0.65	0.44			
C5	0.50	0.46	0.33	0.77		
a_{280}	0.87	0.86	0.86	0.57	0.41	
DOC	0.72	0.77	0.65	0.64	0.51	0.78

All the correlations are significant at the 0.01 level, and four highest DOC values were excluded

late January to early February were shown in Table 3. DOM levels at N13 (as a reference station) varied little, although a_{280} and humic-like component levels were slightly higher on February 2nd and 8th, 2009 than on other dates. DOM characteristics at N14 were similar to N13 on February 2nd, 2009, suggesting the freshwater from upstream played a more important role than the algal bloom at this site. The protein-like fraction at sites N(13–14) (40.1 ± 2.0%) was also similar with that of basin-scale investigations of North Stream in November (40.1 ± 2.8%) and February (40.4 ± 2.2%). The majority of DOC, a_{280} and

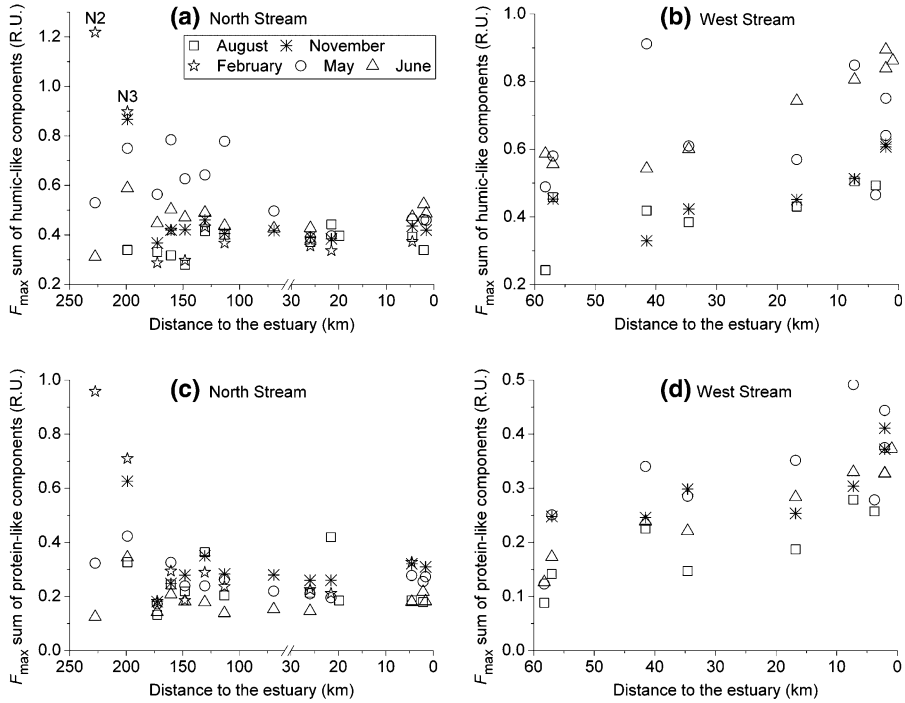

Fig. 4 F_{max} sums of humic-like components (C1, C2 and C3) and protein-like components (C4 and C5, R.U.)

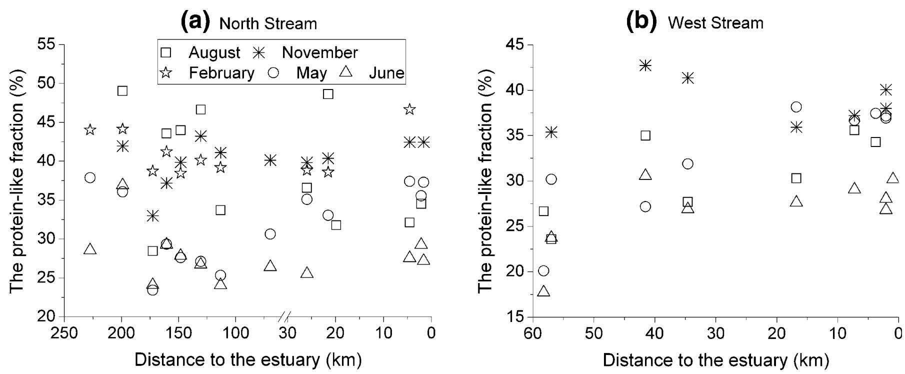

Fig. 5 The variability of the protein-like fraction (%), calculated as the ratio of F_{max} sum of protein-like components (C4 and C5) to F_{max} sum of all the five components

the protein-like fraction (43.7 ± 3.6%) were higher at other stations. In particular, DOM levels and the protein-like fraction were highest on February 2nd and 8th, 2009 at N16 (Online Resource 1) and on February 3rd, 2009 at N19, indicating the production of DOM from the algal bloom. Higher values were also found at N(16–18) sometimes after February 17th, 2009, probably due to other sources such as sewage discharges (see following discussion). The F_{max} ratio between C4 and C5 was also calculated for a comparison of DOM composition during and after the algal bloom (see following discussion, Table 3). The mean value during the bloom (0.76 ± 0.22, from February 2nd to 10th, 2009) was higher than after the bloom (0.56 ± 0.11, from February 17th to 26th, 2009).

Discussion

Spatial variation of DOM and anthropogenic impacts

In North Stream, large differences in DOC concentration and a_{280} were observed between N1 and highly polluted stations N(2–3) (Fig. 2a). N1 was a limpid and shallow station at the head of North Stream with little anthropogenic pollution, while N2 was located

Table 3 Results of algal bloom monitoring in February, 2009, mean values with standard error in parenthesis were presented for similar results at each station

Station	Sampling dates	DOC (mg l^{-1})	a_{280} (m^{-1})	F_{max} sum of protein-like components (R.U.)	F_{max} sum of humic-like components (R.U.)	The protein-like fraction (%)	F_{max} ratio of C4 and C5
N13	Feb 2nd and 8th	1.5 (0.0)	5.1 (0.0)	0.21 (0.00)	0.33 (0.01)	38.0 (0.00)	0.66 (0.01)
	Feb 17th, 20th, 23rd and 26th	–	4.8 (0.1)	0.20 (0.01)	0.30 (0.01)	41.1 (2.0)	0.46 (0.06)
N14	Feb 2nd	1.8	5.2	0.22	0.32	40.4	0.70
N15	Feb 2nd	3.1	11.3	0.64	0.63	50.4	0.44
N16	Feb 2nd	3.3	11.1	0.66	0.59	52.8	0.63
	Feb 7th	2.3	5.9	0.26	0.35	42.8	0.86
	Feb 8th	13.1	9.1	0.50	0.56	46.9	0.42
	Feb 17th and 23rd	–	5.9 (0.5)	0.28 (0.01)	0.35 (0.04)	44.7 (2.1)	0.63 (0.03)
	Feb 20th and 26th	–	8.2 (0.2)	0.43 (0.02)	0.50 (0.01)	45.9 (1.5)	0.44 (0.03)
N17	Feb 10th	1.8	5.6	0.23	0.33	40.9	0.83
	Feb 17th	–	5.8	0.25	0.37	40.6	0.59
	Feb 20th	–	5.8	0.29	0.37	44.0	0.73
	Feb. 23rd and 26th	–	5.4 (0.1)	0.27 (0.00)	0.32 (0.00)	45.9 (0.2)	0.62 (0.03)
N18	Feb 2nd, 7th, 8th and 10th	1.5 (0.5)	5.6 (0.1)	0.25 (0.01)	0.36 (0.01)	40.2 (1.1)	0.75 (0.07)
	Feb 17th, 20th and 23rd	–	6.0 (0.3)	0.29 (0.02)	0.37 (0.00)	41.2 (1.6)	0.65 (0.11)
	Feb 26th	–	5.2	0.23	0.33	46.6	0.51
N19	Feb 3rd	3.0	6.6	0.33	0.37	46.7	1.48
	Feb 8th and 10th	1.4 (0.4)	5.5 (0.1)	0.24 (0.00)	0.36 (0.00)	39.7 (0.5)	0.73 (0.03)
N21	Feb 2nd	1.9	5.4	0.28	0.33	45.2	0.86

within Longyan City (with ~235,000 people in 24.4 km^2) and N3 was a station at Yanshi Bridge receiving heavy pollution from animal cultivation, domestic and industrial sewage, which contained abundant DOM (especially protein-like substances, Baker 2001; Hudson et al. 2007). DOM concentrations at N(2–3) (including CDOM and FDOM) were notably high in the drought months, indicating the accumulation of sewage pollution due to reduced river discharge, which might cause the potential of water quality degradation (such as reduced oxygen content due to organic matter degradation) with ecological implications. This was eased in the flood season, since the increased river discharge could transport DOM away from the polluted stations effectively.

West Stream is a tributary receiving moderate to high anthropogenic impacts. A notable feature is the overall increase of both humic-like and protein-like components downstream, especially from station W4 downward (Fig. 4b, d). However, there were no similar increases of DOC and a_{280} (Fig. 2b, d). This suggested a downstream increase of the fluorescence quantum yield. Huang and Chen (2009) find that the fluorescence quantum yield was highest in industrial DOM endmembers, followed by Golf course and residential endmembers, and lowest in forest and wetland endmembers. Hence, the phenomena in this study was probably because stations from W5 downstream were close to Zhangzhou City with a population of ~0.6 million and industrial production of over 3 billion Yuan, and the anthropogenic inputs accumulated along this stretch of river. This indicated the influence of anthropogenic inputs on the freshwater DOM composition.

The effects of storm events on DOM concentration and composition

Abundant DOM can be flushed from land to the river during storm events, due to the large dynamic energy of stormflow and the shift of hydrologic flowpaths to the river from lower, mineral soil horizons during baseflow conditions to litter and upper soil horizons during storms (Vidon et al. 2008; Wiegner et al. 2009; Fellman et al. 2009b; Spencer et al. 2010). The increases in DOC and a_{280} were most notable in May in both tributaries, followed by June in West Stream (Fig. 2). This, in combination with the sediment and nutrient flushing, was likely to affect the aquatic optical properties and fuel the aquatic production. However, the precipitation during the storm event was not heaviest in May among the three investigations after storms. The strong DOM flushing in May was likely because it was closest to the onset of the flood season and after a long period of drought (middle October, 2008–early March, 2009), and the DOM flushing would decrease with subsequent storm events. Spencer et al. (2010) find a large decrease in riverine DOM levels during post flush periods in a tropical rainforest river. In the present study, DOM flushing was not notable in August and riverine DOM levels did not increase at most stations, likely associated with the intense flushing during the preceding several heavy precipitation events between the onset of the flood season and August. Storm events occurred on June 13th–14th and July 7th–8th, 2008, in addition to other heavy precipitation events on June 16th–17th, June 25th–28th and July 18th–20th, 2008 (Fujian Meteorological Bureau and Fujian Climate Center 2009).

At the end of West Stream from station W7 downstream, the impacts of storms on DOC and a_{280} were also not significant in May and were only evident on a_{280} in June. This was probably due to the dam between W6 and W7 which separated the waterbodies, considering the small distance between them ($\sim$3.5 km). Similarly, the impacts of storms on DOM concentration were more evident in the upper North Stream in May. This was likely due to several dams between N2 and N9 as well as higher hill-slopes in the upper watershed which facilitated the storm flushing (i.e., more notable change in the hydrologic flowpath to the river and faster response time of riverine constituents to precipitation). The rainfall in May, after the droughts, was largely retained in many reservoirs. The dams could block the river flowpath, slow down the river flow and increase the water residence time in the river watershed. When one dam occupied the entire river flowpath, the water was largely retained behind the dam. Hence, in the medium-sized Jiulong watershed with increased water residence time due to dam constructions, the biogeochemical impacts of storm-enhanced DOM inflow would be intensified in the river watershed while weakened for the estuary. Such an effect would be strengthened by the strong solar radiation after storms in summer, which could accelerate the photochemical cycles of freshwater DOM. The influences of DOM and DOM degradation on freshwater production and carbon cycle would be enhanced (Bushaw et al. 1996; Moran and Zepp 1997; Stedmon et al. 2007; Stubbins et al. 2008). Further studies to quantify those impacts are needed. Therefore, the Jiulong River is different from those coastal rivers without impacts of dams where the exports of DOM during storms have more impacts on the coastal ecosystems (e.g., Wiegner et al. 2009).

Storms also impacted DOM composition. Terrestrial humic-like substances were effectively flushed to the river in May and June, 2009 (Figs. 4a, b, 6). The protein-like fluorescent substances in the river could either be diluted by precipitation or increase due to the enhanced inflow from anthropogenic sources (Figs. 4c, d, 6). Overall, the protein-like fraction was lowered after the storms at most stations in May and June (Figs. 5, 6). This implied a decrease in the percent of biodegradable DOM (and hence its environmental role), since the latter is positively correlated with the protein-like fraction (Balcarczyk et al. 2009; Fellman et al. 2009a, b; Hood et al. 2009), although the regional relationship in Jiulong river should be established in future. These results were similar to those in the tropical, temperate and northern high-latitude rivers where the DOM is more aromatic (e.g., Vidon et al. 2008; Spencer et al. 2010) and less labile (e.g., Wiegner et al. 2009) during the storm, although the contrast is also found in some wetland streams (Fellman et al. 2009b).

The effects of algal bloom event on DOM

The increased nutrient levels due to low freshwater discharge in drought led to water quality degradation, which, together with other environmental conditions favored the algal growth (such as abnormal warm temperature), triggered the algal bloom from January 29th to February 13th, 2009 in this study. This would affect the dynamics of DOM, since the latter

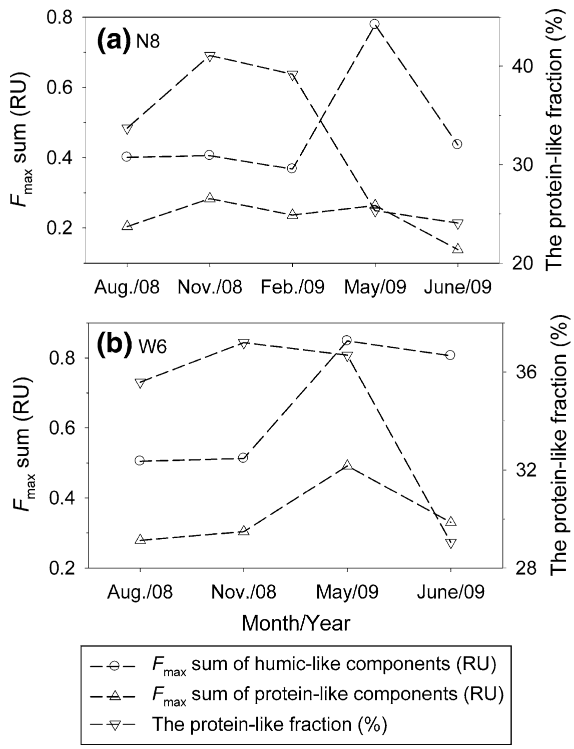

Fig. 6 Temporal variation of F_{max} sums and the protein-like fraction at two selected stations. **a** At N8, F_{max} sum of humic-like components increased after storms in May and June, 2009, while the protein-like component was diluted by precipitation in Augutst, 2008 and June, 2009 and the protein-like fraction decreased after storms. **b** At W6, both F_{max} sums of humic-like and protein-like components increased after storms in May and June, 2009 and the protein-like fraction decreased notably in June, 2009

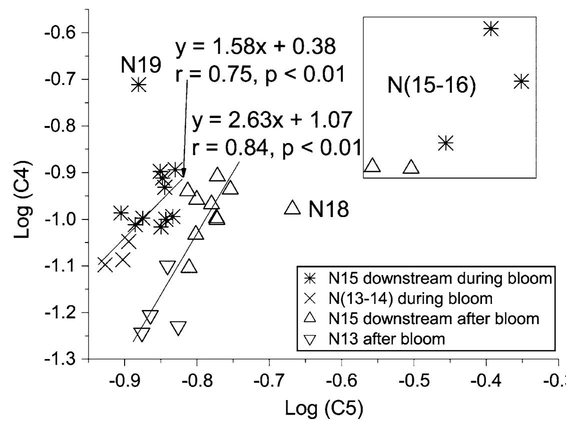

Fig. 7 Logarithmic relationship between F_{max} of C4 and C5 for the algal bloom monitoring, note that most samples could be fitted into two lines (during the bloom and after the bloom, with higher log (C4) at any given log (C5) during the bloom)

(including CDOM and FDOM) can be produced during both algal growth and degradation (Coble 2007; Zhang et al. 2009; Romera-Castillo et al. 2010). On February 2nd or 3rd, 2009, significantly higher DOM abundance was observed at N(15–16), N19 and N21, indicating the production of DOM from the algal bloom, considering that the sewage discharge was strictly prohibited after the occurrence of algal bloom. Additionally, the protein-like fraction increased to >45% concurrent at those stations, indicating a more rapid production of protein-like substances and implying an increase in the bioavailability of DOM (Balcarczyk et al. 2009; Fellman et al. 2009a, b).

Higher CDOM and FDOM concentration and the protein-like fraction were also found at N(16–18) sometimes after February 17th, 2009. This should be attributed to other DOM inputs such as increased sewage discharge, considering the low algal abundance after February 14th (B.Q. Huang unpublished data). A differentiation between DOM characteristics during and after the algal bloom was achieved by examining the logarithmic relationship between the two protein-like components (C4 and C5, Fig. 7). Most samples could be fitted into two lines and thus grouped into two categories: during and after the bloom (i.e., before and after February 13th, 2009). Log (C4) at any given log (C5) was higher during the bloom, suggesting a higher production rate of C4 from the algal bloom. Therefore, the F_{max} ratio between C4 and C5 was expected to be higher during the bloom than after the bloom (mean: 0.76 ± 0.22 vs. 0.56 ± 0.11). Although the protein-like fraction did not increase at sites N(13–14) during bloom, the logarithmic relationship between C4 and C5 at those two sites also fitted well into the two lines, suggesting different DOM characteristics (likely associated with different sources). Some exceptions with much higher log (C4) and/or log (C5) were found at site N19 on February 3rd and sometimes at sites N(15–16) and N18 (Fig. 7), when the source intensity was greatest or other processes such as microbial reworking might also play important roles under certain circumstances.

Conclusions

Anthropogenic inputs of DOM were evident from the much higher concentrations at study sites N2 and N3 in drought months, in comparison with the lowest levels at the pristine site at the head of North Stream (N1). Both storm events (especially those after droughts) and algal growth exerted notable influences on the concentration and composition (hence the reactivity) of DOM in the watershed. Dams increased the residence time of DOM in the watershed and hence the biogeochemical effects of DOM flushing during storm events would be enhanced in the river while weakened in the estuary (in comparison with other watersheds without dams). Hence, the quantity and composition of DOM in the watershed are variable due to human activities, storm events, drought and algal growth. These results have implications for understanding biogeochemical processes in the watershed and highlight the need for effective watershed managements (especially in the dry season when less freshwater discharge leads to the accumulation of pollutants and concurrent water quality degradation). In particular, this study has implications for a number of other rivers that share similar characteristics, including some globally significant ones such as Changjiang River.

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References

Andersson CA, Bro R (2000) The N-way toolbox for MATLAB. Chemom Intell Lab Syst 52(1):1–4

Baker A (2001) Fluorescence excitation-emission matrix characterization of some sewage-impacted rivers. Environ Sci Technol 35(5):948–953

Baker A, Inverarity R (2004) Protein-like fluorescence intensity as a possible tool for determining river water quality. Hydrol Process 18(15):2927–2945

Balcarczyk K, Jones J, Jaffé R et al (2009) Stream dissolved organic matter bioavailability and composition in watersheds underlain with discontinuous permafrost. Biogeochemistry 94(3):255–270

Bushaw KL, Zepp RG, Tarr MA et al (1996) Photochemical release of biologically available nitrogen from aquatic dissolved organic matter. Nature 381(6581):404–407

Chen NW, Hong HS, Zhang LP et al (2008) Nitrogen sources and exports in an agricultural watershed in Southeast China. Biogeochemistry 87(2):169–179

Coble PG (2007) Marine optical biogeochemistry: the chemistry of ocean color. Chem Rev 107(2):402–418

Coble PG, Del Castillo CE, Avril B (1998) Distribution and optical properties of CDOM in the Arabian Sea during the 1995 Southwest Monsoon. Deep Sea Res II 45(10–11): 2195–2223

Fellman JB, Hood E, D'Amore DV et al (2009a) Seasonal changes in the chemical quality and biodegradability of dissolved organic matter exported from soils to streams in coastal temperate rainforest watersheds. Biogeochemistry 95(2):277–293

Fellman JB, Hood E, Edwards RT et al (2009b) Changes in the concentration, biodegradability, and fluorescent properties of dissolved organic matter during stormflows in coastal temperate watersheds. J Geophys Res 114:G01021. doi: 10.1029/2008JG000790

Fujian Meteorological Bureau and Fujian Climate Center (2009) Fujian climate bulletin 2008. http://61.4.185.113/fujian/zxfw/qhgb/03/283126.shtml. Accessed 11 May 2010

Fujian Meteorological Bureau and Fujian Climate Center (2010) Fujian climate bulletin 2009. http://61.4.185.113/fujian/zxfw/qhgb/03/289408_2.shtml. Accessed 11 May 2010

Guo WD, Stedmon CA, Han YC et al (2007) The conservative and non-conservative behavior of chromophoric dissolved organic matter in Chinese estuarine waters. Mar Chem 107(3):357–366

Guo WD, Xu J, Wang JP et al (2010) Characterization of dissolved organic matter in urban sewage using excitation emission matrix fluorescence spectroscopy and parallel factor analysis. J Environ Sci China 22(11):1728–1734

Guo WD, Yang LY, Hong HS et al (2011) Assessing the dynamics of chromophoric dissolved organic matter in a subtropical estuary using parallel factor analysis. Mar Chem 124(1–4):125–133

Hansell D, Carlson C (eds) (2002) Biogeochemistry of marine dissolved organic matter. Academic, New York

Holbrook RD, Yen JH, Grizzard TJ (2006) Characterizing natural organic material from the Occoquan Watershed (Northern Virginia, US) using fluorescence spectroscopy and PARAFAC. Sci Total Environ 361(1–3):249–266

Hong HS, Wu JY, Shang SL et al (2005) Absorption and fluorescence of chromophoric dissolved organic matter in the Pearl River Estuary, South China. Mar Chem 97(1–2):78–89

Hood E, Fellman J, Spencer RGM et al (2009) Glaciers as a source of ancient and labile organic matter to the marine environment. Nature 462(7276):1044–1047

Huang W, Chen RF (2009) Sources and transformations of chromophoric dissolved organic matter in the Neponset River Watershed. J Geophys Res 114:G00F05. doi:10.1029/2009JG000976

Hudson N, Baker A, Reynolds D (2007) Fluorescence analysis of dissolved organic matter in natural, waste and polluted waters—a review. River Res Appl 23(6):631–649

Jaffé R, McKnight D, Maie N et al (2008) Spatial and temporal variations in DOM composition in ecosystems: the importance of long-term monitoring of optical properties. J Geophys Res 113:G04032. doi:10.1029/2008JG000683

Kowalczuk P, Durako MJ, Young H et al (2009) Characterization of dissolved organic matter fluorescence in the South Atlantic Bight with use of PARAFAC model: interannual variability. Mar Chem 113(3–4):182–196

Lawaetz AJ, Stedmon CA (2009) Fluorescence intensity calibration using the Raman scatter peak of water. Appl Spectrosc 63(8):936–940

Moran MA, Zepp RG (1997) Role of photoreactions in the formation of biologically labile compounds from dissolved organic matter. Limnol Oceanogr 42(6):1307–1316

Raymond PA, Bauer JE (2000) Bacterial consumption of DOC during transport through a temperate estuary. Aquat Microb Ecol 22(1):1–12

Romera-Castillo C, Sarmento H, Álvarez-Salgado XA et al (2010) Production of chromophoric dissolved organic matter by marine phytoplankton. Limnol Oceanogr 55(1):446–454

Spencer RGM, Stubbins A, Hernes PJ et al (2009) Photochemical degradation of dissolved organic matter and dissolved lignin phenols from the Congo River. J Geophys Res 114:G03010. doi:10.1029/2009JG000968

Spencer RGM, Hernes PJ, Ruf R et al (2010) Temporal controls on dissolved organic matter and lignin biogeochemistry in a pristine tropical river, Democratic Republic of Congo. J Geophys Res 115:G03013. doi:10.1029/2009JG001180

Stedmon CA, Bro R (2008) Characterizing dissolved organic matter fluorescence with parallel factor analysis: a tutorial. Limnol Oceanogr Meth 6:572–579

Stedmon CA, Markager S (2005) Resolving the variability in dissolved organic matter fluorescence in a temperate estuary and its catchment using PARAFAC analysis. Limnol Oceanogr 50(2):686–697

Stedmon CA, Markager S, Bro R (2003) Tracing dissolved organic matter in aquatic environments using a new approach to fluorescence spectroscopy. Mar Chem 82(3–4):239–254

Stedmon CA, Markager S, Tranvik L et al (2007) Photochemical production of ammonium and transformation of dissolved organic matter in the Baltic Sea. Mar Chem 104(3–4):227–240

Stubbins A, Hubbard V, Uher G et al (2008) Relating carbon monoxide photoproduction to dissolved organic matter functionality. Environ Sci Technol 42(9):3271–3276

Stubbins A, Spencer RGM, Chen HM et al (2010) Illuminated darkness: molecular signatures of Congo River dissolved organic matter and its photochemical alteration as revealed by ultrahigh precision mass spectrometry. Limnol Oceanogr 55(4):1467–1477

Vidon P, Wagner LE, Soyeux E (2008) Changes in the character of DOC in streams during storms in two Midwestern watersheds with contrasting land uses. Biogeochemistry 88(3):257–270

Wiegner TN, Tubal RL, MacKenzie RA (2009) Bioavailability and export of dissolved organic matter from a tropical river during base- and stormflow conditions. Limnol Oceanogr 54(4):1233–1242

Zhang YL, van Dijk MA, Liu ML et al (2009) The contribution of phytoplankton degradation to chromophoric dissolved organic matter (CDOM) in eutrophic shallow lakes: field and experimental evidence. Water Res 43(18):4685–4697