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Characterizing DOC sources in China's Haihe River basin using spectroscopy and stable carbon isotopes☆

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ABSTRACT

The Haihe River Basin is a polluted area affected by the developing industry and intensive agricultural activities in China. Dissolved organic matter (DOC) and light-absorbing characteristics of chromophoric dissolved organic matter (CDOM) were monitored in different tributaries of China within the Haihe River basin during spring and autumn. The concentration of DOC during spring was higher than during autumn ($p < 0.01$), and the evaporation was an important factor affecting the concentration of DOC in the basin. By contrast, the proportion of inputs due to terrigenous plants during autumn was higher than during spring. Carbon stable isotope analysis $\delta^{13}C$ and C: N ratio of DOC, evidenced the inputs of DOC in the Haihe River basin from different sources including sewage, terrestrial plants, soil, and plankton. Isotopic analysis of $\delta^{13}C$ and excitation-emission matrix (EEM) with fluorescence regional integration (FRI) analysis supported the hypothesis that allochthonous inputs contributed substantially to the inputs of DOC in the Haihe River basin, coming largely from sewage (9.8%–81.2%) and terrestrial plants (13.3%–65.8%). Depending on the source of DOC and contribution, four types with different EEM spectra were set. Type I, river water from sewage (81.2%); Type II, river water with input from terrestrial plants (65.8%); Type III, river water with plankton (36.4%), and Type IV, river water with soil-derived DOC (33.9%). The results demonstrated that the combined methodology using ^{13}C stable isotope and EEM-FRI can be used to characterize the components of DOC in river waters. This approach was important for tracking the concentration and composition of DOC in river waters from different input sources and for better understanding concerning the local regulation of the terrestrial carbon cycle.

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1. Introduction

In aquatic ecosystems, dissolved organic carbon (DOC) is a key source of energy for driving ecosystem functioning. DOC is sensitive to many processes that drive global changes (Parr et al., 2019). In boreal lakes, an increasing trend of the concentration of DOC is forecasted, with unpredictable influence for the global carbon cycle (Larsen et al., 2011; Monteith et al., 2007; Roulet and Moore, 2006; Worrall et al., 2003). It is now widely recognized that fluvial organic carbon (OC) is an important component in the terrestrial carbon budget (Worrall et al., 2003). Globally, the delivery of OC by rivers to the oceans has been estimated in approximately in 500 Tg per year (Guo and Macdonald, 2006). Against this background, there is a growing interest for understanding the role of OC derived from multiple sources, in coastal and inland systems, in response to global changes (Guo and Macdonald, 2006; Mayorga et al., 2005; Watanabe and Kuwae, 2015). To the extent that the sources of fluvial OC can be identified, key aspects of the terrestrial carbon cycle may be revealed.

The concentration level and composition of DOC can vary considerably, being the result of net effects due to multiple drivers, including change of sulfate deposition with precipitation and temperature, soil sensitivity to acids, the hydrologic conditions in a basin, eutrophication, or the changes in the use of land and management (Artifon et al., 2019; Cool et al., 2014; Dawson et al., 2008; Driscoll et al., 2016; Gavin et al., 2018; Kellerman et al., 2014;

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Monteith et al., 2007; Song et al., 2018a; Zhang et al., 2018). The identification of sources is critical for the control of DOC concentrations in rivers, being subject of several studies. Carbon stable isotope ratio $^{13}C/^{12}C$ in DOC (expressed as $\delta^{13}C$) remains a useful tool for tracking the carbon sources, runoff processes, and flow paths (Minet et al., 2017). In the case of higher plants, these fall into two categories with different $\delta^{13}C$ values (Smith and Epstein, 1971). Municipal sewage contains matter with $\delta^{13}C$ values that differ concerning the background conditions in the receiving environment (Wayland and Hobson, 2001). The challenge lies in being able to identify the different sources of carbon when multiple sources coexist (Breas et al., 2002). To reduce uncertainty, several source apportionment models using $\delta^{15}N$ and $\delta^{18}O$ were developed with different success, while the isotopic analysis of carbon sources should use appropriate statistical tools for data interpretation (Cabral et al., 2019; Kendall et al., 2001; Minet et al., 2017). The $\delta^{13}C$ and C:N ratios were also used to identify the endmember sources of carbon in river water, with success in different environmental scenarios (Albuquerque and Mozeto, 1997; Kendall et al., 2001). More recently, the chromophoric dissolved organic matter (CDOM) parameter was applied to determine the composition of DOM in fluvial systems (Baker, 2001; Dalmagro et al., 2017; Spencer et al., 2007), and as a tracer for both, quantitative and qualitative changes occurring in the DOC pool as a whole (Song et al., 2019; Zhao et al., 2018). It has been shown that the ratio of fluorescence peaks of both humic-like and protein-like components provide the identification of contaminated river waters due to sewage (Henderson et al., 2009). CDOM absorption was associated with the allochthonous components in river water. In eutrophic high-mountain lakes, CDOM fluorescence characteristics were mostly related to the spectral signatures of terrestrial humic-like components (Zhang et al., 2010). Management improvement of the aquatic environment and the terrestrial carbon cycle depends on a better knowledge of the various sources of DOC, concentration, and composition (Mayorga et al., 2005; Zhang et al., 2018).

Although the progress on the optical properties, concentration, sources, cycles, and remote sensing estimations of DOC in different aquatic environments (Artifon et al., 2019; Spencer et al., 2007; Zhang et al., 2010), no significant breakthroughs have yet been made regarding the optical properties and composition changes of DOC in hydrographic basins. Rivers can transport OC to the oceans being a prominent piece in the global carbon cycle (Cole et al., 2007; Tranvik et al., 2009; Raymond et al., 2013). The bulk DOC is predominantly derived from terrestrial plants and from humic and fulvic acids. Various studies have shown that the allochthonous carbon from the watershed often prevails over autochthonous carbon derived from primary producers in streams and rivers; however, it has not been described the quantitative contribution of different DOC sources. During the change of seasons, the optical properties, and the changes in the composition of DOC in rivers may exhibit large fluctuations due to weather conditions, and anthropogenic pressures (Dawson et al., 2008; Mao et al., 2018; Wayland and Hobson, 2001). This study aimed to investigate the composition and sources of DOC during spring and autumn in a large northern highly polluted river system (Haihe River Basin, China), and quantify the contributions of sewage endmember source to DOC in river water in a whole hydrographic net.

The Haihe River Basin, in northeastern China, is a polluted area according to the report presented by the Haihe River Water Conservancy Commission in 2017. The point emissions and diffuse pollution, due to different pressures, including industrial and urban development, and agricultural intensification, aggravate the situation (Xu et al., 2016). There is a need for identifying the carbon sources causing the deterioration of the river. This study addresses the identification of DOC sources and the seasonal influence on the concentration and composition of DOC in the Haihe River basin. The objectives are to (1) explore the seasonal influence and the impact of sewage discharge on the composition of DOC; (2) evaluate the contributions of the allochthonous and autochthonous matter to the total concentration of DOC.

2. Material and methods

2.1. Study sites and sample collection

The Haihe River drains an area of over 320,000 km^2 in northeastern China (Fig. 1), which is an important heavy industry zone. It covers all or parts of 355 counties and districts. In 2010, the total population in the Haihe basin was 1.40×10^8, the total gross domestic production (GDP) was about 1.4×10^{12} RMB (Xu et al., 2016). The basin contains numerous river systems, and the total reserve of surface water resources is about 12.83 billion m^3. The annual average temperature ranges from 1.5 to 14 °C. The annual precipitation is about 539 mm; abundant precipitation takes place in summer.

Water sampling was conducted during spring (April and May 2017) at 59 locations, and during autumn (September and October 2017) at 26 locations in the Haihe River basin (Fig. 1). Table S1 shows a detailed inventory and description of the sampling sites. At each location, sampling was repeated twice in one season. Surface water was sampled at a depth of 0.1–0.3 m. The location of each sampling station was recorded with an UniStrong G3 GPS. At each station, a portable multi-parameter water quality analyzer (YSI 6600, U.S) was positioned 0.1 m below the water surface to determine the following parameters: temperature (°C), specific conductivity (μS/cm), salinity (PSU), and pH value.

2.2. Water quality measurements

Dissolved total carbon (DTC), DOC and total carbon (TC) were analyzed using an analyzer for total organic carbon (TOC-VCPN, Shimadzu Corporation, Japan). Total dissolved nitrogen (TN) and total phosphorus (TP) were analyzed according to APHA et al.

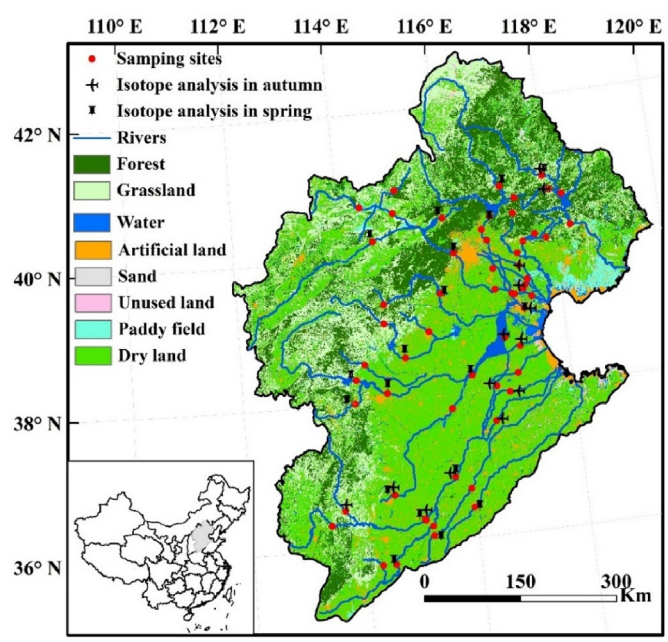

Fig. 1. Study area, locations and sampling sites in the Haihe River basin, China.

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(1998). Chlorophyll-a (*Chl-a*) concentration was determined using an acetone extraction based method and a spectrophotometer (UV−2660PC Shimadzu Inc., Kyoto), details can be found in Wen et al. (2019). During sample collection, Secchi disk depth (SD) was measured at each sampling point and recorded using a black-and-white disk. The trophic state of sampling water stations was evaluated using the Carlson's trophic state index (TSI) (Aizaki et al., 1981; Carlson, 1977; Jaiswal and Pandey, 2019). Detailed information on water quality measurements is provided in the supporting information.

2.3. Carbon stable isotope ($\delta^{13}C$) analysis

Water samples were preserved using paraffin to prevent isotope fractionation. Samples were analyzed in the lab using a Thermo Fisher MAT253 stable isotope-ratio mass spectrometer (precision of ±0.2‰ for $\delta^{13}C$) and the results were expressed in the δ notation according to the Vienna Standard Mean Ocean Water. Stable isotope ratio (δ) is expressed as the deviation from standard in parts per thousand (‰) with the equation, where R is the ratio of $^{13}C/^{12}C$:

$$\delta^{13}C = (R_{sample} \big/ R_{standard} - 1) \times 10^3$$

2.4. CDOM absorption and fluorescence measurements

Details about CDOM absorption, fluorescence and the corresponding measurements of FRI -EEMs can be found in the supporting information and Zhao et al. (2018). Based on FRI analysis, EEM maps were divided into five regions (Table S2). The sum of the fluorescence intensities, divided by these five components is expressed as F_T (unit: nm). The integral volume of each region was expressed by Fi, and the corresponding percentage of fluorescence respect to the total fluorescence intensity as Pi (i = 1, 2, 3, 4, and 5). Besides, the specific UV absorbance at 254 nm ($SUVA_{254}$) is defined as the absorbance at 254 nm (a_{254}) divided by the DOC concentration (mg/g) (Weishaar et al., 2003), which is used to characterize CDOM aromaticity.

2.5. Supporting data acquisition and analysis

Data of the total precipitation and evaporation during spring, summer, and autumn in 2017 was obtained from the National Meteorological Information Center. We used data from a digital elevation model (DEM) and the ArcGIS10.0 software package (Redland, Ca, USA) to delineate the catchment boundaries for the Haihe River basin. The soil organic matter (SOM) data itself was derived from the second national soil census, which was conducted during 1979−1994 (Dai and Huang, 2006; Li et al., 2012). The physiochemical properties of soils, geomorphology, and land use were recorded for each station in this census. In our study, since the SOM percentages for the top 20 cm of the soils were retrieved, they were interpolated using a Kriging algorithm in the ArcGIS10.0 software. After this, an average SOM was calculated by overlaying the catchment boundary of each river on the interpolated map. The land use was obtained from the GLOBELAND 30.

We defined four potential sources: terrestrial source (C3 and C4 plants), SOM, sewage, and autochthonous matter (algal and plankton). The classification according to C:N ratios and $\delta^{13}C$ signatures, for each source has been reported in previous studies (Deines, 1980; Dover et al., 1992; Kendall et al., 2001; Paul, 2007; Rostad et al., 1997; Smith and Epstein, 1971; Wayland and Hobson, 2001). The samples collected during spring and autumn were taken as a whole when we analyzed the proportional contributions of carbon sources to the DOC. Based on the C:N ratio and δ13C signature, river water samples were classified into four types. Stable isotope analysis (IsoSource software) was used to determine the proportional contribution of the potential carbon sources to the bulk DOC, based on $\delta^{13}C$ signature (Phillips and Gregg, 2003; Phillips et al., 2005). ANOVA was conducted to evaluate the seasonal influence, spring versus autumn, on DOC concentration, a_{320}, and $SUVA_{254}$.

3. Results and discussion

3.1. Seasonal variations of DOC concentration in the rivers

The median concentration of DOC in spring was 5.45 mg/L with a range of 0.76−40.04 mg/L; significantly higher than in autumn (4.56 mg/L) ($p < 0.01$) (Fig. 2). Similar variation of DOC was observed in Yukon River (Guo and Macdonald, 2006), where such change was closely related to the environmental conditions. The Haihe River basin distributes in the temperate monsoon climate zone. The river flow is sustained mainly by surface runoff and the tiny amount of groundwater (Xu et al., 2016). This basin received lower levels of precipitation during spring and autumn in 2017 (Fig. S1), and the DOC level in groundwater was much lower than that in the surface runoff (Tao, 1998). The precipitation in spring was lower than in autumn, while the evaporation was relatively higher (Fig. S1 and Fig. S2). This was possibly the product of the evapo-concentration of DOC during spring, resulting in a high mean concentration. Comparing the coefficients of variation of daily flows (CV_Q) of these rivers between spring and autumn, it is shown that the CV_Q values, in most sampling sites, were higher in spring than in autumn (Botter et al., 2013). This means that the flow was more erratic in spring; and spring drought had an important impact on water quality and flow.

Besides, the distribution and seasonal comparison of DOC concentrations in 25 sampling sites (50 data) indicate that most rivers had a higher value in spring than in autumn (Fig. S3). In six sites, the DOC concentration was higher in autumn than in spring (highlighted with black circle in Fig. S3). The change of trophic status, from mesotrophic in spring to eutrophic in autumn, may be the cause of this phenomenon. Carlson's index reflected the eutrophic conditions in most sites during autumn, while in only six sites, water bodies changed the trophic status from mesotrophic

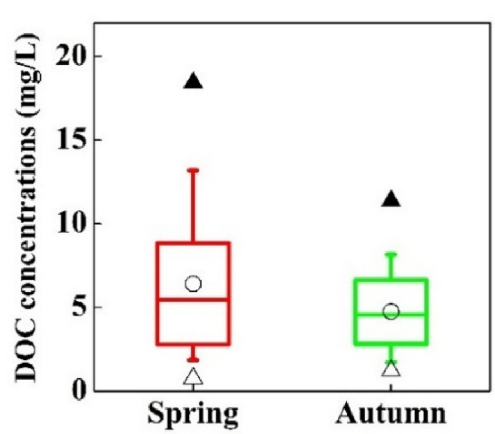

Fig. 2. Box plot of DOC concentrations in the rivers of the Haihe River basin during spring and autumn. The solid line inside the box represents the median and the black circle represents the mean. The horizontal edges of the boxes denote the 25th and 75th percentiles, the whiskers denote the 10th and 90th percentiles, and the solid and hollow triangles represent the max and the min value, respectively.

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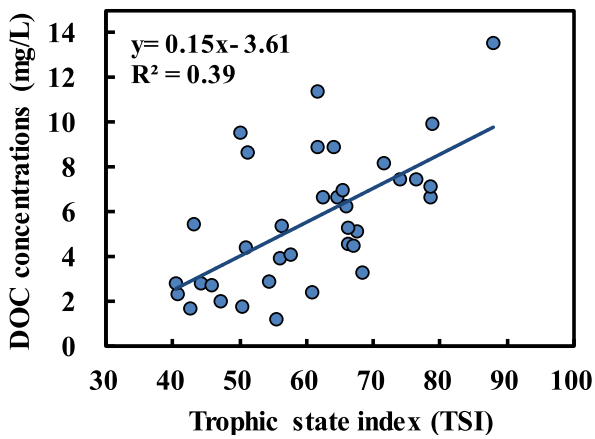

Fig. 3. Relationship between DOC concentrations and TSI.

conditions in spring to eutrophic status in autumn. Recent studies have pointed out that a water body under eutrophic conditions tends to have higher DOC values than meso- and oligotrophic waters (Song et al., 2018b; Sugiyama et al., 2004), because of the release of DOC from phytoplankton during the decay process (Danhiez et al., 2017; Ye et al., 2010). In this study, the positive relationship between DOC concentrations in rivers and TSI proved this assumption (Fig. 3).

3.2. DOC optical characteristics in the Haihe River basin

ANOVA was conducted to evaluate the seasonal influence. The median/mean values of a_{320} exhibited no significant difference between spring and autumn (Fig. 4a). In this regard, there is a growing interest in the use of CDOM parameters to address DOM or DOC composition in different catchments (Song et al., 2019; Spencer et al., 2009; Zhang et al., 2018). The high $SUVA_{254}$ values are related to high input of terrigenous plants, whereas low $SUVA_{254}$ values are associated with low inputs of terrigenous plants (Spencer et al., 2012; Weishaar et al., 2003). The mean $SUVA_{254}$ values ranged from 0.28 to 6.78 mg C^{-1} m^{-1}; Using ANOVA, it was shown that $SUVA_{254}$ (median/mean ± S.D.: 3.43/3.51 ± 1.03 L mg C^{-1} m^{-1}) was significant lower in spring than in autumn (4.72/4.44 ± 1.35 L mg C^{-1} m^{-1}) ($p < 0.01$) (Fig. 4b). This result implies that the DOC may come from different sources depending on the seasonal period. We can infer that the CDOM had more allochthonous sources in autumn than in spring (Weishaar et al., 2003). The higher precipitation in autumn could bring more soil and matter from plants to rivers by surface runoff (Fig. S1), contributing in a lesser portion to the total CDOM during the spring.

Previous studies have shown that CDOM absorption in a range of spectra could be used as a proxy for DOC in many rivers (Griffin et al., 2011; Griffin et al., 2018; Spencer et al., 2010, Zhao et al., 2018). The results in our study once again support this relationship in the river waters of the Haihe River basin. Either in spring or in autumn, the positive relationships between DOC concentrations and a_{320} or a_{254} showed high degree of fitting (R^2) (Fig. 5). The slope of the relationship in autumn was higher than in spring (Fig. 5). Both in spring and in autumn, the R^2 between a_{254} and DOC was higher than R^2 between a_{320} and DOC. The strong relationship between CDOM absorption coefficient and DOC concentration have been reported in various aquatic environments, especially in scenarios dominated by terrigenous inputs contributing to DOM (Hestir et al., 2015, Spencer et al., 2010, Spencer et al., 2012, Zhang et al., 2007; Song et al., 2019). In this study, the relative contribution of terrestrial -like components to F_T of CDOM was higher in autumn than in spring ($p < 0.05$) (Fig. 8). This, in turn, may also lead to a higher R^2 in autumn than in spring (Fig. 5). However, it is not the most important factor for a higher R^2; FDOM only accounted for a small fraction of CDOM. It has been proven that the positive relationship between CDOM and DOC could be affected by the proportion of the biological sources in CDOM (Danhiez et al., 2017; Mannino et al., 2008; Vantrepotte et al., 2015). The dissolved compounds released from phytoplankton in summer may remain in the water, and influence the CDOM absorption in autumn. Furthermore, the photo-degradation process could also modulate the relationship between CDOM and DOC (Cawley et al., 2012; Cory et al., 2015). Sunlight could be rapidly attenuated in high-CDOM waters (Miller, 1998).

Resulting in a relatively low DOC photo-degradation in the water column (Cory et al., 2015).

The a_{320} and $SUVA_{254}$ of CDOM were higher in autumn than in spring (Fig. 4a and b), leading to different relationships between CDOM and DOC depending on the season, having thus different sunlight attenuation in the water.

3.3. Source analysis of DOC in the Haihe River basin

The $\delta^{13}C$ signature showed low variability (ranging from −30.17‰ to −17.21‰ with a median/mean of −27.40‰/-27.03‰, CV = 48%), increasing in autumn (mean value: 24.78‰) and depleting in spring (mean value: 27.65‰) (Fig. 6). For one

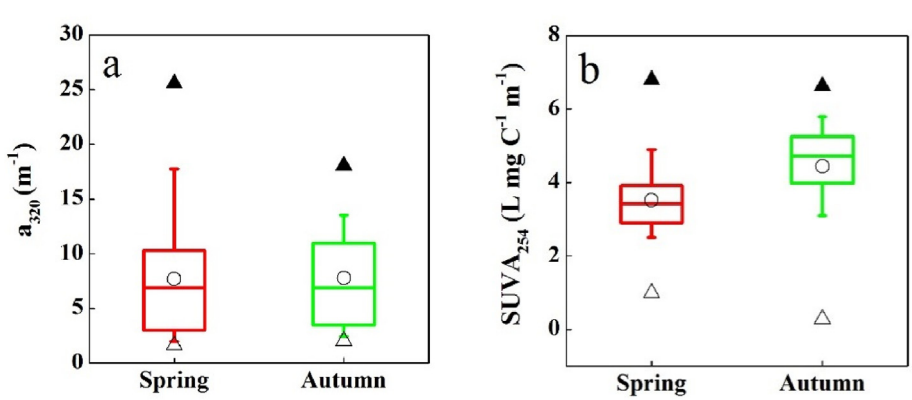

Fig. 4. Seasonal distribution of CDOM absorption coefficient and FRI-extracted CDOM fluorescence components in river waters of the Haihe River basin. The solid line inside the box represents the median and the black circle represents the mean. The horizontal edges of the boxes denote the 25th and 75th percentiles, the whiskers denote the 10th and 90th percentiles, and the solid and hollow triangles represent the max and the min value, respectively. (a) Box plots of CDOM absorption coefficient a_{320}, (b) Box plots of $SUVA_{254}$.

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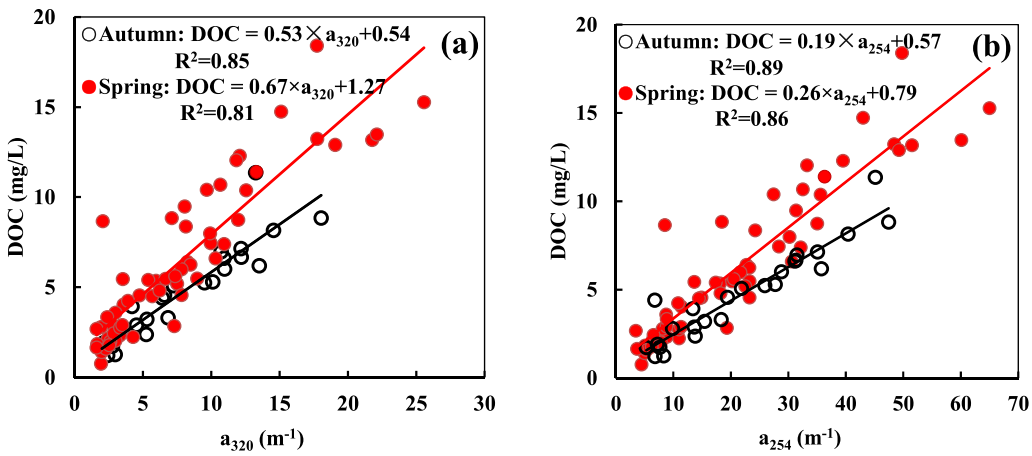

Fig. 5. Relationships between CDOM absorption and DOC concentration; a, between a_{320} and DOC; b, between a_{254} and DOC.

outlier, the spatial difference between the minimum and maximum values of $\delta^{13}C$ was lower than 8‰. There was no significant correlation between $\delta^{13}C$ and DOC concentration neither in spring nor in autumn. The carbon isotopic analysis and C:N ratio provided the identification of four endmember sources of DOC. We divided the four sources into autochthonous sources (plankton) and allochthonous sources (sewage, terrestrial plants, and soil organic materials). It was found that DOC mainly came from the allochthonous sources (Fig. 6). Based on the partition of the C:N and $\delta^{13}C$, river samples were divided into four types: Type I, when the DOC came primarily from the sewage input; Type II, from the input of terrestrial plants; Type III from autochthonous sources, and Type IV from soil erosion (Fig. 6). The percentages of Type II and Type IV were 32.35% and 38.24%, respectively. The percentage of Type I and Type III was 14.71% for each one.

The proportional contribution of each potential carbon source to the DOC in river waters was analyzed based on the $\delta^{13}C$ signature (Fig. 7 and Table S4). The results indicated that 81.2% of DOC in the river samples classified as Type I, came from the sewage input, followed by the input of terrestrial plants (13.3%). While, in those classified as Type II, 65.8% of DOC came from terrestrial plants, followed by the contribution of soil erosion (19.4%). For those Type III, 36.4% of DOC came from autochthonous production, followed by soil erosion (23.5%) and terrestrial plants (22.1%). In the case of Type IV, 33.9% of DOC came from soil erosion, followed by terrestrial plants (29.7%) and sewage input (26.2%). In all the river samples, the allochthonous matter had a significant contribution to the DOC. Previous studies also concluded that watershed inputs were the principal source of organic matter in the river ecosystems (Albuquerque and Mozeto, 1997; Elder et al., 2000). Sewage and terrestrial plants represent the larger contribution of DOC in the rivers of the Haihe River basin (Fig. 7 and Table S4). These results could presumably be due to environmental conditions. The discharge of sewage in the Haihe River basin is in the order of several gigatonnes per year, and increases from year to year (Fig. S4). Although the chemical oxygen demand (COD_{Mn}) in this sewage decreased in the recent years, the water pollution index of the Haihe River basin was still moderate due to the COD_{Mn} discharge in 2017, according to the report on the State of Ecological Environment in China. The close positive relationship between DOC and COD in surface water across China has been reported in the literature (Song et al., 2018a). Indirectly, it has been proved that sewage discharge had an important contribution to the DOC in water, in the Haihe River basin. The findings of our study and from other previous studies suggest that the stable carbon isotope might be an effective tool for tracing organic matter derived from sewage in riverine ecosystems (Lee et al., 2017; France, 1999). However, this method depends to a great extent on the dilution of the effluent in the river and the difference in the order of magnitude of the $\delta^{13}C$ signature between sewage and natural river water (Dover et al.,

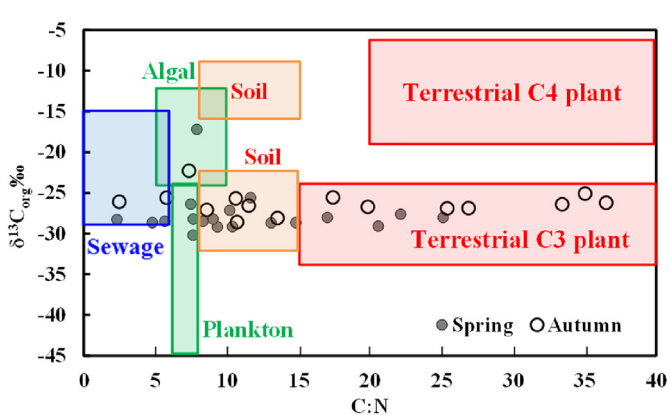

Fig. 6. River water $\delta^{13}C$ signatures and C:N values for the sampling sites. The normal ranges of $\delta^{13}C$ values used in this figure are collected from the following references: (Deines, 1980; Dover et al., 1992; Kendall et al., 2001; Smith and Epstein, 1971; Wayland and Hobson, 2001); The normal ranges of C:N values used in this figure are collected from the references: (Paul, 2007; Rostad et al., 1997).

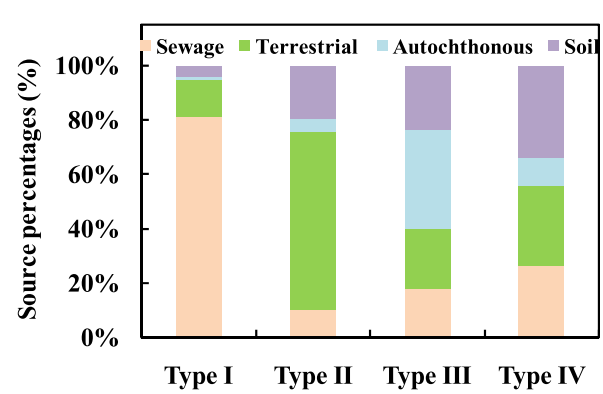

Fig. 7. Proportional contribution (mean value) of each potential carbon source to the DOC in river waters with different types. Type I, river water with a high sewage input; Type II, river water with higher input of terrestrial plants; Type III, river water with higher autochthonous contribution; Type IV, river water with higher soil erosion.

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1992; Wayland and Hobson, 2001).

The Haihe River basin is an area with an intense agricultural activity (Fig. 1). Farmland is accounted for 70.7%, followed by land cover type forest (Fig. 1). The land use and cover can become the underlying cause of the contribution of terrestrial plants in the DOC. The plant litter is often delivered to the river through surface runoff, and leachate of rotting leaves. In the Haihe River basin, the area with plants C3 is higher than that with plants C4 (Table S3), and consequently, the terrestrial input due to C3 plants is higher than that from C4 plants (Fig. 6). The SOM was relatively lower in the Haihe River basin (Fig. S3 b), thus possibly resulting in a low contribution of soil to DOC in the rivers. Besides, although the trophic status for most of the river samples was eutrophic, the contribution due to autochthonous sources was low (Table S3). The flow heterogeneity of the rivers played an important role in the distribution of plankton and persistence (Walks, 2007). The slow-moving waters of the rivers provide favorable habitat for plankton. Statistically, about 60% of the Haihe River basin is characterized by plateaus and mountains, but also by steep terrain and fast flow, which do not favor the persistence of the plankton, and presumably explain the lower contribution of the plankton to DOC.

3.4. Source analysis of CDOM in the Haihe River basin

In this study, the FRI-based EEMs in spring and autumn river waters of the Haihe River basin was analyzed to track the trends in CDOM fluorescence characteristics in relation to seasonal variation (Fig. 8, Fig. S5). F_T ranged from 4.96×10^{10} to 5.98×10^{12} nm for all water samples. The median/mean F_T ($3.49/4.77 \times 10^{11}$ nm) was significantly higher in spring than in autumn ($2.91/3.88 \times 10^{11}$ nm) ($p < 0.01$). The humic acid-like F5 (terrigenous component) dominated the fluorescence composition in the samples collected in both spring and autumn (Fig. 8), being consistent with previous findings (Zhang et al., 2010; Zhao et al., 2017). The correlations between the fluorescence intensity corresponding to the five components were analyzed, resulting in a strong autocorrelation (Fig. S6). Therefore, the five FDOM components were classified into two groups: F_3+F_5 and F_1+F_2+F_4. The terrestrial -like (F3 and F5) accounted (80.89 ± 6.41)% in spring and (87.32 ± 7.94)% in autumn of the F_T (Fig. 8). There was a significant difference in the relative contribution of terrestrial -like components (F3 and F5) to F_T between spring and autumn ($p < 0.05$). The median/mean humification index (HIX) value obtained for the samples collected in spring (5.51/5.94) was lower than those collected in autumn (7.06/7.42) (Fig. 8), evidencing that the allochthonous contribution to CDOM was higher in autumn than in spring (Fig. 8) (Bilal et al., 2010).

The total fluorescent intensities of CDOM and DOC concentrations showed a strong positive linear correlation ($R^2 = 0.75$, Fig. S7). The positive linear relationships were also observed between F_{3+5} and DOC concentrations (Fig. S7 b), and for F_{1+2+4} and DOC concentrations (Fig. S7 c). However, the degree of fitting between $\log F_{3+5}$ and logDOC ($R^2 = 0.725$) was higher than that obtained between $\log F_{1+2+4}$ and logDOC ($R^2 = 0.56$). It has been described the important role of the rivers for transporting the terrestrial carbon into the oceans, being DOC, the bulk part of this carbon (Zhao et al., 2018). In river water, the allochthonous carbon often prevails over the autochthonous carbon (Worrall et al., 2003; Zhao et al., 2017). It may, in part, depend on the flooded land during river flooding period, where some soil materials would be washed down from land into river. Besides, the carbon analysis based on $\delta^{13}C$ signature proved that the contribution due to the inputs derived from soil and the terrestrial matter represent the main source of DOC in rivers (Fig. 7).

The four types of river samples showed different EEM fluorescence spectra (Fig. 9, Fig. S1). F_T decreased from 6.22×10^{11} nm to 1.97×10^{11} nm for four types with the highest value in Type I and

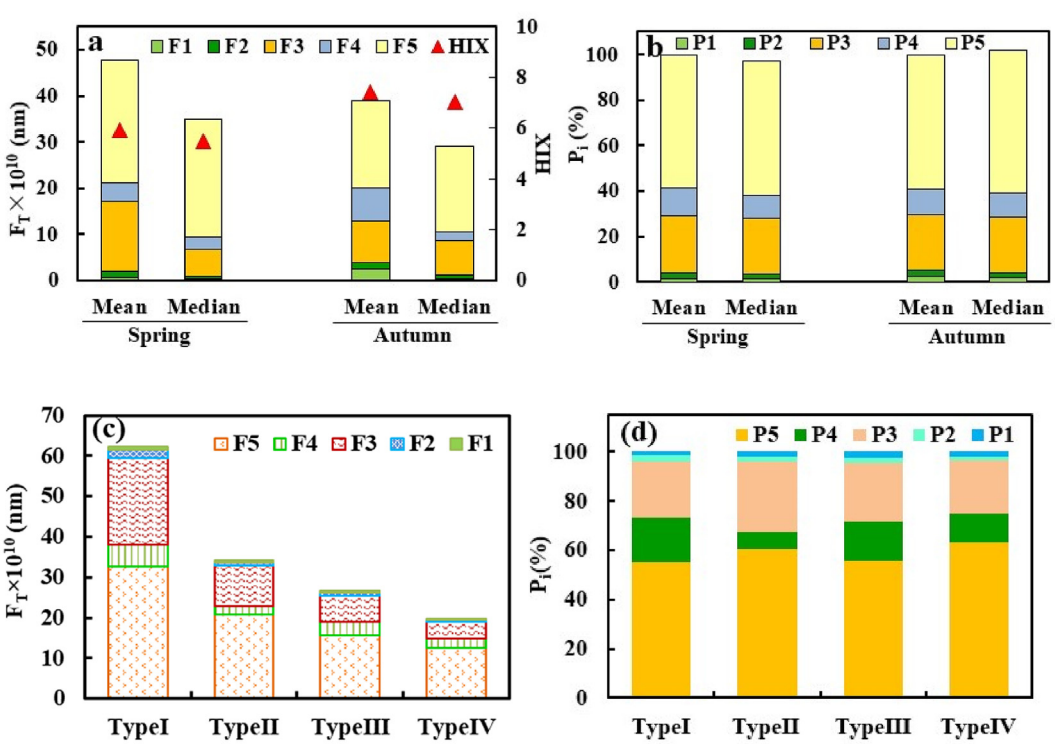

Fig. 8. Seasonal distribution of FRI-extracted CDOM fluorescence components in river waters of the Haihe River basin. (a) The total fluorescence intensities (F_T) in spring and autumn, (b) the percentages of FRI-extracted CDOM fluorescence components (P_i) in spring and autumn, (c) F_T in four typical waters, (d) percentages of FRI-extracted CDOM fluorescence components in four typical waters.

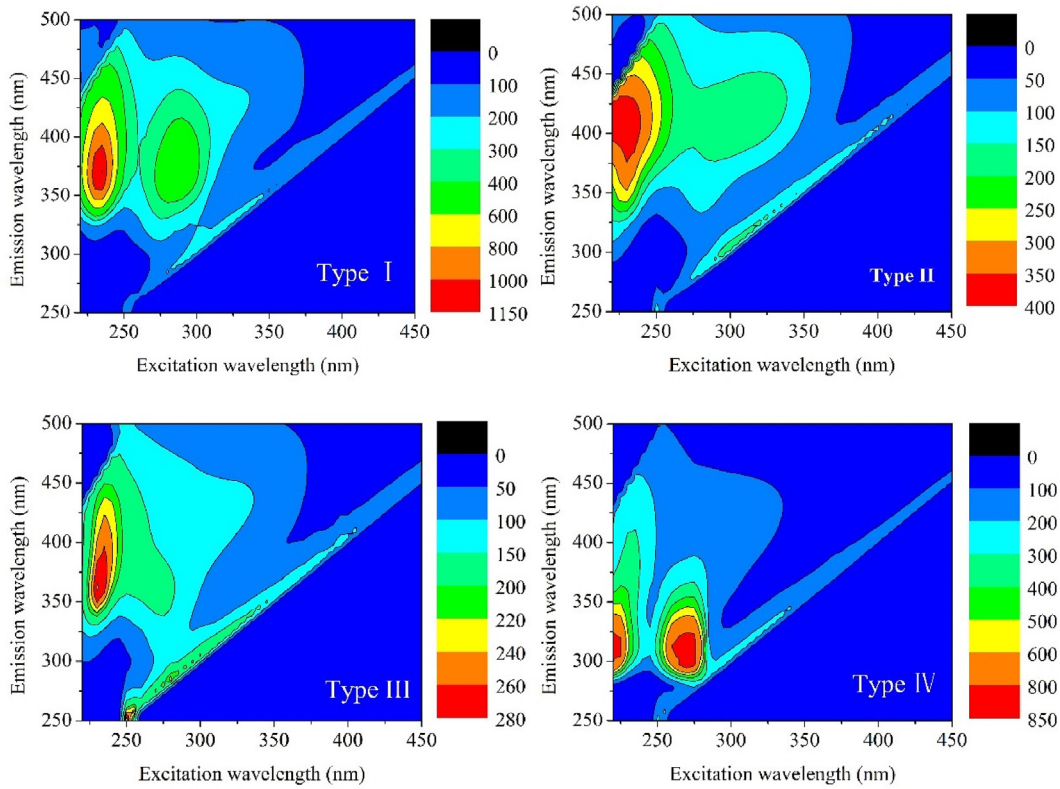

Fig. 9. EEM fluorescence spectra and FRI distribution of four typical waters in the Haihe River basin. Type I, river water with high sewage input; Type II, river water with higher input of terrestrial plants; Type III, river water with higher algal decay; Type IV, river water with higher soil erosion.

the lowest value in Type IV (Fig. 8c). The relative contribution of each component to F_T also differed from type to type (Fig. 8d). In all types, humic acid-like F5 dominated the fluorescence composition (58.37%–62.95%) of CDOM. The sum of the fulvic and humic acid-like (F3 and F5) accounted for 78.29%–89.36%. The three protein-like components (F1, F2, and F4) just accounted for 10.64–20.46% in the four types. A previous study showed that the municipal sewage contained matter with $\delta^{13}C$ values differing from background conditions in the receiving environment (Wayland and Hobson, 2001). The river samples classified as type I were characterized by the higher sewage-derived DOC (81.2% in Fig. 7). Meanwhile, these samples (Type I) were also characterized by the highest F_T and protein-like components proportion (Fig. S2). The sewage-derived organic matter contained more fluorescence components, including detergents, antiseptics, and personal care products. Many protein and amino acids came from the domestic sewage and provide the contribution of F1, F2, and F4 (Dover et al., 1992; Wayland and Hobson, 2001). In type II, the contribution of DOC was mainly attributed to the input of organic matter from terrestrial plants (65.8% in Fig. 7). It was consistent with the FRI analysis, which showed that terrestrial sources accounted for the highest proportion in fluorescent DOC among all types (Fig. 8d). It is assumed that the matter from terrestrial plants may have a strong fluorescence characteristic, which is related to the relatively slow biodegradation (Benner and Kaiser, 2011). Autochthonous sources dominated the DOC in Type III (36.4% in Fig. 7) with the P_{1+2+4} of only 19.23% (Fig. 8d). This may further prove that autochthonous DOC has a weak fluorescence characteristic than the DOC from terrestrial plants. The DOC in Type IV was mainly derived from the soil erosion, showing the lowest F_T (Figs. 8c and 7). This type usually had a high turbidity. Thus the SOM in the river basin may result higher than in other types of rivers (Wang et al., 2012).

4. Conclusions

Water samples were systematically collected in different tributaries of the highly polluted different tributaries across the Haihe River basin, both spectroscopy and stable carbon isotopes were used to characterize DOC and CDOM in spring and autumn, aiming to quantify anthropogenic carbon source to the river water DOC and CDOM in the Haihe River basin. DOC concentrations in spring river waters of the Haihe River was higher than in autumn ($p < 0.01$) due to the higher evaporation in spring, and much of DOC was derived from sewage and terrestrial plant matters. Both in spring and autumn, humic acid-like component dominated the fluorescence composition of CDOM. Our analysis indicated that the combination of spectroscopy and stable carbon isotopes was effective for identifying the endmember sources of DOC in river water, and first successfully quantified the contributions of different endmember sources to DOC in a whole hydrographic net. The results of the study clarified that the allochthonous carbon from the watershed prevailed over autochthonous carbon derived from algae in Haihe River ecosystem, and precisely delineated the proportion of sewage -derived organic matter to riverine DOC, which is important for the management and remediation of river water pollution. In fact, this great effort may be attractive to worldwide audience and help to motivate new studies using this same strategy in other riverine systems of the globe, contributing to the understanding of the effect of rivers ecosystem on global carbon cycle. Further, the method used in this study for quantifying anthropogenic DOC input to ocean through river flow may provide an effective tool for partition different C source, particularly for these river systems which have been severely polluted or disturbed by human being. This study also confirmed a strong relationship between DOC and CDOM for the highly polluted Haihe River, thus remote sensing might be used

to track DOC through the linkage of CDOM for the Haihe River and also other large rivers, and to trace DOC and CDOM at high temporal observations with different satellite platforms or airborne platforms using optical sensors.

Data statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Declaration of competing interest

No conflict of interest exits in the submission of this manuscript, and manuscript is approved by all authors for publication. All authors read and approved the final manuscript. I would like to declare on behalf of my co-authors that the work described was original research that has not been published previously, and not under consideration for publication elsewhere, in whole or in part.

CRediT authorship contribution statement

Zhidan Wen: Writing - review & editing, Data curation, Writing - original draft, Conceptualization, Methodology, Funding acquisition. **Kaishan Song:** Funding acquisition, Formal analysis, Writing - review & editing, Conceptualization. **Ge Liu:** Investigation, Data curation. **Lili Lyu:** Investigation, Data curation. **Yingxin Shang:** Investigation, Data curation. **Chong Fang:** Investigation. **Jia Du:** Investigation.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.envpol.2019.113684.

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