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Special Section:
Biogeochemistry of natural organic matter

Key Points:
- Main controls on DOM removal were flocculation and photo degradation (microbial degradation and photo degradation) at moderate (high) discharge
- CDOM can be used to trace dissolved lignin at high discharge, whereas at moderate discharge, CDOM and dissolved lignin were decoupled
- At high (moderate) discharge, 17.0% (6.1%) of DOC, 24.2% (32.3%) of dissolved lignin, and 14.5% (0.8%) of CDOM were degraded

Supporting Information:
- Supporting Information S1

Correspondence to:
Y. Wu,
wuying@sklec.ecnu.edu.cn

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Sources, Transport, and Transformation of Dissolved Organic Matter in a Large River System: Illustrated by the Changjiang River, China

Xiaona Wang[1], Ying Wu[1], Hongyan Bao[1,2], Shuchai Gan[1,3], and Jing Zhang[1]

[1]State Key Laboratory of Estuarine and Coastal Research, East China Normal University, Shanghai, China, [2]State Key Laboratory of Marine Environmental Science, Xiamen University, Xiamen, China, [3]Guangdong Provincial Key laboratory of Emergency Test for Dangerous Chemicals, Guangdong Institute of Analysis, Guangzhou, China

Abstract The sources, transport, and transformation of terrestrial dissolved organic matter (DOM) in large river systems are of great interest due to their importance in the regional and global carbon cycles. However, knowledge of these factors is limited, especially for different DOM compositions coupling with hydrodynamics at the basin scale. To investigate the dynamics of different DOM compositions in a large river system, we characterized the dissolved organic carbon (DOC), chromophoric DOM (CDOM), and dissolved lignin at both moderate (September–October 2009) and high (August 2012) discharges in the Changjiang River basin. We found that extensive soil erosion resulted in the increased DOC concentration in the middle to lower reaches in 2012. In 2009, the transformation of DOM was dominated by flocculation and photo degradation due to the low flow velocity and depressed particle suspension. In 2012, the degradation of CDOM and dissolved lignin was coupled and dominated by microbial degradation and photo degradation. In 2012, CDOM (absorbance and fluorescence) and dissolved lignin concentrations were positively correlated, demonstrating the potential of using CDOM to quantitatively estimate dissolved lignin. Mass balance estimations of the DOM fluxes further confirmed that 17.0% (6.1%) of DOC, 24.2% (32.3%) of dissolved lignin, and 14.5% (0.8%) of CDOM were degraded at high (moderate) discharge. This study reveals contrasting transformation processes of DOM compositions with different sources and reactivities along the Changjiang River under different hydrological conditions, and it provides new insights into the linkage between the chemical and optical properties of DOM in large river systems.

1. Introduction

Large fluvial systems transport substantial amounts of dissolved organic matter (DOM) to the ocean and play important roles in the regional and global carbon cycle (Hedges et al., 1997; Jaffé et al., 2012). Many studies have reported the spatial and temporal variations of DOM in large fluvial systems (Bao et al., 2015; Bianchi et al., 2004; Duan et al., 2007; Spencer et al., 2008), Riverine DOM concentrations and compositions are closely related to climate, temperature, topography, land use, soil type, vegetation cover, and hydrology (Mann et al., 2014; Spencer et al., 2008; Spencer, Aiken, et al., 2009; Wilson & Xenopoulos, 2009; Yamashita, Maie, et al., 2010; Yamashita et al., 2011). Large fluvial systems also act as active DOM dynamic reactors. The pulse-shunt concept describes the transport of DOM along the river continuum under different hydrologic events (Raymond et al., 2016). At low and moderate discharges, DOM inputs into a river can be significantly altered within the river system, whereas at high discharge, DOM is shunted through the river prior to significant transformation (Raymond et al., 2016; Ward et al., 2017). Although the optical characteristics and molecular composition of DOM might represent sensitive indicators of biogeochemical processes, including hydrological controls (Lu et al., 2016; Spencer et al., 2008, 2010), the interactions of hydrology and DOM compositions with different characteristics and reactivities are not clear. Few studies have compared the response of DOM compositions to different hydrological conditions along large river continuums (Bao et al., 2019; Shen et al., 2012; Spencer et al., 2008, 2010).

Microbial degradation and photo degradation are important processes for the removal of terrestrial DOM, including chromophoric DOM (CDOM) and dissolved lignin phenols (Benner & Kaiser, 2011; Lu et al., 2016; Opsahl & Benner, 1998; Spencer, Stubbins, et al., 2009). However, most of the studies that evaluate the fate of terrestrial DOM perform incubation experiments, which simplify the natural fluvial system. In natural fluvial system, other factors can impact the riverine DOM composition, such as the flow velocity, freshwater flocculation, allochthonous, and autochthonous inputs. The interactions of hydrology with DOM are more complicated due to the coupling of multiple processes within the fluvial system (e.g., microbial degradation, photo degradation, and flocculation) with widely varying contributors (e.g., tributaries and groundwater systems); therefore, such interactions merit detailed surveys and studies.

CDOM is the light-absorbing fraction of DOM (Stedmon & Markager, 2003). The optics (absorbance and fluorescence) of CDOM provide useful information about the aromaticity, molecular weight, source, and degradation state of DOM (Catalá et al., 2015; Coble, 1996; Fellman et al., 2010). The optical properties of CDOM result from complex mixtures of compounds derived from allochthonous or autochthonous inputs (Stedmon & Nelson, 2015), CDOM contains labile, semilabile, and more recalcitrant moieties (Cory & Kaplan, 2012). Some pioneering studies have used CDOM optical properties to quantitatively estimate terrestrial DOM export by rivers (Mann et al., 2016; Spencer et al., 2013).

Lignin phenols are biomarkers of vascular plant-derived organic compounds, and dissolved lignin phenols are widely used to investigate DOM sources and transformation in fluvial systems (Hedges & Mann, 1979; Hernes & Benner, 2003; Jex et al., 2014). The monomeric composition of lignin phenols provides useful information about the vegetation sources and degradation state of DOM (Feng et al., 2016; Hedges & Mann, 1979; Opsahl & Benner, 1995). Compared with CDOM, lignin represents a specific recalcitrant polymer and can be linked to specific types of plants, such as, gymnosperms or angiosperms vascular plants (Ruiz-Dueñas & Martínez, 2009; Stedmon & Nelson, 2015).

Combining the optical proxies and biomarkers to characterize DOM, especially the linkage between CDOM (absorption or fluorescence) and dissolved lignin, has drawn the attention of researchers; however, most studies have focused on estuaries and coastal regions (Fichot et al., 2016; Lu et al., 2016; Osburn & Stedmon, 2011; Walker et al., 2009). Except for studies conducted in arctic rivers, which showed high dissolved organic carbon (DOC) concentrations, few studies have linked the optical and chemical properties of DOM in large fluvial systems (Mann et al., 2016; Spencer, Aiken, et al., 2009; Stubbins et al., 2015).

The Changjiang River represents an ideal model to study the interactions of riverine DOM with lakes and groundwater systems within the watershed. Extensive studies about the impacts of the Three Gorges Dam (TGD) on the river flow regime of the Changjiang River have found significant sediment trapping, increased nutrient retention and light transmittance (Liu et al., 2016; Yang et al., 2014). However, the variability of DOM composition in the Changjiang River under different hydrological conditions, which are regulated by TGD operations, is poorly characterized on the molecular level.

This study aims to characterize the chemical and optical composition of DOM in the Changjiang River, study the sources and transformation of DOM within the river, and reveal the linkage between CDOM and dissolved lignin under different hydrological conditions. Studying the sources and processing of DOM in the Changjiang River, which is one of the largest rivers in the world, can help reveal the transformation of terrestrial DOM in large fluvial systems.

2. Materials and Methods

2.1. Study Area and Sample Collection

The Changjiang River, which is also known as Yangtze River, originates in the Tibetan Plateau and flows 6,300 km through various geomorphologies to the East China Sea. It has a catchment area of 1.8×10^6 km^2 and annual average discharge of 960 km^3 (Zhang et al., 2014). The river basin is located in the temperate zone (24.5–35.5°N), and the average annual precipitation is 1,100 mm (70–90% of which occurs during the wet season of May to October; Zhang et al., 2014). Approximately half of the precipitation is lost due to evaporation (Yang et al., 2014). Influenced by the East Asian monsoon and its basin topography, the river exhibits a gradual change in precipitation and hydrology from west to east. Based on the geomorphological characteristics, the Changjiang River can be divided into two parts: the upper reaches characterized by mountains and the middle to lower reaches characterized by extensive fluvial plains with lakes (Dai et al., 2010). The upper reaches end at Yichang, which is 1,750 km upstream of the river mouth. The TGD was constructed 44 km upstream of Yichang. Major croplands and industrial areas are concentrated in the middle to lower reaches of the river basin (Liu et al., 2016). Two lake systems (Dongting Lake and Poyang Lake) and

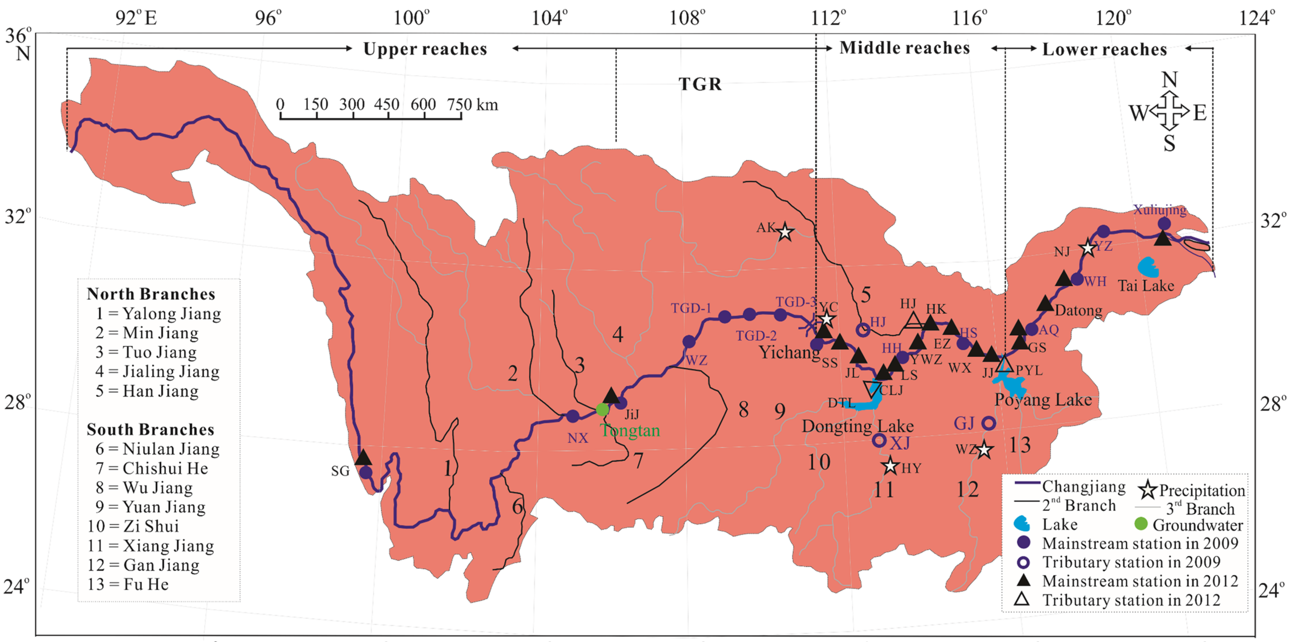

Figure 1. River basin map of the Changjiang River, showing the main stream and main tributaries. The collection of water samples along the main stream and tributaries is indicated on the map. The blue solid circles, the blue blank circles, and the green solid circles indicate the sampling stations in the main stream, tributaries, and groundwater in moderate discharge in 2009, respectively, whereas the black solid triangles and the black blank triangles indicate the samples collected in the main stream and tributaries in high discharge in 2012 respectively. The precipitation data collected stations were marked with black iris star.

the Hanjiang River are the large tributaries in the middle to lower reaches (Figure 1). The Changjiang River transports the greatest amount of terrestrial DOM during the high discharge period from June to September (Bao et al., 2015).

Field sampling was conducted during two different hydrological periods, September to October 2009 and August 2012. The precipitation in the 2009 sampling period was lower than that in 2012 (CWRC (Changjiang water resources commission of the ministry of water resources), 2009; CWRC, 2012; Table S1 in the supporting information). The field sampling in 2009 was conducted during a moderate discharge period, and the discharge during the sampling period was similar to the average discharge of Datong Station from 1956 to 2016 (CWRC, 2016; Figure 2). Seventeen sample stations covered the whole river main stream and three important tributaries (Dongting Lake, Hanjiang River, and Poyang Lake), and a groundwater sample was also collected from a well near the main stream at Tongtan Station (Figure 1). The field sampling in 2012 was conducted during a high discharge period; the discharge during the sampling period was similar to the monthly peak discharge of Datong Station from 1956 to 2016 (CWRC, 2016; Figure 2). In 2012, 18 sample stations located in the middle to lower reaches, including 3 tributary sampling stations, were investigated (Figure 1). The Changjiang River experiences strong spatial/temporal variability in precipitation (Jiang et al., 2007). Water discharge from the upper to middle to lower reaches is coupled with the control of precipitation and flow regulation of the TGD. Samples in September and October 2009 were collected during TGD impoundment period, and a large amount of water and sediment from the upper reaches were trapped by the dam, whereas the samples in 2012 were collected during the high discharge period, and water and sediment from the upper reaches freely flowed through the dam and were transported with shorter retention time to the middle to lower reaches. DOC, CDOM, dissolved lignin, total suspended matter (TSM), and chlorophyll *a* (Chl *a*) analyses were performed for samples collected during both periods.

2.2. Methods

In 2009, surface water samples (0–50 cm) were collected in the main stream of the river channel with an acid-washed polyethylene bottle, kept at ~0 °C and transported to the laboratory within several hours for filtration. In 2012, surface water samples (0–50 cm) were filtered directly in a laboratory on the sampling boat.

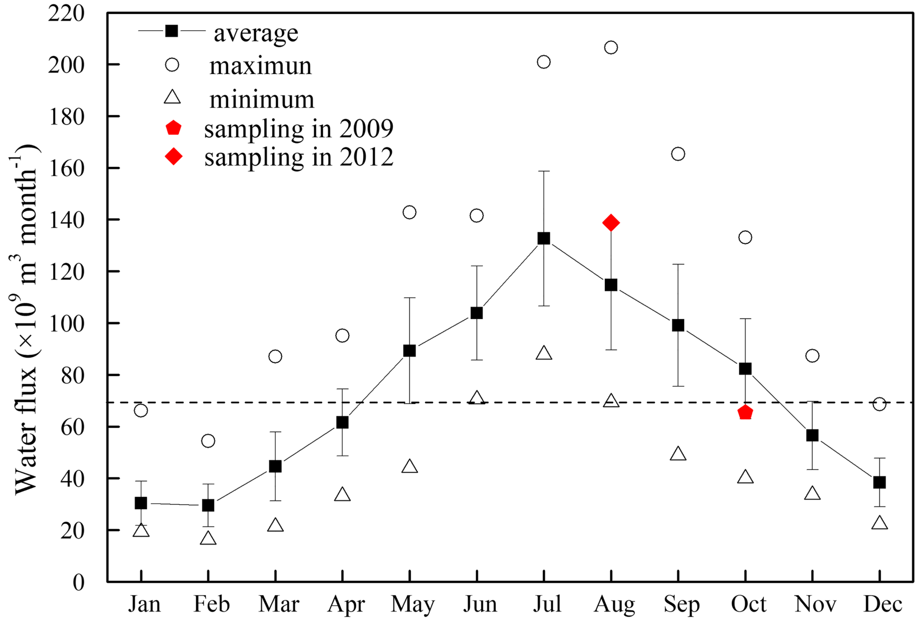

Figure 2. The average, maximum, and minimum values of monthly Changjiang River water discharge over 60 years at Datong Station and the water discharge during the sampling periods in 2009 and 2012. The dashed line is the average discharge value of Datong Station from 1956 to 2016 (CWRC (Changjiang water resources commission of the ministry of water resources), 2016).

DOC samples were filtered through 0.45-μm nylon filters (Rephile, Shanghai, China), and CDOM samples were filtered through 0.22-μm polyether sulfone filters (Millipore, Darmstadt, Germany). Dissolved lignin samples were filtered through 0.7-μm GF/F filters (Whatman, Kent County, England) and concentrated using 1-g styrene-divinylbenzene copolymer (PPL) sorbent (Agilent, CA, USA) according to the method developed by Dittmar et al. (2008). All samples were stored in a freezer at −20 °C before analysis. The short-term (60 days) frozen storage had a limited impact on the CDOM parameters (Table S2).

The concentration of Chl *a* was measured using a Cary 100 UV-Vis spectrophotometer (Varian, CA, USA) after extraction with 90% acetone at −20 °C for 24 hr in the dark with a precision of ±0.1 μg/L (Sartory & Grobbelaar, 1984).

The DOC samples were acidified and oxygen purged to remove dissolved inorganic carbon prior to analysis with a total organic carbon (TOC) analyzer (Shimadzu TOC-L, Kyoto, Japan) using the high-temperature catalytic oxidation method. The details are described in Wang et al. (2017).

Absorption spectra for CDOM were measured with a Cary 100 UV-vis spectrophotometer (Varian, CA, USA). Napierian absorption coefficient (a_λ) was calculated from $a_\lambda = 2.303 \times A_\lambda \div l$, where l is the path length in meters and A_λ is the absorbance at wavelength λ. The absorption coefficient at 254 nm (a_{254}) were measured to represent the CDOM concentration. The spectral slope coefficient, $S_{275–295}$, was calculated over the range of 275–295 nm following the exponential function and using a linear fit of a log-linearized a_λ: $a_\lambda = a_{\lambda_0} e^{-S(\lambda-\lambda_0)}$ (Helms et al., 2008). The $S_{275–295}$ was used as a tracer of the molecular weight of DOM, with a higher value indicating a lower molecular weight of DOM (Helms et al., 2008). The $S_{275–295}$ increased with the degradation of CDOM (Yamashita et al., 2013).

Excitation Emission Matrix Spectroscopy was measured with an F-4500 fluorescence spectrophotometer (Hitachi, Tokyo, Japan). The spectra of ultrapure water were subtracted as a blank. The fluorescence intensity was calibrated by dividing the Raman scatter band of ultrapure water, which was collected at 350-nm excitation and integrated over 380 to 420 nm. The fluorescence intensity was reported in Raman units. A parallel factor analysis (PARAFAC) was applied to decompose the spectra into individual fluorescent components according to the method established by Stedmon and Bro (2008). Split-half validation was used to determine the number of components. The fluorescence index (FI) is a ratio of emission intensities (450 and 500 nm) at 370-nm excitation, and it can measure the structural features of the carbon skeleton that are influenced by the source of organic matter (McKnight et al., 2001). Since the FI reflects the relative contribution of aromatic and nonaromatic DOM, it also provides information about the degradation degree of the DOM. Microbial degradation typically leads to an increase in the FI, whereas photo degradation reduces the FI (Fellman et al., 2010; Hansen et al., 2016; Kellerman et al., 2015).

Lignin phenols were determined using the CuO oxidation method as described in Bao et al. (2014). In brief, an extracted DOM sample is reacted with sodium hydroxide along with an excess of CuO. Ferrous ammonium sulfate as an oxygen scavenger is added to the vessel to prevent super oxidation of lignin during the reaction. After oxidation, the contents of the reaction vessels are centrifuged to separate solids from the eluent. The latter is subsequently acidified and extracted with ethyl acetate to isolate the lignin oxidation products and then analyzed using gas chromatography (Agilent 6890N, CA, USA) with a flame ionization detector.

In our study, the concentration of dissolved lignin phenols (Σ6) utilized the sum of three vanillyl phenols (V) and three syringyl phenols (S). The relative contribution of vascular plant-derived material to organic matter can be accessed by the carbon-normalized lignin phenols concentration Λ6 (mg (100 mg OC)$^{-1}$). Vanillyl phenols are ubiquitous, whereas syringyl phenols are unique to angiosperm tissue and cinnamyl phenols (C) are prevalent in herbaceous tissues and absent from woody tissues (Hedges & Mann, 1979). Vanillyl phenols are ubiquitous in vascular plants; therefore, a total vanillyl phenol end-member mixing model was used to calculate the percentage of vascular plant tissue (Hernes et al., 2007). The average vanillyl phenol concentration of various vascular plant tissues collected in the Changjiang River basin is 2.7 mg (100 mg OC)$^{-1}$ (Yu et al., 2007), and we use this value as the end-member that represents 100% vascular plant-derived DOM. The syringyl-to-vanillyl (S/V) and cinnamyl-to-vanillyl (C/V) phenol yields ratios that provide useful information about the tissue source (Lobbes et al., 2000; Opsahl & Benner, 1995). Demethylation by brown-rot fungi leads to a loss of methoxylated phenols (vanillyl and syringyl phenols), whereas nonmethoxylated phenols (p-hydroxyl phenols, P) are not affected (Dittmar & Lara, 2001). Thus, the ratio of p-hydroxyl phenols to the sum of vanillyl phenols and syringyl phenols (P/(V+S)) is an important indicator of microbial degradation (Dittmar & Lara, 2001). Among the additional CuO oxidation products, 3, 5-dihydroxybenzoic acid (DHBA) is known to originate from tannin and other flavonoids and DHBA accumulates as a degradation byproduct of fresh vascular plant tissue (Farella et al., 2001; Prahl et al., 1994). Hence, the ratio of DHBA to vanillyl phenols (DHBA/V) characterizes the degradation state of terrigenous organic matter (Farella et al., 2001; Pautler et al., 2010). The ratio of vanillin acid to vanillin ((Ad/Al)v) increases as side-chain oxidation increases (Hedges & Mann, 1979; Wu et al., 2015; Yu et al., 2011).

2.3. Box Model

The water discharge at the Changjiang River gauge stations is measured by the Changjiang Water Resources Commission of the Ministry of Water Resources (CWRC, http://www.cjw.gov.cn/zwzc/bmgb/). A box model was applied to evaluate the contribution of water resources to the middle to lower reaches of the Changjiang River (Bao et al., 2015). Briefly, the major water resources for the middle to lower reaches are the upper reaches (represented by the discharge at Yichang Station), three tributaries in the middle to lower reaches (Dongting Lake, Hanjiang River, and Poyang Lake), and groundwater. The water discharge at Xuliujing Station represents the discharge of the Changjiang River into the East China Sea. The groundwater discharge is calculated via the water balance box model in the middle to lower reaches. The difference between the water input (the sum of the discharges at Yichang Station and the three tributaries) and the output (discharge at Datong Station, which is the most seaward gauging station and approximately 500 km upstream of Xuliujing Station) is calculated as groundwater.

Based on the box model, we multiplied concentrations by discharge to calculate the DOC, CDOM, and lignin fluxes in the middle to lower reaches. In 2009, the CDOM samples were not collected successfully at Dongting Lake; thus, the CDOM flux of Dongting Lake was calculated based on the difference between Yichang Station (before Dongting Lake) and Honghu Station (after Dongting Lake), which may have produced a larger error.

2.4. Statistical Analysis

IBM SPSS Statistics Version 23.0 and MATLAB Version 7.0 with the DOMFluor toolbox were used for the data analysis. Differences in the DOM parameters between high and moderate discharges were tested for

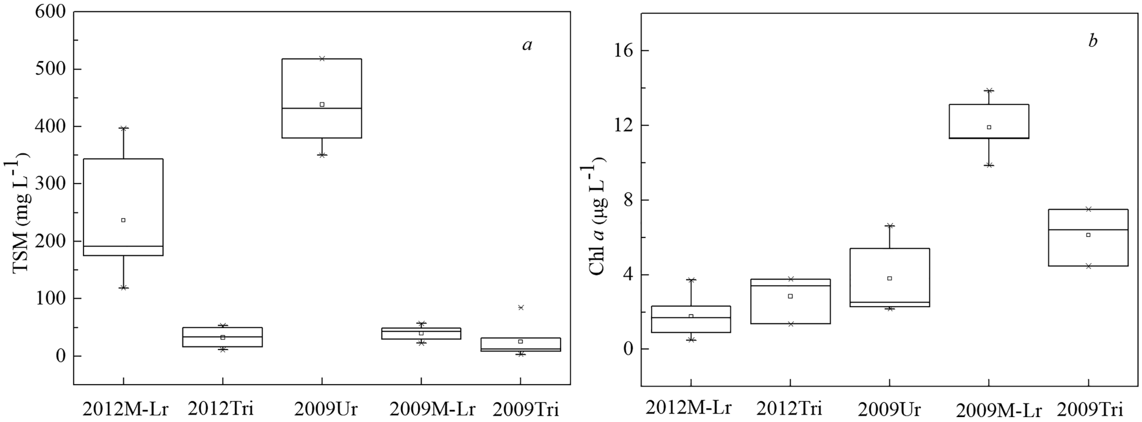

Figure 3. The distribution of (a) total suspended matter (TSM) and (b) Chl *a* concentration in upper reaches and middle to lower reaches and tributaries in Changjiang River (2012: samples collected at high discharge in 2012; 2009: samples collected at moderate discharge in 2009; Ur: upper reaches; M-Lr: middle to lower reaches; Tri: tributaries).

significance by Student's *t* test, and Pearson's correlation coefficient was used to examine the relationship between two variables (e.g., Σ6 and a_{254}, the FI and P/(V+S), DHBA/V and $S_{275–295}$).

3. Results

3.1. Bulk Parameters

The TSM, which contains the inorganic fraction (silt and clay, Dekker et al., 2001) and the organic fraction (detritus and algae, Dekker et al., 2001), showed large spatial and seasonal variations in the Changjiang River (Figure 3a). At moderate discharge, the TSM concentrations were higher in the upper reaches and decreased in Three Gorges Region (TGR) (Figure S1a). At high discharge, the TSM concentrations in the middle to lower reaches were higher than the values at moderate discharge (Figure 3a), and the TSM concentrations showed a decreasing trend in the middle to lower reaches (Figure S1a). In the middle to lower reaches, the Chl *a* concentrations were 11.9 ± 1.9 μg/L at moderate discharge, which were higher than the concentrations at high discharge (1.8 ± 1.1 μg/L, Figure 3b).

At moderate discharge, DOC increased dramatically in TGR, the DOC concentrations were 0.97 ± 0.11 mg/L in the upper reaches and 1.31 ± 0.09 mg/L in the middle to lower reaches (Figure 4a). At high discharge, the DOC concentrations were 1.59 ± 0.10 mg/L (Figure 4a), which were significantly higher than at moderate discharge ($p < 0.001$). The DOC concentrations in the tributaries were lower than that in the main stream (Figure 4a). The DOC concentration of the groundwater sampled in Tongtan Station was 0.76 mg/L.

3.2. Optical Properties of DOM

CDOM concentrations were highly variable among sites, especially in the upper reaches of the Changjiang River (Figure 4b). At moderate discharge, the a_{254} increased from 5.33 to 8.44 m^{-1} along the upper reaches, and there was a dramatic increase in the TGR, which was similar to the DOC patterns (Figures 4a and 4b). A slight decrease in the a_{254} values occurred from the middle to the lower reaches along the river basin (Figure 4b). In the middle to lower reaches, the CDOM concentrations were 11.50 ± 0.65 m^{-1} at high discharge and 8.94 ± 0.73 m^{-1} at moderate discharge (Figure 4b), and they were significantly higher at high discharge than at moderate discharge ($p < 0.001$). At moderate discharge, the a_{254} values were 4.19 and 8.91 m^{-1} in the Hanjiang River and Poyang Lake, respectively, whereas at high discharge, the a_{254} values ranged from 10.08 to 11.17 m^{-1} in the tributaries (Figure 4b). For groundwater collected at Tongtan Station, the a_{254} was 3.90 m^{-1}.

Five fluorescent components were identified using the PARAFAC model. C1, C2, and C4 are typical recalcitrant humic-like components, whereas C3 and C5 are identified as protein-like components (Aiken, 2014; Coble, 1996; Dainard et al., 2015; Fellman et al., 2010; Li et al., 2015; Osburn & Stedmon, 2011; Yamashita, Scinto, et al., 2010; Table S3). C3 is labile tyrosine-like matter and represents the freshly produced compounds, whereas C5 is tryptophan-like matter that contains labile, semilabile, and recalcitrant

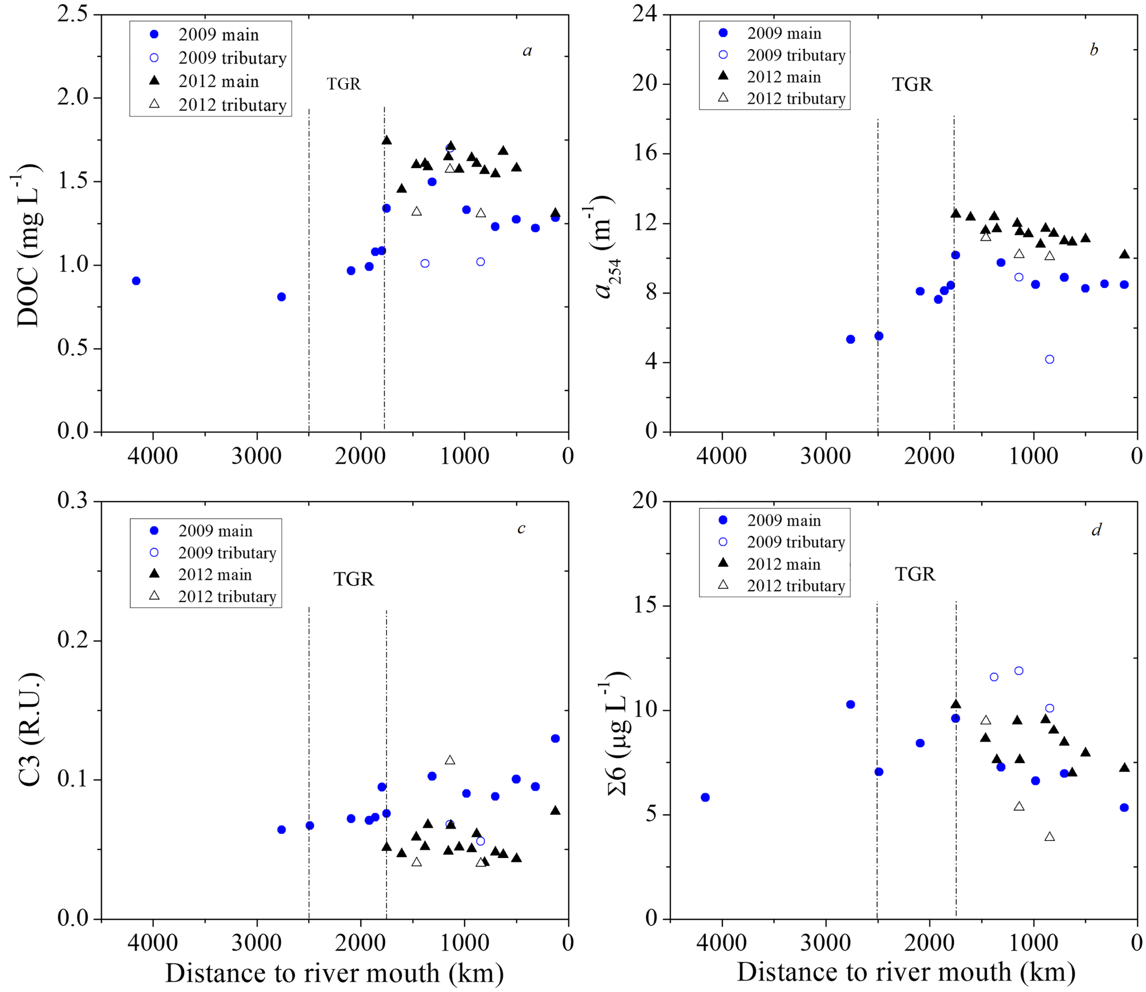

Figure 4. The variations of (a) dissolved organic carbon (DOC), (b) absorption coefficient at 254 nm (a_{254}) of chromophoric dissolved organic carbon (CDOM), (c) humic-like component C3, and (d) dissolved lignin concentrations along the Changjiang River (The region between vertical lines is Three Gorges Region (TGR); the dark solid and empty triangles: samples collected in the main stream and tributaries at high discharge in 2012; the blue solid and empty circles: samples collected in the main stream and tributaries at moderate discharge in 2009).

compounds (Cory & Kaplan, 2012). All components identified in our study have been reported in previous PARAFAC models (Table S3), and these five components have been successfully matched in the OpenFluor database with similarity scores >0.95 (Murphy et al., 2014).

In the middle to lower reaches, the concentrations of labile component C3 at high discharge were significantly lower than that at moderate discharge ($p < 0.001$, Figure 4c), whereas the concentrations of humic-like components C1, C2, and C4 were significantly higher at high discharge than at moderate discharge ($p < 0.001$, Table 2 and Figure S2). At high discharge, 82 ± 2% of the fluorescent matter were recalcitrant humic-like matter, which was higher than that at moderate discharge (75 ± 3%).

Ultraviolet A (320–400 nm) and Ultraviolet B (280–320 nm) can reach the surface of the Earth, whereas Ultraviolet C (200–280 nm) is absorbed in the atmosphere (Meunier, 1999). During the photo degradation process, the largest losses of absorption and fluorescence occurred at the wavelength of incident irradiation (Del Vecchio & Blough, 2002); therefore, fluorescent matter that is excited at longer wavelengths is more susceptible to photo degradation. In our study, C4 (253/468 nm) was typically Ultraviolet C humic-like matter, whereas C2 (274(343)/468 nm) contained Ultraviolet A and Ultraviolet B matter. The fluorescence intensity ratio of C4 and C2 (C4/C2) was therefore calculated to indicate the photo degradation process, with an increased ratio indicating enhanced photo degradation. The short-term frozen preservation does not significantly alter the C4/C2 ratio (Table S2). At high discharge, the C4/C2 ranged from 1.32 to 1.81 (Table 1 and

Table 1
The DOM Parameters in the Changjiang River in 2012 and 2009

Station	Distance[a] (km)	Λ6 (mg (100 mg OC)$^{-1}$)	V (mg (100 mg OC)$^{-1}$)	FI	C1 (R.U.)	C2 (R.U.)	C4 (R.U.)	C5 (R.U.)	C4/C2
Middle to lower reaches of 2012 (high discharge)									
YC[1]	1,750	0.59	0.34	1.80	0.24	0.19	0.26	0.09	1.33
SS	1,607	ND	ND	1.82	0.24	0.20	0.26	0.09	1.32
JL	1,465	0.54	0.39	1.67	0.21	0.20	0.34	0.10	1.72
CLJ	1,380	ND	ND	1.58	0.20	0.16	0.22	0.09	1.41
LS	1,355	0.48	0.29	1.67	0.22	0.19	0.30	0.11	1.55
YWZ	1,158	0.58	0.38	1.65	0.20	0.18	0.29	0.09	1.65
HK	1,135	0.45	0.29	1.67	0.21	0.19	0.35	0.10	1.81
EZ	1,052	ND	ND	1.71	0.21	0.19	0.31	0.10	1.66
WX	934	ND	ND	1.65	0.20	0.18	0.31	0.10	1.73
JiJ	885	0.59	0.38	1.64	0.24	0.21	0.36	0.12	1.70
GS	807	0.58	0.37	1.69	0.20	0.19	0.31	0.10	1.67
AQ	704	0.55	0.35	1.58	0.20	0.18	0.31	0.10	1.71
DT[2]	630	0.42	0.29	1.54	0.20	0.18	0.30	0.10	1.72
WH	501	0.50	0.34	1.67	0.21	0.19	0.32	0.10	1.67
XLJ[3]	125	0.55	0.44	1.55	0.19	0.16	0.28	0.14	1.71
Tributaries of 2012 (high discharge)									
DTL[4]	1,460	0.72	0.52	1.70	0.20	0.15	0.22	0.08	1.40
HR[5]	1,140	0.34	0.22	1.65	0.16	0.11	0.16	0.11	1.50
PYL[6]	8,44	0.30	0.23	1.55	0.16	0.13	0.18	0.08	1.47
Upper reaches of 2009 (moderate discharge)									
SG	4,161	0.64	0.41	ND	ND	ND	ND	ND	ND
NX	2,761	1.27	0.73	1.78	0.11	0.09	0.11	0.05	1.28
JJ	2,489	ND	0.29	1.76	0.10	0.08	0.11	0.05	1.34
WZ	2,092	0.87	0.22	1.56	0.14	0.12	0.18	0.07	1.49
TGD-1	1,917	ND	0.49	1.69	0.19	0.15	0.19	0.08	1.22
TGD-2	1,859	ND	ND	1.69	0.19	0.16	0.20	0.08	1.26
TGD-3	1,796	ND	ND	1.70	0.16	0.12	0.14	0.07	1.17
Middle to lower reaches of 2009 (moderate discharge)									
YC[1]	1,751	0.72	0.28	1.68	0.17	0.15	0.19	0.07	1.32
HH[7]	1,313	0.49	0.33	1.48	0.16	0.14	0.25	0.08	1.78
HS	981	0.50	0.28	1.50	0.21	0.17	0.20	0.08	1.20
AQ	704	0.57	0.22	1.33	0.15	0.16	0.35	0.10	2.26
WH	501	ND	ND	1.51	0.16	0.12	0.16	0.08	1.29
YZ	317	ND	ND	1.48	0.14	0.13	0.22	0.09	1.66
XLJ[3]	125	0.42	0.23	1.49	0.15	0.13	0.22	0.09	1.70
Tributaries of 2009 (moderate discharge)									
DTL[4]	1,380	1.15	0.55	ND	ND	ND	ND	ND	ND
HR[5]	1,140	0.70	0.41	1.77	0.10	0.08	0.10	0.04	1.32
PYL[6]	844	0.99	0.48	1.78	0.10	0.08	0.10	0.05	1.30

Note. [1]Yichang, [2]Datong, [3]Xuliujing, [4]Dongting Lake, [5]Hanjiang River, [6]Poyang Lake, [7]Honghu. ND: No data.
[a]Distance to the river mouth.

Figure S1b), and the TSM concentrations showed a significant negative correlation with C4/C2 ($r^2 = 0.645$, $p < 0.001$; Figure S1c).

At moderate discharge, the $S_{275–295}$ increased significantly along the river ($r^2 = 0.477$, $p = 0.005$, Figure 5a), whereas at high discharge, the $S_{275–295}$ was lower and discrete (Figure 5a). Both at moderate and high discharges, the FI decreased significantly along the river (Figure 5b).

3.3. Dissolved Lignin Phenols

At moderate discharge, the Σ6 concentrations ranged from 6.99 to 10.25 μg/L in the main stream, whereas at high discharge, the Σ6 concentrations ranged from 5.33 to 10.28 μg/L in the main stream (Figure 4d). At moderate and high discharges, the dissolved lignin concentrations (Σ6 and Λ6) in main stream were similar ($p \geq 0.05$, Table 2). At moderate discharge, the Λ6 and vanillyl phenols concentrations were higher in the tributaries than the main stream of the middle to lower reaches (Table 1) and the vascular plant-derived

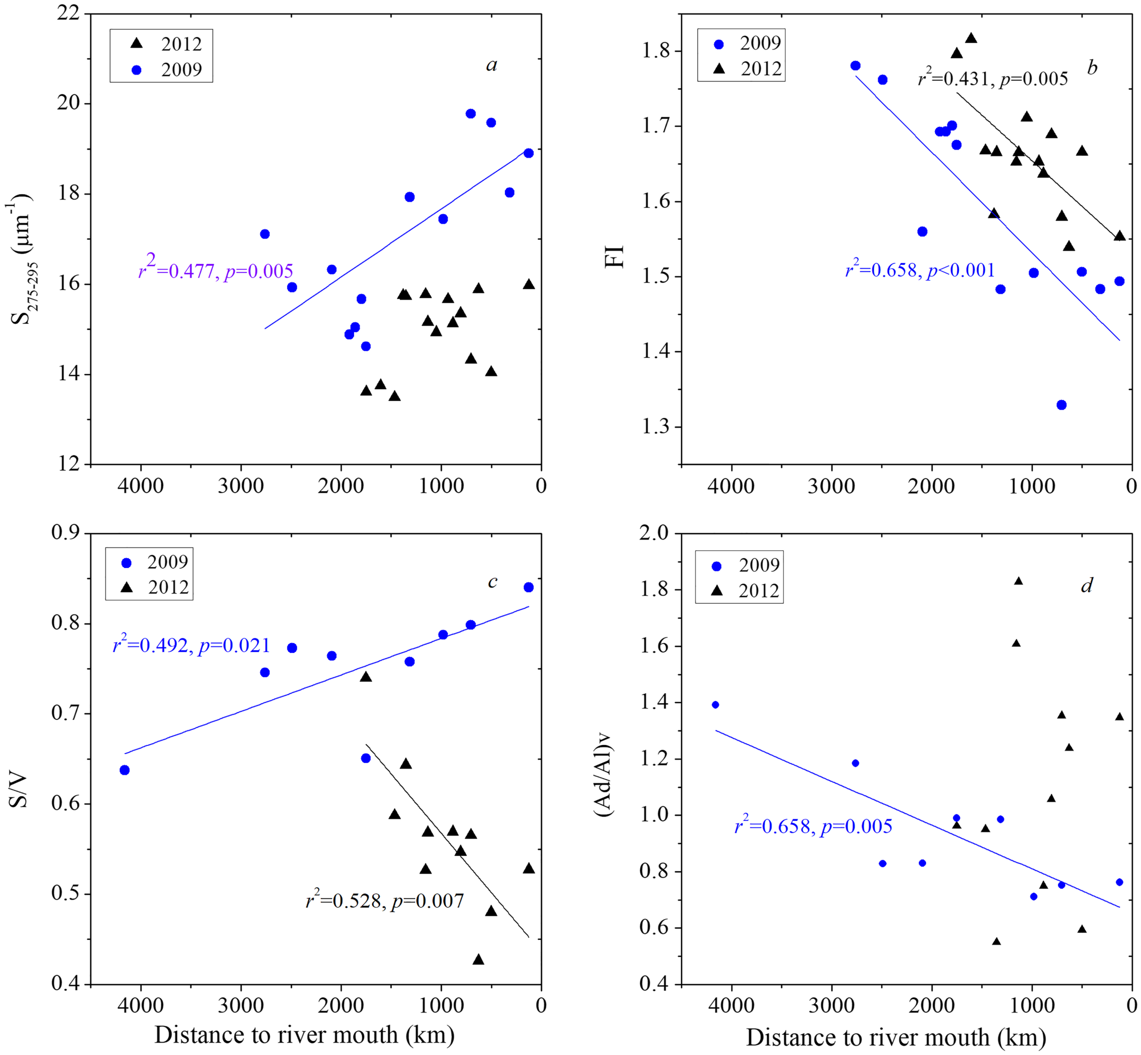

Figure 5. The variations of (a) $S_{275–295}$, (b) fluorescence index (FI), (c) S/V, and (d) (Ad/Al)v along the Changjiang River (The dark triangles: samples collected at high discharge in 2012; the blue circles: samples collected at moderate discharge in 2009).

proportions were higher in the tributaries (from 15.0% to 20.3%) than the main stream of the middle to lower reaches (from 8.3% to 12.1%).

The S/V and C/V ratios were significantly different between the moderate and high discharge periods ($p < 0.001$, Table 2). The S/V at high discharge was lower than at moderate discharge (Figure 5c).

Table 2
T Test Analysis of All Parameters

Significance level	$p < 0.001$	$0.001 \leq p < 0.05$	$p \geq 0.05$
Difference between upper and middle to lower reaches in 2009	Chl a, DOC, FI	TSM, a_{254}, $S_{275–295}$, C3, C4, C5	C1, C2, Σ6, Λ6, P/(V+S), S/V, C/V, (Ad/Al)v, (Ad/Al)s, DHBA/V
Difference of middle to lower reaches in 2009 and 2012	Chl a, DOC, a_{254}, C1, C2, C3, C4, C5, FI, $S_{275–295}$, S/V, C/V, DHBA/V	TSM	Σ6, Λ6, P/(V+S), (Ad/Al)v, (Ad/Al)s

Note. TSM: total suspended matter; Chl a: chlorophyll a; DOC: dissolved organic carbon; a_{254} and a_{350}: absorption coefficients of chromophoric dissolved organic matter at 254 and 350 nm; $S_{275–295}$: spectral slope coefficient over the range of 275–295 nm; C1, C2, C3, C4, and C5: five components identified by the PARAFAC, C1, C2, and C4 are humic-like matter, C3 and C5 are protein-like matter; FI: fluorescence index; Σ6: the sum concentrations of three vanillyl phenols and three syringyl phenols; Λ6: carbon-normalized yields of lignin phenols; S/V: ratio of syringyl to vanillyl phenols; C/V: ratio of cinnamyl to vanillyl phenols; P/(V+S): ratio of p-hydroxyl phenols to the sum of vanillyl and syringyl phenols; Ad/Al: ratio of acid to aldehyde; DHBA/V: the ratio of DHBA to vanillyl phenols.

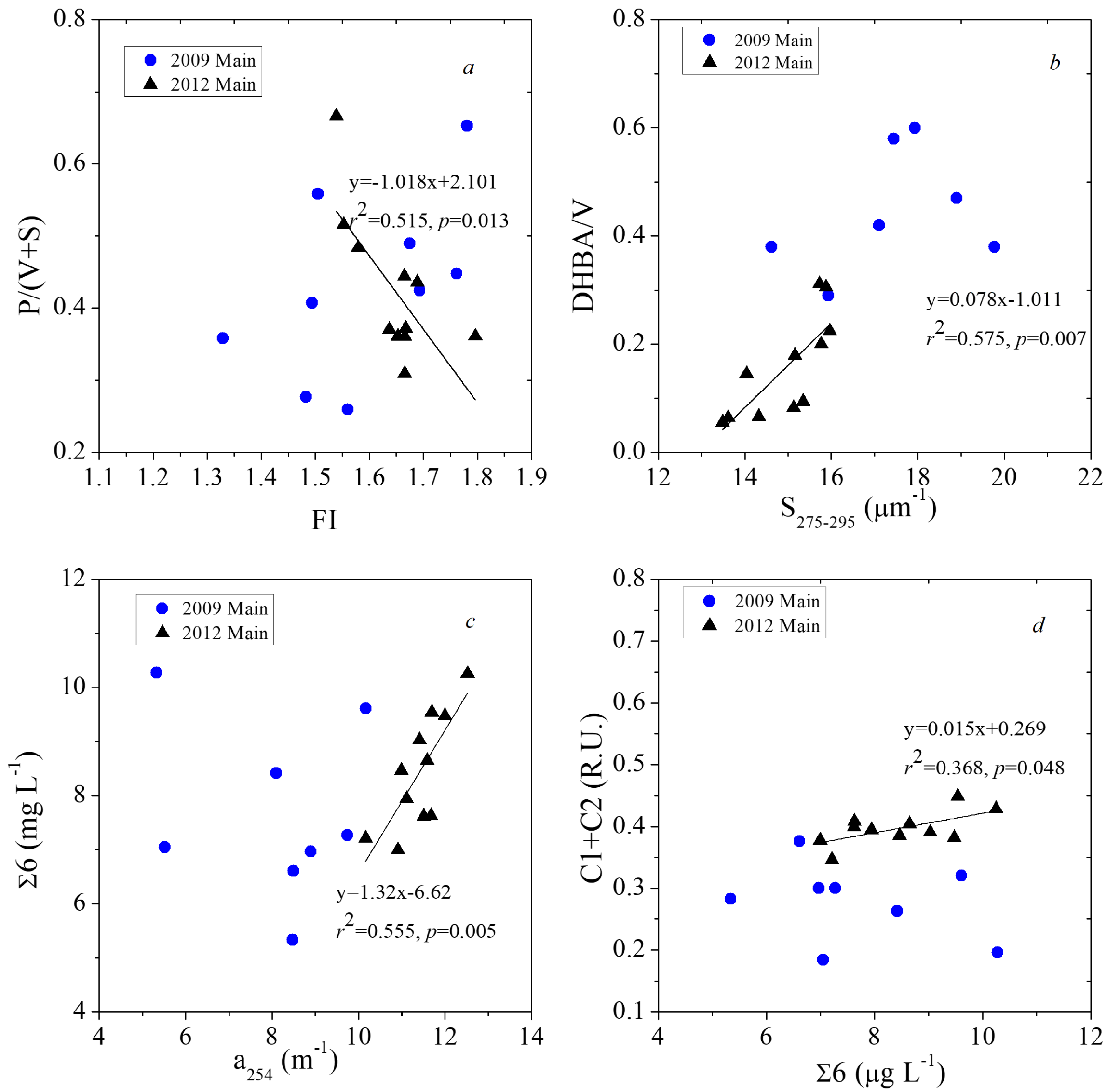

Figure 6. The correlation between (a) P/(V+S) and FI, (b) DHBA/V and $S_{275–295}$, (c) Σ6 and a_{254}, and (d) the sum of two humic-like components (C1 and C2) and Σ6 in the Changjiang River (Blue circles: samples collected in main stream at moderate discharge in 2009; dark triangles: samples collected in main stream at high discharge in 2012; black line: the regression line at high discharge).

Although the dissolved lignin concentrations in the main stream were similar, the composition of dissolved lignin phenols varied significantly under different hydrological conditions. The composition of dissolved lignin varied along the river (Figures 5c and 5d). In the main stream, the S/V showed a significant decreasing trend along the river at high discharge (r^2 = 0.528, p = 0.007; Figure 5c), whereas the S/V increased along the river at moderate discharge (r^2 = 0.492, p = 0.021; Figure 5c). At moderate discharge, the (Ad/Al)v decreased significantly along the river (r^2 = 0.658, p = 0.005; Figure 5d), and the P/(V+S) scattered along the river (Figure S3), whereas at high discharge, the (Ad/Al)v scattered along the river (Figure 5d), and the P/(V+S) increased along the river (Figure S3). At high discharge, the FI was significantly negatively correlated with P/(V+S) (r^2 = 0.515, p = 0.013; Figure 6a). In the middle to lower reaches, the DHBA/V ratios were significant higher at moderate discharge than at high discharge (p < 0.001; Figure 6b). At high discharge, the DHBA/V showed a significant positive correlation with $S_{275–295}$ (r^2 = 0.575, p = 0.007, Figure 6b).

Table 3
The DOM Concentrations in Large Fluvial Systems

Rivers	DOC (mg/L)	a_{254} (m^{-1})	Σ6 (ug/L)	Λ6 (mg (100 mg OC)$^{-1}$)	References
Amazon River	3.8–10.8	ND	25.8 ± 15.5	0.97 ± 0.32	Hedges et al. (2000)
Mississippi River	2.9–4.1	18.3–39.6	38.1 ± 26.8	0.65 ± 0.54	Spencer, Butler, et al. (2012) and Cai et al. (2015)
Congo River	2.7–10.7	16–32	65.66 ± 3.43	0.70 ± 0.17	Spencer et al. (2010), Spencer, Hernes, et al. (2012) and Lambert et al. (2015)
Yukon River	2.6–17.0	35–123	49.42 ± 63.00	0.49 ± 0.53	Amon et al. (2012), Stubbins et al. (2015), and Mann et al. (2016)
Yenisey River	4.0–9.8	25–88	103.08 ± 82.45	0.97 ± 0.89	Amon et al. (2012), Stubbins et al. (2015), and Mann et al. (2016)
Lena River	7.7–17.5	52–147	127.67 ± 113.1	0.93 ± 2.10	Amon et al. (2012), Stubbins et al. (2015), and Mann et al. (2016)
Ob River	7.3–8.5	50–67	60.67 ± 55.50	0.56 ± 0.51	Amon et al. (2012), Stubbins et al. (2015), and Mann et al. (2016)
Kolyma River	2.6–10.7	12–83	46.30 ± 38.14	0.60 ± 0.85	Amon et al. (2012), Stubbins et al. (2015), and Mann et al. (2016)
Mackenzie River	4.3–5.0	32–44	12.07 ± 11.70	0.27 ± 0.20	Amon et al. (2012), Stubbins et al. (2015), and Mann et al. (2016)
Changjiang River	0.81–1.74	4.19–12.52	8.17 ± 1.95	0.62 ± 0.23	This study

Note. ND: No data.

3.4. Box Model Calculation

At moderate discharge, groundwater from terrestrial aquifers injected into middle to lower reaches at a flux of 0.45×10^9 m^3/day, which accounted for 25.3% of the total water discharged in the middle to lower reaches (Table S4). At high discharge, ~0.04×10^9 m^3/day river water continuously seeped into the aquifers located at the middle to lower reaches, and this groundwater discharge only accounted for 0.8% of the total water discharge (Table S4). Thus, groundwater played a more important role at moderate discharge. The water discharge calculated based on the box model indicates that the upper reaches represent a crucial water source to the middle to lower reaches, and Dongting Lake is the most important tributary in the middle to lower reaches (Table S4).

Based on the box model, we calculate the DOM fluxes from the upper reaches and tributaries to the middle to lower reaches. The groundwater DOM flux is discussed later. The Changjiang River transported 6.45×10^9 g/day of DOC and 35.47×10^6 g/day of dissolved lignin to the East China Sea at high discharge, and the CDOM (a_{254}) flux was 50.04×10^9 m^2/day, whereas it transported 2.29×10^9 g/day of DOC, 9.49×10^6 g/day of dissolved lignin, and 15.09×10^9 m^2 day of CDOM (a_{254}) to the East China Sea at moderate discharge (Table S4). Thus, the DOM flux at high discharge was approximately threefold higher than the flux at moderate discharge.

4. Discussion

4.1. Composition and Sources of DOM in the Changjiang River

The DOC concentrations in this study (0.81–1.74 mg/L, Figure 4a) are comparable to the concentrations observed before the TGD began operations in 1997 and 2003 (1.36 ± 0.22 mg/L and 1.55 ± 0.19 mg/L, respectively, Wu et al., 2007). The DOC concentrations in the Changjiang River are lower than the concentrations in the Amazon River, Mississippi River, Congo River, Yukon River, and other arctic rivers (Amon et al., 2012; Cai et al., 2015; Hedges et al., 2000; Lambert et al., 2015; Spencer, Aiken, et al., 2009; Stubbins et al., 2015, Table 3). The a_{254} value in the Changjiang River is lower than the values in the Mississippi River, Congo River, and arctic rivers (Spencer et al., 2010, Spencer, Butler, et al., 2012, Spencer, Hernes, et al., 2012; Stubbins et al., 2015, Table 3). The Σ6 in the Changjiang River is lower than that in other large rivers, whereas the Λ6 in the Changjiang River is similar to that in the Mississippi River, Ob River, and Kolyma River (Amon et al., 2012; Hedges et al., 2000; Mann et al., 2016; Spencer, Butler, et al., 2012, Table 3). Compared to other large rivers, the DOM concentrations in the Changjiang River are at a low level, while the proportions of lignin in DOM are at a moderate level.

Riverine DOM could be derived from in situ production, leachates from soils, wetlands, and anthropogenic sources (Bao et al., 2015; Bianchi et al., 2004; Jaffé et al., 2012; Raymond & Spencer, 2014; Spencer et al., 2008). In our study, the spatial and temporal variations of the TSM and Chl a concentrations implied that high soil erosion occurred in the upper reach and high in situ production occurred in the middle to lower reaches at moderate discharge (Figure 3). Since the observation of high discharge was only conducted in the middle to lower reaches, we compared the variation of DOM in the middle to lower reaches between moderate and high discharges to investigate the impact of different hydrological conditions.

In the middle to lower reaches, precipitation was higher at high discharge and high concentrations of DOM originating in the upper soil horizons leached into rainwater and were flushed into the river (Brooks et al., 1999; Qualls & Haines, 1992). The higher concentrations of TSM, DOC, and humic-like components at high discharge (Figures 3a, 4a, and S2) indicate that these components were strongly influenced by soil erosion. Recalcitrant terrestrial derived matter predominated in riverine DOM (Bianchi et al., 2004). In this study, DOM at high discharge tends to be more recalcitrant due to the high proportion of humic-like matter (Hertkorn et al., 2006; Nebbioso & Piccolo, 2013). Allochthonous inputs of more recalcitrant organic matter generally increased during the higher discharge period.

The increased primary production at moderate discharge increased the production of biologically autochthonous labile materials (Yamashita et al., 2008). At high discharge, however, light attenuation was caused by the high TSM concentrations, which limited the growth of phytoplankton (Cloern, 1987; Devlin et al., 2008). The higher concentrations of Chl *a* and labile tyrosine-like component C3 at moderate discharge (Figures 3b and 4c) indicate the active autochthonous production at moderate discharge. However, the C3 concentrations were not correlated with the Chl *a* concentrations in this study, which may be due to the degradation of labile component C3, especially during the moderate discharge. At moderate discharge, the flow velocity is slower and water residence time is longer; therefore, DOM was transformed more extensively before entering the coastal region.

Variation in the hydrological conditions did not alter the total dissolved lignin concentrations, which is consistent with a previous study of minor seasonal lignin variation in the Changjiang River (Wu et al., 2015). The significant lower S/V in 2012 seemed to indicate a higher contribution of gymnosperm tissues at high discharge (Table 2 and Figure 5c). However, dramatic changes in land use did not occur in the Changjiang River basin between 2009 and 2012. The areas of forest cover (0.68×10^6 km^2) and grassland (0.79×10^6 km^2) were the same as that in the basin in 2009 and 2012, and the area of cropland was 0.54×10^6 km^2 and 0.56×10^6 km^2, respectively (data sources: http://data.stats.gov.cn/index.htm and http://tongji.cnki.net/kns55/Dig/Dig.aspx). The apparent paradox may be resolved by considering the modification of lignin monomers during transport under different hydrological conditions. The source parameters were altered and can be explained by degradation processes under different hydrological conditions. The transformation of lignin monomers along the river is discussed later.

Agriculture also has an effect on the dissolved lignin composition. Rice, a typical nonwoody angiosperm plant, is grown in the middle to lower reaches as the main crop twice per year. The reported S/V and C/V ratios for paddy soil are 1.3 and 0.4 (Bierke et al., 2008), which are higher than the S/V and C/V ratios observed in the Changjiang River (0.6 ± 0.1 and 0.2 ± 0.1, respectively). At high discharge, the sampling period coincided with the growth period of the second rice cropping cycle, which is when the paddy soils are usually submerged, whereas at moderate discharge, the sampling coincided with the harvest period of the second rice crop, which is when the water from the paddy field had drained into the main stream of the Changjiang River through the tributaries; thus, the S/V and C/V ratios may have increased. At moderate discharge, the vascular plant tissue proportions in the tributaries were higher than that in the main stream, which further indicates the impact of paddy soil drainage on the tributaries.

At high discharge, the dominant source of bulk DOM was allochthonous input derived from extensive soil erosion, whereas at moderate discharge, an important source of DOM was autochthonous DOM derived from the elevated in situ primary production, especially for labile organic matter. The dissolved lignin concentrations in the Changjiang River exhibited minor variations under different hydrological conditions, whereas the dissolved lignin composition was modified along the river. Agriculture activities also affect the composition of dissolve lignin, especially in the tributaries.

4.2. Transformation of DOM in the Changjiang River and Its Controls

During transport from the headwaters to the ocean, the riverine DOM pool is transformed continually due to flocculation, microbial degradation, and photo degradation (Hernes & Benner, 2003). These processes determined the fate of DOM in a fluvial system. The transformation of DOM during the transport in this study is noticeable, the source parameter of dissolved lignin, S/V, is changed significantly during transport both at high and moderate discharges (Figure 5c). Previous studies offer various opinions about the impact of degradation on DOM composition (Benner & Kaiser, 2011; Fichot & Benner, 2014; Hernes & Benner, 2003; Lu et al., 2016). However, the responses of DOM compositions with different characteristics and reactivities to these degradation processes under different hydrological conditions are not yet clear, especially in natural large fluvial systems. Thus, it is crucial to evaluate the impacts of degradation processes on different DOM compositions under different hydrological conditions in the Changjiang River to provide insights on the DOM transformation in large fluvial systems.

The dissolved lignin composition was transformed significantly along the river, especially at moderate discharge. At moderate discharge, (Ad/Al)v decreased significantly along the river (Figure 5d), which can be explained by the flocculation. The affinities of clay minerals with lignin monomer phenols were different, with clay minerals such as montmorillonite preferentially absorbing the more oxidized lignin monomers, which would result in the preferential removal of acidic phenols (Clemente & Simpson, 2013; Kaiser et al., 2004; Robinson, 2010). In the middle to lower reaches of the Changjiang River, 58.6 $\pm$ 4.3% of the suspended particulate matter is clay minerals (Ding et al., 2014), and clay mineral particles are important composition of flocs (Eisma, 1986). The preferential sorption of vanillic acid during the flocculation may explain the decrease of (Ad/Al)v along the river. In our study, the dissolved lignin concentrations showed a positive correlation with effective densities at moderate discharge (Figure S4); thus, dissolved lignin concentrations were correlated negatively with the floc sizes (Ali & Hill, 2006; Guo & He, 2014), indicating that the flocculation process is effective at removing dissolved lignin from water at moderate discharge. Previous studies have demonstrated that photo degradation can also rapidly decompose dissolved lignin (Lu et al., 2016). However, the photo degradation of lignin phenols would decrease S/V and increase (Ad/Al)v (Opsahl & Benner, 1998), which differed from our results, suggesting that flocculation dominated the transformation of dissolved lignin composition at moderate discharge.

The CDOM composition was also transformed significantly along the river at moderate discharge. Compared with the findings at high discharge, the $S_{275–295}$ was higher and FI was lower at moderate discharge (Figures 5a and 5b). The lower TSM concentration would promote the transmittance of light in water and enhance photo degradation. Photo degradation would lead to an increase of $S_{275–295}$ and decrease of the FI (Hansen et al., 2016; Helms et al., 2008; Yamashita et al., 2013). The observed higher $S_{275–295}$ and lower FI at moderate discharge suggest that photo degradation of CDOM was more intense at moderate discharge. At moderate discharge, the increased $S_{275–295}$ along the river (Figure 5a) suggests a decreasing trend in the DOM molecular weight caused by flocculation (Asmala et al., 2014).

DOM composition was transformed along the river at high discharge. The TSM concentration showed a significant negative correlation with C4/C2 (Figure S1c), indicating that high TSM contents prevented the photo degradation of CDOM. A high concentration of TSM reduced the light intensity by reducing the water's transparency. As the TSM concentrations decreased along the river, photo degradation was enhanced and C4/C2 was increased. The high values of C4/C2 observed downstream indicate that strong photo degradation contributed to the removal of CDOM. Moreover, S/V decreased significantly along the middle to lower reaches at high discharge (Figure 5c), whereas (Ad/Al)v was scattered (Figure 5d). Both photo degradation and microbial degradation can decrease S/V, whereas (Ad/Al)v increases with the photo degradation process, and the impact of microbial degradation on (Ad/Al)v varies among studies (Benner & Kaiser, 2011; Lu et al., 2016; Opsahl & Benner, 1998). The scattered (Ad/Al)v and decreased S/V suggest that both photo degradation and microbial degradation affect the DOM composition.

The degradation of CDOM and dissolved lignin was coupled at high discharge. At high discharge, the FI decreased along the Changjiang River (Figure 5b), suggesting increased CDOM degradation along the river. The P/(V+S) increased along the river (Figure S3), suggesting increasing degradation of lignin phenols by microbial activity (e.g., brown-rot fungi, Dittmar & Lara, 2001). The FI of CDOM was significantly negatively correlated with the P/(V+S) of dissolved lignin phenols (Figure 6a), which indicates that the degradation of CDOM and lignin phenols was closely related and microbial degradation may play an important role in DOM degradation at high discharge. The lack of correlation between the FI and P/(V+S) at moderate discharge may be explained by the higher primary production at moderate discharge. The phytoplankton-derived materials may contain CDOM and p-hydroxyl phenols (Yamashita et al., 2008; Yu et al., 2011). The strong positive correlation between the $S_{275–295}$ values and DHBA/V (Figure 6b) also suggested that CDOM and lignin phenols degraded simultaneously at high discharge.

The flocculation at high discharge was much weaker than at moderate discharge (Figure S4). The average flow velocity reported along the Changjiang River was 1.70 m/s at high discharge, with a range of 0.20–2.55 m/s (Guo & He, 2014). Here, we assume that for the same station under different hydrological conditions, the flow velocity was in proportion with the water discharge. The calculated flow velocity at moderate discharge was slower than 1.0 m/s (range from 0.14 to 0.71 m/s). In the Changjiang River, the accretion of velocity would promote flocculation when the flow velocity was slower than 1.0 m/s, whereas the flocs would break up once the velocity surpassed 1.0 m/s (Guo & He, 2014). At high discharge, the fast flow velocity limited the removal of DOM through flocculation.

At moderate discharge, flocculation and photo degradation dominated the transformation of DOM, with flocculation primarily altering the composition of dissolved lignin and photo degradation primarily altering the composition of CDOM. Whereas at high discharge, photo degradation and microbial degradation dominated the transformation of DOM, and the degradation of CDOM was closely coupled with the degradation of dissolved lignin.

4.3. Linking the Optical and Chemical Properties of DOM

Previous studies have shown the potential for utilizing CDOM measurements to estimate the flux of DOC (Hernes et al., 2008; Lambert et al., 2015; Spencer, Aiken, et al., 2009; Spencer et al., 2008), and such a relationship is observed in areas where mixing is strong and the DOC and CDOM gradients are high, such as in estuaries where riverine terrestrial DOM mixes with coastal DOM. However, in this study, the DOC concentrations of the Changjiang River were relatively low and the concentration gradient was quite narrow (Table 3). For all samples collected during moderate and high discharges, the a_{254} was strongly correlated with DOC concentration (Figure S5). The experiential formula for calculating DOC from CDOM concentrations in the Changjiang River was obtained with the method of linearity regression (DOC (mg/L) = 0.11 × a_{254} (m^{-1}) + 0.36; $r^2 = 0.681$, $p < 0.001$; Figure S5), thus demonstrating the feasibility of using the optical properties of DOM to assess the bulk DOC concentrations in the Changjiang River.

At high discharge, the CDOM concentrations showed a robust correlation with the dissolved lignin concentrations. The linearity regression equations between a_{254} and Σ6 were established. At high discharge, Σ6 (mg/L) = 1.32 × a_{254} (m^{-1})−6.62 ($r^2 = 0.555$, $p = 0.005$; Figure 6c), suggesting the potential of utilizing CDOM as a proxy for dissolved lignin at high discharge. The intercept of the regression lines on the horizontal ordinate indicates that the absorbance of CDOM can be caused by other chromophores in addition to lignin phenols, such as flavins, melanin, and tannins (Stedmon & Nelson, 2015). Moreover, the sum of two humic-like components (C1 and C2) and dissolved lignin concentrations were positive correlated (r^2 = 0.368, $p = 0.048$; Figure 6d), indicating that lignin phenols constitute an important part of the humic fluorescent components at high discharge. Stubbins et al. (2014) illustrated that a humic-like peak C (C2 in this study) was correlated with lignin-derived phenols. Boyle et al. (2009) also concluded that the optical properties commonly associated with terrestrial humic substances and CDOM arise primarily from an ensemble of partially oxidized lignin phenols. This study represents a first attempt to establish the linkage between CDOM and dissolved lignin phenols in the Changjiang River. The established correlations are important because they indicated that CDOM, which can be measured rapidly and easily, can be used to quantitatively estimate the dissolved lignin concentrations and fluxes. To more accurately estimate dissolved lignin with CDOM, additional data are required to predict and calibrate the equation.

Both the absorbance and fluorescence of CDOM were not correlated with the dissolved lignin concentrations at moderate discharge (Figures 6c and 6d). The longer water residence time resulted in more extensive degradation of DOM at moderate discharge. Photo degradation dominated the degradation of CDOM, whereas flocculation dominated the variation of dissolved lignin. The decoupled degradation processes result in the absence of a monotonic relationship at the moderate discharge. In addition, phytoplankton released lignin-free CDOM into the water (Yamashita et al., 2008); thus, the high in situ production of phytoplankton also contributed to the decoupling of CDOM and dissolved lignin at moderate discharge.

4.4. DOM Fluxes in the Middle to Lower Reaches

It is essential to calculate the groundwater DOM flux in order to calculate the DOM fluxes in the middle to lower reaches of the Changjiang River. Groundwater DOM has been subject to extensive modification processes (e.g., sorption/desorption and microbial degradation), and it flows through deep soil horizons with low organic matter content (Matiasek et al., 2017; Ward et al., 2017), and groundwater DOM contains more amino sugar-like compounds while river water contains more lignin-like compounds (Stegen et al., 2018). Thus, the dissolved lignin concentration in groundwater is much lower than that in river water. Based on the lignin and DOC concentrations reported in Shen et al. (2015), the average lignin/DOC proportion by weight was 0.033% in groundwater. Since the groundwater samples were only sufficient to analyze DOC and CDOM and insufficient to analyze dissolved lignin, we use the DOC flux of groundwater and the average lignin/DOC proportion in groundwater to calculate the dissolved lignin flux of groundwater.

The DOM flux of groundwater was calculated with two different end-members to evaluate the proportion of groundwater transport to the middle to lower reaches. The first calculation used groundwater samples collected at the Tongtan Station, and the groundwater transported 0.34×10^9 g/day of DOC, 0.11×10^6 g/day dissolved lignin, and 1.76×10^9 m^2/day of CDOM (a_{254}) to the middle to lower reaches at moderate discharge (Table S4 and Figure 7). The DOC flux of groundwater was higher than the fluxes of tributaries, indicating that groundwater is a nonnegligible source of DOM to the middle to lower reaches, especially during the moderate charge period. The second calculation used the average DOC and CDOM concentrations of groundwater sampled in the Jianghan Plain (2.33 mg/L and 10.06 m^{-1}; Huang et al., 2015), which is located in the Changjiang River basin. The DOC, dissolved lignin, and CDOM (a_{254}) fluxes of the groundwater at moderate discharge were 1.05×10^9 g/day, 0.34×10^6 g/day, and 4.53×10^9 m^2/day (Table S4 and Figure 7), respectively, which are higher than the former calculation results based on Tongtan groundwater. The high DOM fluxes of groundwater, especially the high DOC and CDOM fluxes, suggest that the lignin-depleted groundwater plays an important role in the alteration of the riverine DOM composition. Thus, additional studies about groundwater DOM should be performed to gain a better understanding of its role in the regional carbon cycle.

River water seeped into aquifers at high discharge, and the discharge was only approximately a tenth of the flux at the moderate discharge period, which resulted in a relatively low DOM flux of groundwater at high discharge. The DOC, dissolved lignin, and CDOM (a_{254}) fluxes seeping to the groundwater at high discharge were 0.03×10^9 g/day, 0.01×10^6 g/day, and 0.16×10^9 m^2/day respectively, which were estimated based on the groundwater collected at Tongtan Station (Table S4 and Figure 7). The other estimation based on the groundwater in the Jianghan Plain indicated that 0.09×10^9 g/day of DOC, 0.03×10^6 g/day of dissolved lignin, and 0.40×10^9 m^2/day of CDOM (a_{254}) seep into groundwater at the high discharge period (Table S4 and Figure 7). However, Dongting Lake transported 1.99×10^9 g/day of DOC, 14.32×10^6 g/day of dissolved lignin, and 16.87×10^9 m^2/day of CDOM (a_{254}) to the middle to lower reaches (Table S4), which were approximately 26%, 31%, and 29% of the total input of the middle to lower reaches, respectively. During the high discharge period, Dongting Lake played a more important role in altering the riverine DOM. Groundwater and Dongting Lake served as important regulators under the different hydrological conditions.

Based on the transformation of the DOM composition, we infer that at moderate discharge, flocculation and photo degradation dominate the removal of DOM and resulted in the loss of 6.1% DOC, 32.3% dissolved lignin, and 0.8% CDOM (a_{254}), whereas at high discharge, microbial degradation and photo degradation were the major removal processes and resulted in the loss of approximately 17.0% DOC, 24.2% dissolved lignin, and 14.5% CDOM (a_{254}) (Table S4 and Figure 7). The removal proportion of dissolved lignin was higher at moderate discharge (Table S4), which can be explained by the longer water residence time and more extensive degradation processes during transport along the river. However, the removal proportions of DOC and CDOM were lower at moderate discharge (Table S4), which may be explained by the large water discharge from the groundwater and the high in situ production at moderate discharge. Since groundwater accumulates more amino sugar-like rather than lignin-like compounds and autochthonous DOM contains more labile rather than recalcitrant matter (Stegen et al., 2018; Yamashita et al., 2008), both groundwater and in situ production may add lignin-depleted DOM to the water. The addition of groundwater DOM and autochthonous DOM under moderate discharge altered the composition and reactivity of the riverine DOM. The

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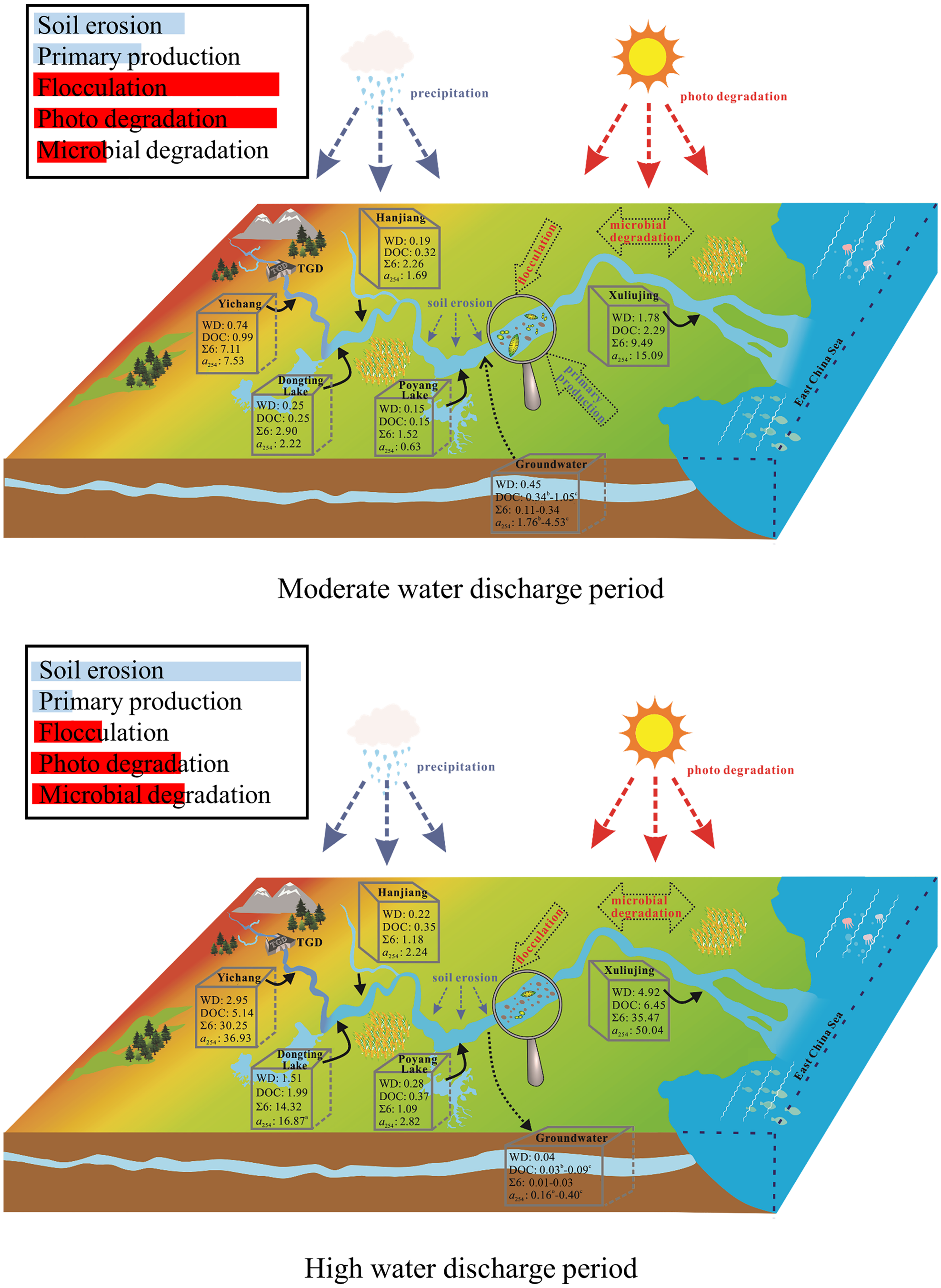

Figure 7. The conceptual model of the sources and transformation processes of terrestrial DOM in Changjiang River drainage basin during the moderate and high water discharge periods (WD: water discharge, 10^9 m^3/day; DOC: 10^9 g/day; Σ6: 10^6 g/day; a_{254}: 10^9 m^2/day).

responses of different DOM compositions (CDOM and dissolved lignin) with different sources and reactivities were significantly different at moderate and high discharges in the Changjiang River.

5. Conclusions

The riverine transport of terrestrial DOM is an important process in the global carbon cycle. Here, we reported a detailed investigation of the chemical and optical properties of DOM within the Changjiang River under different hydrological conditions. In the Changjiang River, the DOC and CDOM concentrations at high discharge were higher than that at moderate discharge because of the higher soil erosion. At moderate discharge, high in situ production contributed to the labile tyrosine-like component C3, and large discharge from groundwater added lignin-depleted DOM into the water. This study indicates that both soil erosion and in situ production are important sources of DOM in the Changjiang River and groundwater served as an important regulator during the moderate discharge period.

In our study, flocculation and photo degradation dominate DOM degradation at moderate discharge, while photo degradation and microbial degradation dominate DOM degradation at high discharge. At moderate discharge, the elevated S/V and decreased (Ad/Al)v along the river demonstrated that flocculation altered the DOM source information and dominated the degradation of dissolved lignin. The $S_{275-295}$ values also increased along the river, indicating the impact of photo degradation on CDOM. At high discharge, the negative correlation between P/(V+S) and FI and the positive correlation between DHBA/V and $S_{275-295}$ indicated that the degradation of dissolved lignin and CDOM were closely coupled at high discharge. The S/V ratio decreased along the river, whereas (Ad/Al)v was scattered, indicating the impact of both microbial degradation and photo degradation.

Understanding the linkage between the chemical and optical properties of DOM under different hydrological conditions is crucial and low-cost optical techniques can be used to estimate DOM chemical properties. In this study, we first attempt to link CDOM with DOC and dissolved lignin in the Changjiang River. The dissolved lignin concentrations were positively correlated with CDOM absorbance and fluorescence at high discharge, whereas dissolved lignin and CDOM were decoupled at moderate discharge. The correlation between CDOM and dissolved lignin highlights the potential to quantitatively estimate dissolved lignin from CDOM measurements.

At moderate discharge, the Changjiang River transported 2.29×10^9 g/day of DOC, 9.49×10^6 g/day of dissolved lignin, and 15.09×10^9 m^2/day of CDOM to the East China Sea; in addition, 6.1% of DOC, 32.3% of dissolved lignin, and 0.8% of CDOM (a_{254}) were degraded in the middle to lower reaches. At high discharge, the river transported 6.45×10^9 g/day of DOC, 35.47×10^6 g/day of dissolved lignin, and 50.04×10^9 m^2/day of CDOM to the East China Sea; in addition, 17.0% of DOC, 24.2% of dissolved lignin, and 14.5% of CDOM (a_{254}) were degraded in the middle to lower reaches. At moderate discharge, due to the long residence time and extensive degradation, the removal proportion of recalcitrant lignin was higher; however, the contribution from groundwater and in situ production altered the riverine DOM and resulted in lower removal proportions of DOC and CDOM. The responses of different DOM compositions (CDOM and dissolved lignin) with different sources and reactivities were significantly different during different hydrological conditions.

Hydrographic processes regulated by precipitation and dam operations influence the sources and compositions of DOM, whereas flocculation, photo degradation, and microbial degradation exert secondary controls on the fate of DOM in the Changjiang River. Moreover, the aquatic networks within a watershed, such as lake systems or groundwater, could play important roles in the alteration of DOM.

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