Impact of the Three Gorges Dam on the Quality of Riverine Dissolved Organic Matter

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Abstract

The Three Gorges Dam (TGD) is the largest hydropower facility in the world, influencing the riverine hydrology and mass flux in the Yangtze River. Little is known about its impact on the riverine dissolved organic matter (DOM) quality. In this work, the water quality and DOM quality for water samples collected from the upstream and downstream sites of TGD were investigated. The presence of TGD significantly affects the quantity and quality of DOM but has no pronounced effect on nutrient concentrations. Upstream DOM had higher concentration but lower average molecular weight and aromaticity than the downstream DOM. The biological processes in the dam reservoir contribute significantly to upstream DOM. In the downstream sites, terrestrial DOM input raises the average molecular weight and aromaticity of the overall DOM pool. These results suggest that TGD will influence not only the mass flux of organic carbon but also its quality and lability, which has both environmental and ecological significance.

Dissolved organic matter (DOM) is a heterogeneous mixture of aromatic and aliphatic hydrocarbons with abundant functional groups. It originated from biological processes in the aquatic systems and the terrestrial input. Ubiquitous in aquatic systems, DOM is the natural sorbent and carrier for pollutants, affecting their fate, transport, and bioavailability in the environment (Aiken et al. 2011; Liu et al. 2019). It is also the key player in the cycling of carbon and nutrients, being an important ecological indicator (Williams et al. 2010; Tranvik et al. 2009). The quality of DOM controls its interactions with pollutants as well as its lability (Liu et al.

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2019; Gu et al. 2011; Helms et al. 2013). Thus, structural characterization of DOM is the key step for understanding its environmental and ecological significance and implications.

Dams and hydropower facilities are known to alter the riverine hydrology and the flux of nutrients and sediment (Humborg et al. 1997; Nilsson et al. 2005). Its influence on the quality of riverine DOM is still not clear. Several studies investigated the upstream or downstream effect of dams on DOM quality (Sun et al. 2017; Nadon et al. 2015). The biological contribution to DOM in the upstream increased with decreasing distance to the dam (Sun et al. 2017). On the other hand, DOM quality was reported to remain fairly stable at downstream sites of dams (Nadon et al. 2015). There is one study compared DOM quality between the upstream and downstream sites of a dam (Nadon et al. 2015). The authors found that the presence of the dam has no significant influence on DOM quality (Nadon et al. 2015). The result was attributed to the fact that natural variation is more significant than the potential dam effect. The Three Gorges Dam (TGD) is the largest hydropower facility in the world with an installed capacity of 22,500 MW. The dam has a height of 181 m and a gigantic reservoir storing > 39 km^3 water (Nilsson et al. 2005). This megaproject may potentially influence the quality of DOM to downstream ecosystems in the Yangtze River. Nevertheless, there is a lack of comparisons

of DOM quality in the upstream and downstream regions of TGD to examine the dam effect.

In the present study, we investigated the impact of TGD on DOM quality in the Yangtze River. Water samples were collected from both the upstream and downstream sites of TGD. Their DOM properties were examined using spectroscopic methods. Our main objective was to reveal the potential impact of TGD on DOM quality by comparing the DOM structural indices between upstream and downstream samples. The result will provide insights on the impact of hydroelectric waterpower facilities on riverine ecosystems.

Materials and Methods

Water samples were collected from the upstream and downstream sites of TGD in the Yangtze River from 2019/4/18 to 2019/4/21. The detailed geographical distribution of sample sites are shown in Fig. 1 and Table S1. The water samples collected at the upstream sites were named as US1 to US13, and those collected at the downstream sites were named as DS1 to DS12. The in-situ water quality parameters, including temperature, dissolved oxygen, conductivity, pH, oxidation reduction potential, and turbidity, were measured using a portable multi-parameter water quality probe (YSI Instrument® EXO2, USA). A summary of the in-situ water quality data can be found in Table S1. The water samples were filtered through a 0.45-μm membrane (Pall, USA) and transported to the lab on ice within 2 days for further analysis. Dissolved organic carbon (DOC) of the water samples was measured by a total organic carbon analyzer (vario TOC, Elementar, Germany). Chlorophyll-a of the water samples was measured colorimetrically according to a previous study (Visscher and Taylor 1993). T-P was measured according to the Chinese National Standard GB/T 11,893–1989. Phosphate, T-N, NH_3-N and NO_3-N were measured according to the National Environmental Protection Standards of China HJ 669–2013, HJ 636–2012, HJ 535–2009, and HJ 84–2016, respectively.

UV–Vis absorbance spectra of the water samples were measured using an UV-2700 UV–Vis spectrophotometer (SHIMADZU, Japan) in a 1-cm quartz cuvette. Specific UV absorbance, $SUVA_{254}$, was calculated by dividing the absorption coefficient at 254 nm by the DOC of the water sample (Weishaar et al. 2003). Spectral ratios, including E_2/E_3 and E_3/E_4, were calculated from the ratio of absorption at 250 to that at 365 nm and the ratio of absorption at 300 to that at 400 nm, respectively (Peuravuori and Pihlaja 1997; Abbt-Braun et al. 2004). The absorption coefficient was determined as $a(\lambda) = 2.303 \times A/l$, where $a(\lambda)$ is the absorption coefficient at wavelength λ (nm), A is the absorbance, and l is the cuvette path length (m) (Green and Blough 1994, Helms et al. 2008). Spectral slope, S_R, was obtained from

the equation: $a(\lambda) = a(\lambda_0) e^{-S(\lambda-\lambda_0)}$ (Briucaud et al. 1981), where $a(\lambda)$ and $a(\lambda_0)$ are the absorption coefficients at wavelength λ and λ_0 (nm), respectively. $S_{275–295}$ and $S_{350–400}$ were calculated over the range of 275–295 nm and 350–400 nm, respectively (Helms et al. 2008). S_R was calculated by dividing $S_{275–295}$ by $S_{350–400}$.

The fluorescence spectra of the water samples were measured using a fluorescence spectrophotometer (Aqualog®, Horiba, Japan) in a 1-cm quartz cuvette. The fluorescence index (FI) was calculated as the ratio of the fluorescence intensities at emission wavelengths of 450 nm and 500 nm at an excitation wavelength of 370 nm (Mcknight et al. 2001; Cory and Mcknight 2005). The biological fluorescence index (BIX) was calculated as the ratio of the fluorescence intensities at emission wavelengths of 380 nm and 430 nm at an excitation wavelength of 310 nm (Huguet et al. 2009; Du et al. 2018). The freshness index (β/α) was calculated by dividing fluorescence intensity at emission wavelength of 380 nm by the maximum value of fluorescence intensity from 420 to 435 nm at an excitation wavelength of 310 nm (Wilson and Xenopoulos 2009). The humification index (HIX) was calculated as the ratio of the integrated emission intensity from 435 to 480 nm and the sum of integrated emission from 300 to 346 nm and that from 435 to 480 nm at an excitation wavelength of 254 nm (Du et al. 2018; Kalbitz et al. 1999).

The differences of spectroscopic indices between the upstream DOM and downstream DOM groups were examined using Student's t-test. Principal component analysis (PCA) was applied to further reveal the differences between the upstream and downstream DOM samples. PCA analysis was conducted using MATLAB_R2015b. Significance levels can be divided into not significant ($p > 0.05$), significant (*, $0.05 > p > 0.01$) and highly significant (**, $p < 0.01$) (Yao et al. 2011).

Results and Discussion

The water quality parameters of the collected samples were summarized in Table S2, Fig. S1 and Fig. 2. The DOC values of water samples varied from 5.25 mg/L to 12.87 mg/L, generally agree with the average DOC values previously reported near the TGD (1.05 mg/L to 10.20 mg/L) (Jiang et al. 2018a). The DOC values of upstream and downstream water samples were 8.33 ± 2.08 mg/L and 6.06 ± 0.43 mg/L, respectively. DOC of upstream samples was significantly higher than downstream samples ($p < 0.05$). Total phosphorus (T-P) and total nitrogen (T-N) are good indicators of water eutrophication conditions (Liu et al. 2010; Wu et al. 2018). The T-N/T-P ratio varied from 28.4 to 68.7, which is relatively high. Thus, T-P is expected to be the major limiting factor for algal growth in the Yangtze River near the

Fig. 1 Sampling sites in the upstream and downstream regions of the Three Gorges Dam in Yangtze River
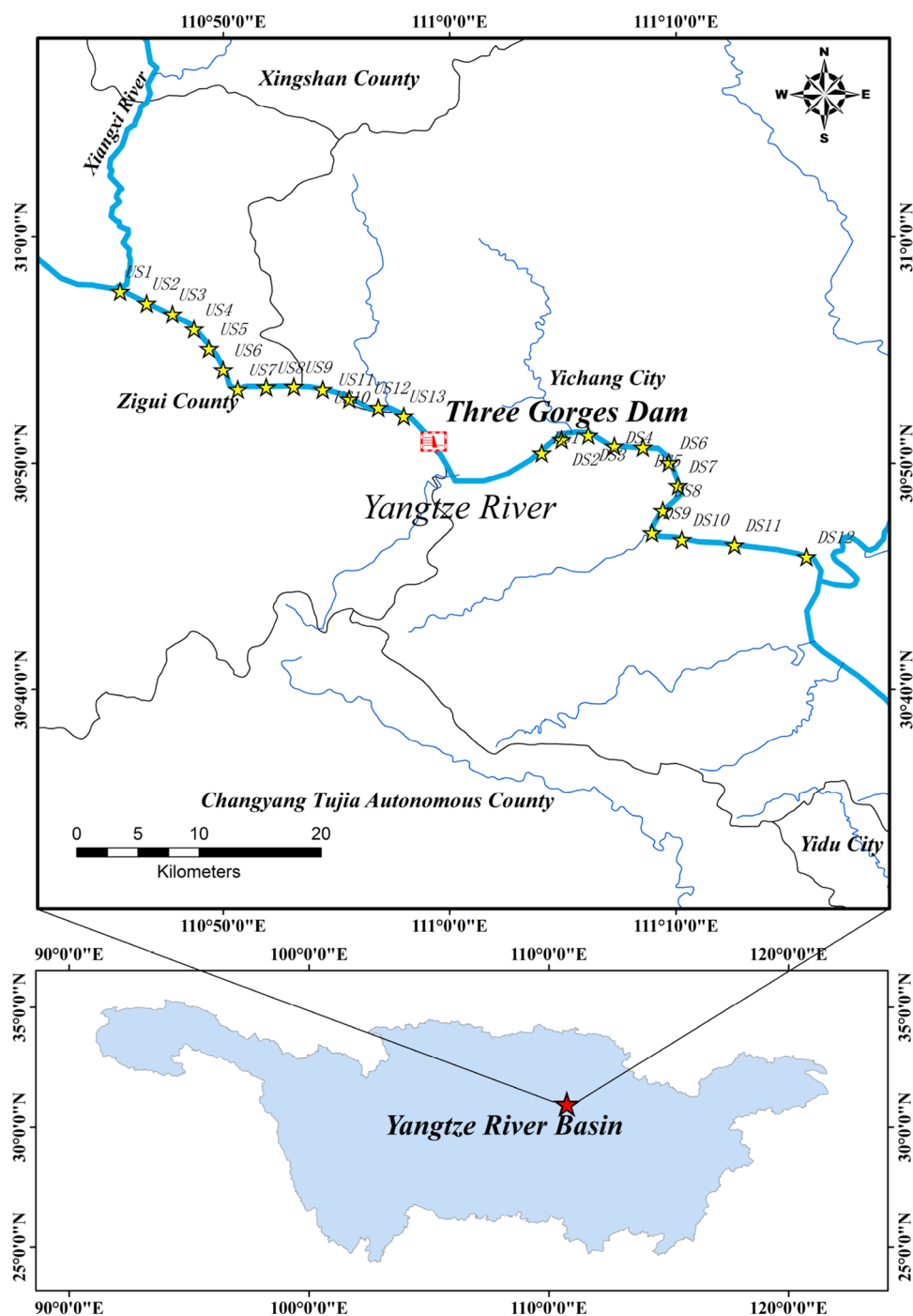
TGD (Downing and McCauley 1992; Guildford and Hecky 2000; Elser et al. 2009). The nutrient concentrations, including T-P, T-N, phosphate, NH_3-N and NO_3-N, were not significantly different between upstream and downstream water samples ($p > 0.05$). Overall, the TGD had minimal effect on the nutrient concentrations.

The structural characteristics of DOM were first examined using absorbance spectroscopy (Table S3). A suit of absorbance indices, including $SUVA_{254}$, E_2/E_3, E_3/E_4, $S_{275-295}$, $S_{350-400}$, and S_R were compared between upstream and downstream DOM samples (Fig. 3). Among these indices, significant difference was found for $SUVA_{254}$ ($p < 0.05$). $SUVA_{254}$ values of all water samples varied from 0.483 to 1.215 L mg^{-1} m^{-1}. These values are within the typical range of freshwater $SUVA_{254}$ values (Jiang et al. 2018a, 2017; Mash et al. 2004; Wei et al. 2008; Gueguen et al. 2012). $SUVA_{254}$ was reported to have a positive correlation with the average molecular weight and aromaticity of DOM
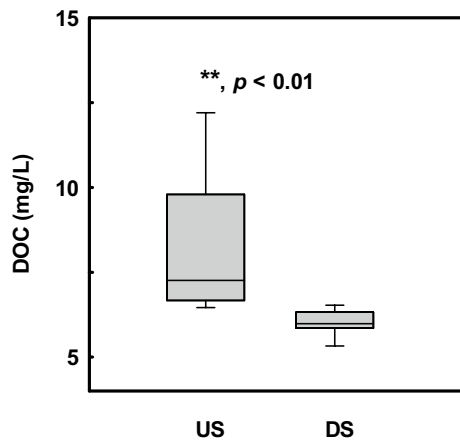
Fig. 2 The DOC was compared between upstream (US) and downstream (DS) sampling sites of the Three Gorges Dam. Line represents median, box upper and lower bound represent 25% and 75% values, and whiskers represent 10% and 90% values

molecular weight and aromaticity of upstream DOM was lower than downstream DOM. The lower average molecular weight and less aromatic portion of DOM pool was often linked to biological processes (Hur et al. 2007). Consistently, a previous study reported that phytoplankton contributes significantly to the DOM in the dam reservoir (Sun et al. 2017). The significant biological processes of TGD reservoir caused by long hydraulic retention time lead to the lower average molecular weight and aromaticity of upstream DOM. There was no significant difference of E_2/E_3, E_3/E_4, $S_{275-295}$, $S_{350-400}$ and S_R for upstream and downstream DOM ($p > 0.05$). Nevertheless, upstream DOM was expected to be more heterogeneous than downstream DOM as suggested by its wider value ranges of these indicators. The results show initial evidence that TGD can influence the quality of riverine DOM.

The structural characteristics of DOM were then examined using fluorescence spectroscopy (Table S4). The fluorescence indices, including BIX, FI, β/α, and HIX, were compared between upstream and downstream DOM samples (Fig. 4). BIX and FI of upstream and downstream DOM were found to be significantly different. These two indices have been widely used to determine the relative contribution of DOM with autochthonous and allochthonous origins. DOM
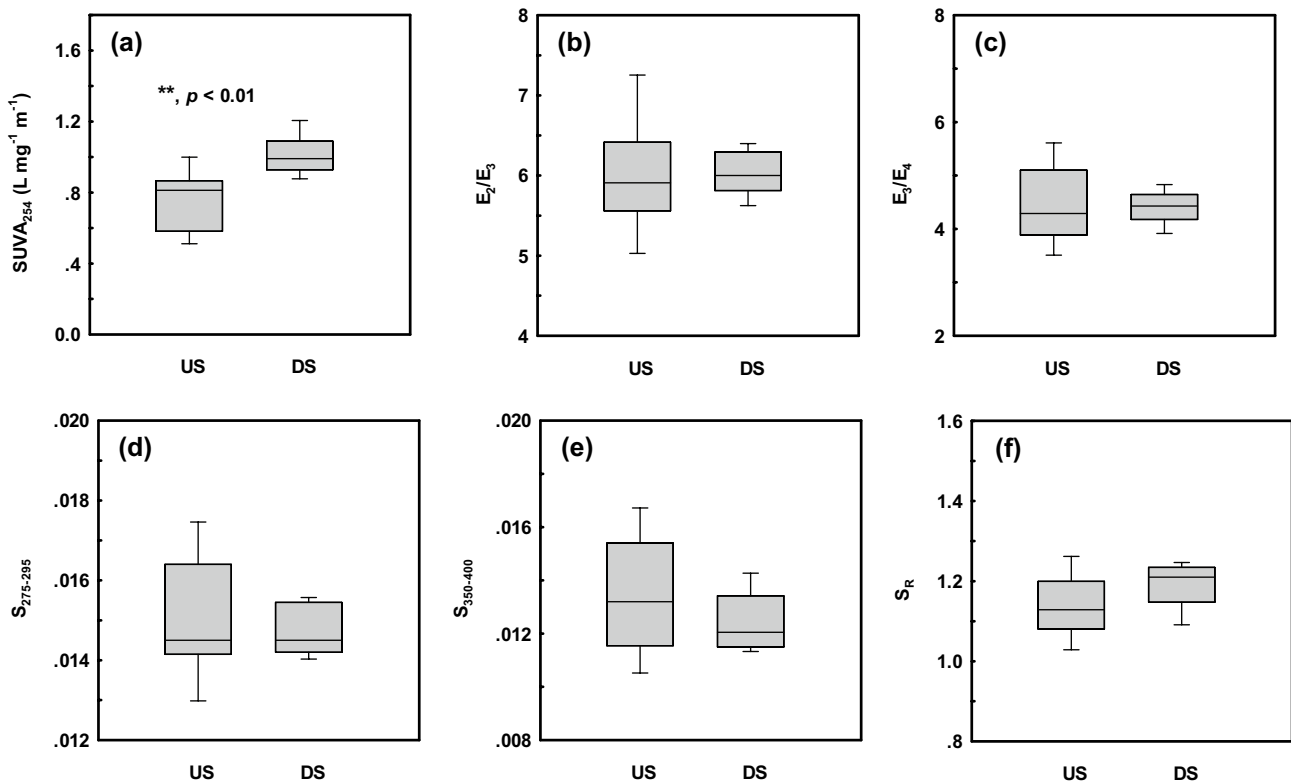
(Weishaar et al. 2003; Du et al. 2018). $SUVA_{254}$ of downstream samples was 1.010 ± 0.109 L mg^{-1} m^{-1}, remarkably higher than those of upstream samples, 0.755 ± 0.169 L mg^{-1} m^{-1} ($p < 0.01$, Fig. 3a). This indicates that the average

Fig. 3 The UV–Vis spectroscopic indices of DOM in natural waters were compared between upstream (US) and downstream (DS) sampling sites of the Three Gorges Dam. Line represents median, box upper and lower bound represent 25% and 75% values, and whiskers represent 10% and 90% values

Fig. 4 The fluorescence spectroscopic indices of DOM were compared between upstream (US) and downstream (DS) sampling sites of the Three Gorges Dam. Line represents median, box upper and lower bound represent 25% and 75% values, and whiskers represent 10% and 90% values
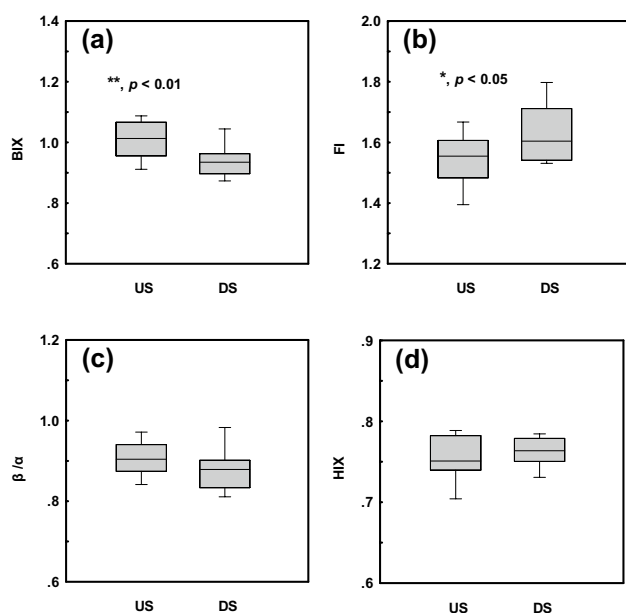

Fig. 5 Principal component analysis of absorbance and fluorescence indices of upstream (stars) and downstream (circles) DOM groups

with BIX in the range above 1.0 is considered to be predominately autochthonous; while that with BIX in the range of 0.6–0.7 has allochthonous origin (Huguet et al. 2009). The autochthonous DOM usually has FI values in the range of 1.7–2.0; while the allochthonous DOM in the range of 1.2–1.5 (Mcknight et al. 2001). The BIX values of all water samples range from 0.868 to 1.088, suggesting that they have more autochthonous characteristics, consistent with previous reports (Sun et al. 2017; Wang et al. 2019; Jiang et al. 2018b). The average BIX value of upstream DOM is 1.008, indicating the strong biological origin of DOM in the upstream (Huguet et al. 2009; Jiang et al. 2018b). It is significantly higher than downstream DOM ($p < 0.01$). The result suggests that upstream DOM contains more autochthonous components than downstream DOM. Consistently, the freshness index (β/α), as an indicator for the contribution of newly produced DOM (Wilson and Xenopoulos 2009), shared the similar trend as BIX, although not significant. The result agrees with the lower SUVA$_{254}$ observed for upstream DOM. The FI values of all samples range from 1.379 to 1.804, falling in the typical range of freshwater FI values (1.4–1.9) (Mcknight et al. 2001; Wang et al. 2019). FI of upstream DOM is significant lower than downstream DOM ($p < 0.05$). Based on the value ranges, this could be taken as evidence for the more abundant autochthonous components in downstream DOM, contradict to the BIX and SUVA$_{254}$ results. The discrepancy can be attributed to the uncertainty of the FI value ranges for DOM with different origins. For
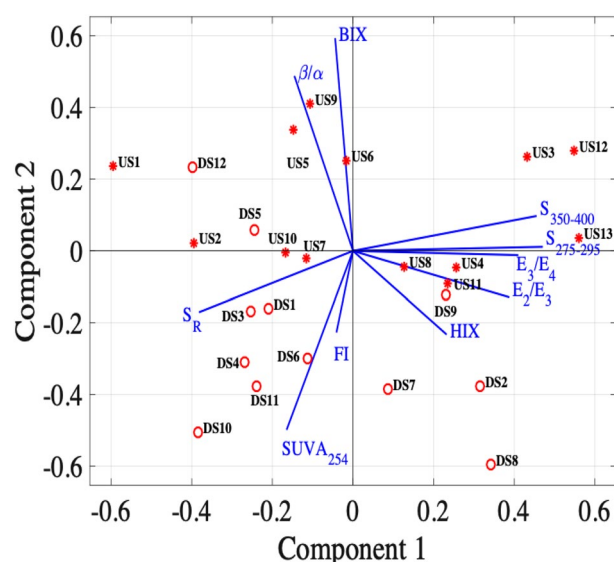
example, in a recent study, it was reported that dissolved black carbon, despite its terrestrial origin and aromaticity, has higher FI values (1.394–1.804) than IHSS aquatic natural organic matter (1.304–1.567) (Du et al. 2018). Another study also pointed out the low sensitivity of FI as an indicator for DOM origins (Jiang et al. 2018b). Thus, we conclude that upstream DOM has more biological components than downstream DOM, which is supported by both SUVA$_{254}$ and BIX indices. Based on the geographical information, it is most likely that upstream samples near deserted canyon area contain rich autochthonous components due to biological processes in the dam reservoir. On the other hand, downstream samples received allochthonous components from the wetlands.

The absorbance and fluorescence indices of upstream and downstream sample groups were subjected to PCA analysis. The PCA scores for all DOM samples are shown in Fig. 5. Principal component 1 (PC1) explained 43.51% of the variance, and principal component 2 (PC2) explained an additional 23.85%. The PCA score plot can generally differentiate the upstream and downstream groups. Upstream DOM samples group on the upper side of the plot, while downstream DOM samples on the lower side. The PCA component loading plot can reflect the impact of indices on the PC1 and PC2 (Fig. 5). BIX and β/α have large positive loadings for PC2. SUVA$_{254}$ and HIX have large negative loadings for PC2. Thus, upstream DOM (upper side of the plot) has higher BIX and β/α, indicating the strong contribution of biological processes. Downstream DOM (lower side of the plot) had higher SUVA$_{254}$ and HIX, suggesting its higher degree of humification and aromaticity. The results are consistent with our previous discussions.

Overall, our results suggest that the TGD had significant impact on both the quantity and quality of riverine DOM mainly due to the changes in riverine hydrology. The upstream DOM samples contained abundant fractions derived from biological processes in the dam reservoir, which is related to the increased hydraulic retention time behind the dam (Mash et al. 2004; Nguyen et al. 2011; Park et al. 2009). Consequently, upstream DOM was more fresh and had lower aromaticity and average molecular weight than downstream DOM. The downstream DOM samples showed more allochthonous features, which can be attributed to the input of terrestrial DOM from the downstream riverine wetlands. The results highlight the profound impacts of TDG on the riverine ecosystem. The alternation of DOM quality due to the interruption of TDG to the riverine longitudinal continuum will change its lability and interactions with chemicals. This process will certainly affect the biogeochemical processes of DOM as well as the bioavailability and fate of pollutants in the downstream region in Yangtze River.

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