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RESEARCH ARTICLE

Temporal-spatial variation of DOC concentration, UV absorbance and the flux estimation in the Lower Dagu River, China

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Abstract Dissolved organic carbon (DOC) is an important component for both carbon cycle and energy balance. The concentration, UV absorbance, and export flux of DOC in the natural environment dominate many important transport processes. To better understand the temporal and spatial variation of DOC, 7 sites along the Lower Dagu River were chosen to conduct a comprehensive measurement from March 2013 to February 2014. Specifically, water samples were collected from the Lower Dagu River between the 26th and 29th of every month during the experimental period. The DOC concentration (C_{DOC}) and UV absorbance were analyzed using a total organic carbon analyzer and the ultraviolet-visible absorption spectrum, and the DOC export flux was estimated with a simple empirical model. The results showed that the C_{DOC} of the Lower Dagu River varied from 1.32 to 12.56 mg/L, consistent with global rivers. The C_{DOC} and UV absorbance showed significant spatial variation in the Dagu River during the experiential period because of the upstream natural processes and human activities in the watershed. The spatial variation is mainly due to dam or reservoir constructions, riverside ecological environment changes, and non-point source or wastewater discharge. The seasonal variation of C_{DOC} was mainly related to the source of water DOC, river runoff, and temperature, and the UV absorbance and humification degree of DOC had no obvious differences among months ($P < 0.05$). UV absorbance was applied to test the C_{DOC} in Lower Dagu River using wave lengths of 254 and 280 nm. The results revealed that the annual DOC export flux varied from 1.6 to 3.76×10^5 g C/km^2/yr in a complete hydrological year, significantly lower than the global average. It is worth mentioning that the DOC export flux was mainly concentrated in summer (~90% of all-year flux in July and August), since the runoff in the Dagu River took place frequently in summer. These observations implied environment change could bring the temporal-spatial variation of DOC and the exports, which would further affect the land-ocean interactions in the Lower Dagu River and the global carbon cycle.

Keywords DOC, temporal-spatial variation, UV absorbance, export flux, Dagu River

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1 Introduction

A major fraction of the organic matter in the river, estuarine, and oceanic waters is presented in dissolved form (Peterson et al., 1994). Therefore, the dissolved organic matter (DOM) plays a significant role in the transport of metal/organic contaminants and provides energy for micro-organisms in the aquatic environment. Specifically, the structure, UV absorbance, and abundance of DOM in the environment dominate many important transport processes. DOM includes dissolved organic carbon (DOC), nitrogen (DON), and phosphorus (DOP), in which DOC is an important component in carbon cycle and energy balance. Previous studies proved that DOC increase in river can lead to increases in organic acid, acid neutralizing capacity, water color, etc., and further affect freshwater aquaculture, drinking water quality, and estuarine and marine ecosystems (Xi et al., 2015).

The DOC concentration (C_{DOC}) of global rivers with a mean value of 5.75 mg/L varied from 1.05 to 12.37 mg/L. Usually, the C_{DOC} mainly influenced by natural factors and human activities in the watershed presented differences among different rivers and reaches (Ran et al., 2013). Hydrologic transport, land cover type, vegetation density, wetland area, and bottom sediment were the key natural factors (Maie et al., 2014; Zhao et al., 2015a). For instance, there was a linear relationship between wetland area and the DOC production from rivers (Clark et al., 2008). 15% of global terrestrial carbon flux from rivers to coastal environments was estimated to be derived from wetlands (Hedges et al., 1997), though wetlands covered only 5%–8% of the earth's land surface (Mitsch and Gosselink, 2007). There are also other results which reveal that the C_{DOC} in streams were principally associated with the distance from the wetlands to stream network, and 73%–85% of them were possibly derived from wetland soil of a riparian zone (Yin et al., 2015). In addition, it was found that hydrologic transport and changes in flow path were also important for controlling the C_{DOC} in streams (Tian et al., 2012). Especially when first-order streams merged together to form a larger-scale stream network, DOC from various landscape source areas were mixed and processed to define the downstream DOC signal observed at the outlet (Schelker et al., 2014). Besides natural factors, artificial interference also has an important effect on the DOC variation in river waters. For example, changes of land use and landscape structure in the drainage basin indirectly affected the C_{DOC} and export flux in rivers by changing soil DOC and hydrological regime (Schelker et al., 2014; Yin et al., 2015); meanwhile, construction of hydraulic structure directly affected the production and loss of water DOC by altering the state of naturally flowing water (Moody et al., 2013). Furthermore, the discharge of industrial and domestic waste water also directly caused the increment of C_{DOC} and export flux in rivers (Wang et al., 2013).

Carbon transportation from land to oceans *via* rivers has been widely investigated (Ran et al., 2013). The DOC flux of global rivers was estimated at about 200 Mt C/yr according to the carbon content of 542 Mt C/yr in the air (Meybeck, 1993). The value was estimated at 170 Mt C/yr by a global model (Harrison et al., 2005), while it was reported over 200 Mt C/yr by Hartmann et al. (2009). The mean value of the DOC flux was estimated at about 2.04×10^6 g C/km^2/yr by the spatial explicit model of the global riverine carbon flux. However, the estimation of global riverine DOC export flux was mostly extrapolated based on the measurement of C_{DOC} of a few rivers, which could not represent all the types of terrestrial ecological environment. Rivers are not passive conduits of DOC, as a matter of fact, since there are a range of processes that can remove, degrade, or add DOC to the flux within streams (Moody et al., 2013). Given that the previous calculation ignored the in-stream processing of DOC, the estimation and analysis had large uncertainties. As the largest river of Shandong Peninsula in China, the Dagu River is a crucial part of the program "Conservation and Development around Jiaozhou Bay". Dagu River is recognized as the mother river of Qingdao City, which has the longest flow path, the largest drainage area (Li et al., 2008), most water functions, and the greatest runoff within Jiaozhou Bay. In recent decades, the Dagu River basin has suffered from severe destruction of the ecological environment due to the influence of nature and human activities, such as intensive reclamation, dam construction and developing activities of the basin (Li et al., 2008). The forest and wetland degradation (Zhao et al., 2015b), increasing amount of industrial, agricultural, and aquaculture waste lead to serious decline in water quantity and deterioration of water quality (Li et al., 2008). The C_{DOC}, UV absorbance and discharge fluxes probably affect freshwater drinking water quality, estuarine and marine ecosystems, etc. However, anthropogenic influence on water environment in the upstream of the Dagu River watershed was not obvious (Wang et al., 2013). Meanwhile, in the Dagu River, the transport processes of DOC within the river system from its source to the river outlet constitute important aspects of the land-ocean interactions in the lower reaches. Therefore, it is critical to study the dynamics of C_{DOC} and UV absorbance, estimate the export flux of DOC, and reveal the influence of human factors in the Lower Dagu River. Herein, the concentration and UV absorbance of DOC were investigated, and the results were compared with a selection of other rivers in the world. Moreover, the effects of runoff and rubber dam in Dagu River were discussed.

2 Methodologies

2.1 Sampling sites

Dagu River was chosen as the target area of this study. The river originates from Fushan Mountain of Zhaoyuan County in Yantai City, then flows through Laixi, Pingdu, Jimo, and Jiaozhou city as well as the Chengyang district in Qingdao City, and finally inflows into Jiaozhou Bay (Fig. 1). The total mainstream length of the Dagu River is 179.9 km and the basin area is 6131.3 km^2, including the South Jiaolai River Basin, with a total area of 1500 km^2 (Jiang, 2007).

According to watershed division and stream order classification, three level reaches and seven sampling sites were selected from north to south with fixed set station method in the Lower Dagu River, China (Fig. 1, Table 1). Among them, R2 and R3 were in the first-order tributaries of the Dagu River, and the others located in the main stream. Within each site, three water samples were randomly chosen in the cross section of mainstream according to the river width and flow condition.

2.2 Sampling and analysis

Water samples were collected monthly from 7 sampling sites during the research period. In order to minimize the interference of floating debris and river bottom sediment, a depth of 0.1 m below the water surface was adopted to collect these water samples. During sampling, the seasonal

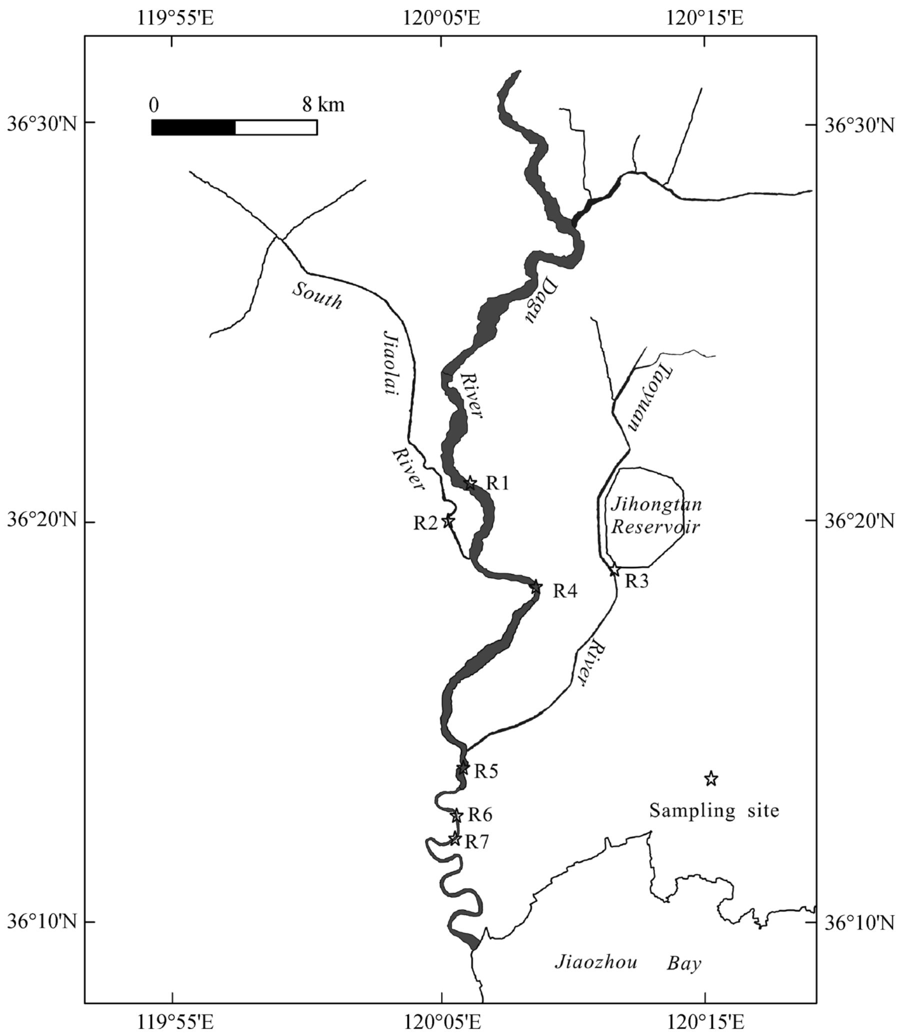

Fig. 1 Schematic map of the study area and the sample sites.

Table 1 The description of sampling locations

Sampling sites	Position	Descriptions
R1	36°22'22.39"N, 120°07'45.85"E	Near the Dagu River rubber dam, north of south Jiaolai River
R2	36°21'45.64"N, 120°07'05.53"E	The outfall of south Jiaolai River into Dagu River
R3	36°20'28.86"N, 120°12'24.02"E	Near the bridge of National Road 204 on the Taoyuan River, south of Jihongtan reservoir
R4	36°20'09.24"N, 120°09'07.92"E	Near the bridge of National Road 204 in the Lower Dagu River
R5	36°15'31.05"N, 120°07'10.25"E	Near the bridge of Provincial Road 395 in the Lower Dagu River
R6	36°14'08.08"N, 120°07'20.11"E	Near the bridge of National Road 22 in the Lower Dagu River
R7	36°13'32.56"N, 120°06'59.10"E	The southern tip of study area in the vicinity of the Dagu River estuary

variations in depth or water levels were also considered. The collected water samples were placed in labeled 1000 mL brown vials, and stored in an ice box for 12 hours.

Water samples were filtered through a glass fiber filter (Whatman GF/F, ignited for 4 hours at 450°C in advance) with low negative pressure on a vacuum glass filter into two separate vials. The pore size of the filter membrane was 0.45 μm, with a diameter of 50 mm. DOC of the filtrate was analyzed using a total organic carbon analyzer (TOCVCPH, Shimadzu, Kyoto, Japan) (Xi et al., 2007). Absorbance of five wavelengths (254, 280, 400, 450, and 650 nm) under the potential of hydrogen (pH) of 7.0 (Ludwig et al., 1996) was also determined using the UV-2600 ultraviolet-visible light detector (US UNICO).

2.3 Flux estimation

The data obtained were analyzed for Analysis of Variance (ANOVA) using SPSS 17.0 software package. The pictorial diagrams of the distribution variables of DOC in the Lower Dagu River were performed using OriginPro 8.0.

The monthly export flux of DOC in the Dagu River was obtained with Eq. (1), and then the yearly export flux was estimated with Eq. (2).

$$F_{\mathrm{DOC}i} = C_{\mathrm{DOC}i} \times Q_i, \tag{1}$$

$$F_{\mathrm{DOC}} = \sum_{i=1}^{12} F_{\mathrm{DOC}i}, \tag{2}$$

where $F_{\mathrm{DOC}i}$ is the export flux of DOC in the i^{th} month of the year, $C_{\mathrm{DOC}i}$ is the measured value of C_{DOC} at site R1 in the i^{th} month of the year, Q_i is the runoff at Nancun station in the i^{th} month in the Dagu River, and F_{DOC} is the export flux of DOC in a full hydrological annual which represents the yearly export flux of DOC in the Dagu River.

3 Results

3.1 Temporal-spatial variation of C_{DOC} in the Lower Dagu River

The statistical characteristics of C_{DOC} from north to south along the Lower Dagu River are shown in Table 2. The C_{DOC} varied from 1.32 to 12.56 mg/L with a mean value of 5 mg/L. Site R1 showed the lowest mean value of C_{DOC} and the standard deviation among the 7 monitoring sections. The maximum and minimum C_{DOC} at R1 were 4.30 and 1.91 mg/L, respectively, indicating relatively small seasonal variations. However, site R3 had the highest mean value and standard deviation among the 7 sites. The maximum and minimum C_{DOC} were 12.56 mg/L and 4.09 mg/L, respectively, which indicated a seasonal fluctuation at R3. At other sites, the mean value of C_{DOC} and the standard deviation was between R1 and R3 with an order of R5 < R6 < R7 < R4 < R2. According to the one-way ANOVA analysis, site R3 showed a significantly different C_{DOC} from other sampling plots ($P < 0.05$), while there was no significant difference between R1 and R4, and between R2, R5, R6, and R7 ($P < 0.05$).

Further analysis showed that the lowest value of C_{DOC} appeared in November and the highest appeared in January during a complete hydrological year, respectively Pearson correlation analysis showed that there was no obvious correlation between C_{DOC} and river runoff among all the sampling plots. Correlation coefficients of C_{DOC} and river runoff at R1, R2, and R4 before confluence of Taoyuan River were 0.018, 0.191, and 0.296, respectively. Meanwhile, the correlation coefficients of R3, R5, R6, and R7 were −0.246, −0.243, −0.558, and −0.242, respectively. The lowest positive correlation coefficient appeared at site R1 (R = 0.018), but the variation of C_{DOC} was partial consistency with that of the river runoff from April to August in 2013. River runoff decreased sharply from August to October, while C_{DOC} showed an increasing trend. However, river runoff did not change much from October to November, although C_{DOC} decreased obviously. From December 2013 to March 2014, river runoff was nearly zero, while C_{DOC} presented an increasing trend. The highest negative correlation coefficient was at site R6 (R =− 0.558), and the opposite trend occurred between the C_{DOC} and the river runoff from March to April, June to July, September to October, and so on in 2013. At the other sites, the correlation coefficient between C_{DOC} and river runoff was moderate.

3.2 Temporal-spatial variation of DOC UV absorbance in the Lower Dagu River

As illustrated in Table 3, the maximum values of Abs_{254}, Abs_{280}, and Abs_{400} among the 7 monitoring sections all appeared at site R3, and the minimum values were at site R1. One-way ANOVA analysis showed that significant differences in Abs_{254}, Abs_{280}, and Abs_{400} were found among R1, R4, and R3 ($P < 0.05$), while there was no remarkable difference between R1, R4 and R2, R5, R6, R7. Also no obvious difference was found between R3 and R2, R5, R6, R7 ($P < 0.05$). The results indicated that significant differences in DOC UV absorbance only

Table 2 Descriptive statistics for C_{DOC} in the Lower Dagu River

Sampling sites	Maximum (mg/L)	Minimum (mg/L)	Mean (mg/L)		Range (mg/L)	Std. Deviation (mg/L)
			Statistic	Std. Error		
R1	4.30	1.91	2.958	0.196	2.39	0.680
R2	7.63	2.13	4.652	0.447	5.50	1.547
R3	12.56	4.09	8.268	0.771	8.47	2.670
R4	5.20	1.32	3.380	0.348	3.88	1.204
R5	6.86	3.64	5.249	0.273	3.22	0.947
R6	6.83	3.63	5.077	0.284	3.20	0.984
R7	7.17	3.73	5.427	0.291	3.44	1.007

appeared among R1, R4 and R3. The mean value of the *E*4/*E*6 ratio in the Dagu River is in the range of 3 to 6, with the minimum at site R1 and R4 and the maximum at site R5. Furthermore, one-way ANOVA analysis showed that no remarkable difference was found in the mean value of *E*4/*E*6 among all the sampling plots in the Lower Dagu River ($P < 0.05$).

In addition, the dynamics changes in UV absorbance of DOC were observed within the months during the sampling period from August 2013 to January 2014 in the Lower Dagu River. As shown in Fig. 2, the Abs_{254}, Abs_{280}, and Abs_{400} dropped slowly from August to November, then increased rapidly from November to December in 2013. The lowest absorbance value of three characteristic wavelengths varied from 0.101 to 0.01 between December 2013 and January 2014. The monthly *E*4/*E*6 ratio displayed a slight change with a shape of "W" throughout the sampling period. Through further one-way ANOVA analysis, no significant difference was found in Abs_{254}, Abs_{280}, Abs_{400}, and *E*4/*E*6 among sampling months ($P < 0.05$). This indicated that the UV absorbance of DOC varied with months, but it changed little on the whole in the Lower Dagu River.

3.3 The flux estimation of DOC in the Dagu River

The estimated annual DOC export flux of the Dagu River in a complete hydrological year was about 9.81×10^8 g. In July the export flux reached the maximum value of 5.89×10^8 g which accounted for about 60% of the annual DOC flux. In August, the DOC export flux deceased to 3.09×10^8 g and accounted for about 30% of the whole year

Table 3 Descriptive statistics for Abs_{254}, Abs_{280}, Abs_{400} and *E*4/*E*6

	Sampling sites	Maximum	Minimum	Mean		Range	Std. Deviation
				Statistic	Std. Error		
Abs_{254}	R1	0.11	0.05	0.0698	0.0087	0.06	0.0213
	R2	0.164	0.102	0.1303	0.0096	0.062	0.0235
	R3	0.396	0.08	0.1857	0.0452	0.316	0.1107
	R4	0.118	0.055	0.0823	0.0092	0.063	0.0225
	R5	0.136	0.11	0.1225	0.0035	0.026	0.0085
	R6	0.126	0.118	0.1212	0.0012	0.008	0.0029
	R7	0.132	0.115	0.1213	0.0025	0.017	0.0062
Abs_{280}	R1	0.07	0.031	0.0455	0.0059	0.039	0.0145
	R2	0.11	0.081	0.0942	0.0047	0.029	0.0115
	R3	0.332	0.06	0.1463	0.0392	0.272	0.0961
	R4	0.072	0.038	0.058	0.0057	0.034	0.0139
	R5	0.095	0.078	0.0857	0.0026	0.017	0.0063
	R6	0.098	0.080	0.086	0.0027	0.018	0.0066
	R7	0.098	0.079	0.0847	0.0031	0.019	0.0075
Abs_{400}	R1	0.011	0.001	0.0057	0.0017	0.01	0.0043
	R2	0.016	0.01	0.0128	0.0009	0.006	0.0023
	R3	0.112	0.01	0.0355	0.0156	0.102	0.0381
	R4	0.02	0.005	0.012	0.0021	0.015	0.0052
	R5	0.015	0.01	0.013	0.0007	0.005	0.0018
	R6	0.016	0.01	0.013	0.0009	0.006	0.0022
	R7	0.015	0.01	0.0122	0.0009	0.005	0.0023
*E*4/*E*6	R1	7.14	0.5	3.2733	1.1320	6.64	2.7728
	R2	7.5	1.67	4.2783	0.9392	5.83	2.3006
	R3	6	2.07	4.1783	0.5783	3.93	1.4166
	R4	6.67	1.5	3.1583	0.7521	5.17	1.8423
	R5	15	2.67	6.485	1.9354	12.33	4.7407
	R6	10	1.67	4.635	1.3149	8.33	3.2208
	R7	8.75	2	5.41	1.2567	6.75	3.0783

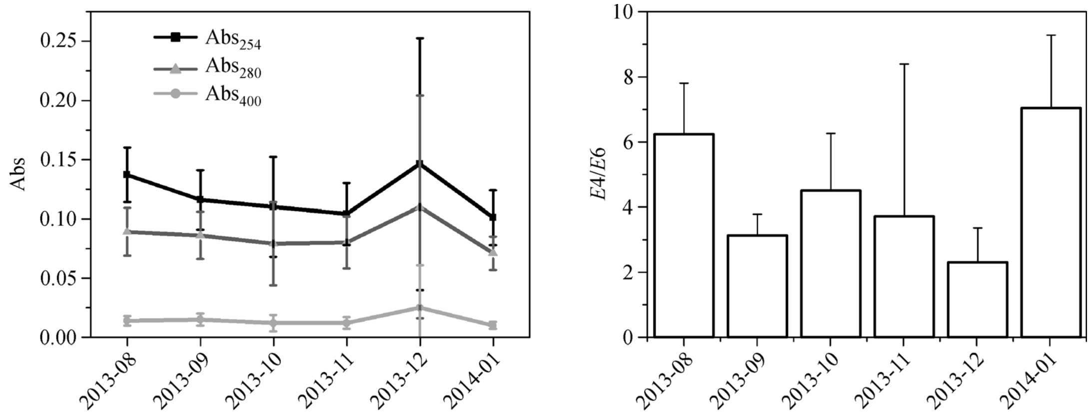

Fig. 2 Monthly dynamics of Abs_{254}, Abs_{280}, Abs_{400} and $E4/E6$ in the lower Dagu River.

export. The minimum export flux appeared in January with a value of 0.72×10^6 g, which was as low as 0.7 ‰ of the annual DOC flux (Fig. 3). River runoff mainly determined the DOC export flux in the Dagu River. The DOC export flux in summer accounted for about 94% of the total because river runoff mainly concentrated in this season. However, in winter, the volume of flow was very low and even nearly zero, thus the DOC export flux only accounted for 0.296% of all-year DOC flux.

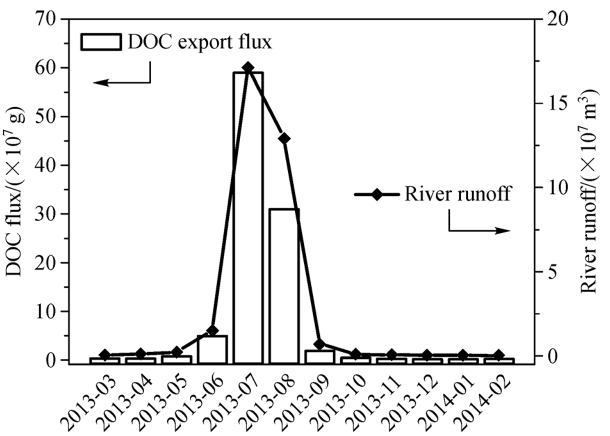

Fig. 3 Monthly changes of DOC export flux and river runoff in the lower Dagu River.

To further investigate the monthly contribution of DOC export flux to the total, DOC cumulative export flux and percentage from March 2013 to February 2014 was calculated (Fig. 4). The cumulative export flux curve varied slightly from March to April 2013. From May, the DOC cumulative export flux began to increase. Particularly, the curve rose rapidly after June and it reached the maximum in August. After that, DOC cumulative export flux varied slightly with the decrease of river runoff. The cumulative export flux of the first nine months accounted for 99.24% of all-year DOC flux, indicating that the latter five months contribute little to the whole flux.

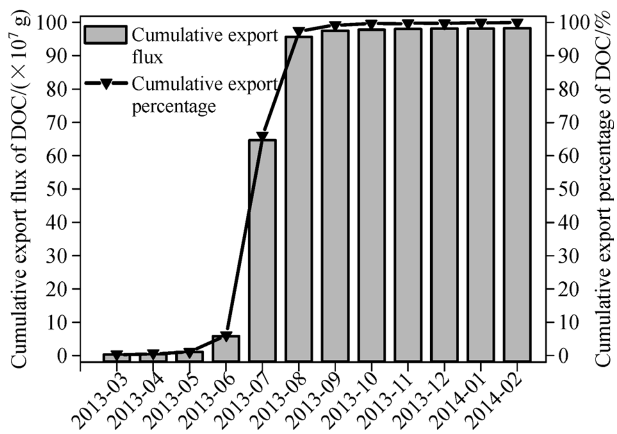

Fig. 4 The cumulative export flux and percentage of DOC in the lower Dagu River.

4 Discussion

The Dagu River basin belongs to a humid warm temperate monsoonal climate zone. Its C_{DOC} was higher than that of other rivers in the non-monsoonal region. Meanwhile, different reaches of the Dagu River have different C_{DOC} due to the large watershed area and different regions where the river flows.

Among the 7 monitoring sections, R3 was the most prominent position in the tributary of the Taoyuan River which flows through the largest wetland of Jihongtan reservoir and the densely populated area with highly developed agricultural activities. The high C_{DOC} of this river was due to wetland plant residue, root exudates, and soil organic matter in the river valley. Moreover, reservoir construction can extend water residence time and reservoir trapping, which results in the promotion of DOC production (Ran et al., 2013). In addition, non-point source and sewage or waste water discharge may also bring large amounts of organic pollutants to the aquatic environment (Guo et al., 2010; Wang et al., 2013). Unlike

R3, less wetland area and strong agricultural activity appeared at site R2 because it lay at the outfall of the south Jiaolai River and was in the catchment area. The contributions of *in-situ* biological activity (e.g., plankton, macrophytes) and anthropogenic discharge to the Jiaolai River were less than those to the Taoyuan River. That was why C_{DOC} of R3 was higher than that of R2, which were both in the first-order tributaries of the Dagu River. The other 5 monitoring sections were located on the main stream of the Dagu River. R1 located at the most northerly area was next to a rubber dam, where the regional environment was affected by riverside development and construction, sand-borrow activity, and so on. The construction of a ladder-like barrage or dam on the Dagu River caused more DOC loss by strengthening the infiltration (Wang et al., 2013) and mineralization process (Moody et al., 2013). In addition, the exogenous DOC derived from the leaching of litters and plant residue in the river valley was also at a low level. All of these effects led to the lowest C_{DOC} at site R1 among the 5 monitoring sections. The C_{DOC} of R4 and R5 rose significantly due to high DOC content. Meanwhile, the C_{DOC} had no significant differences from R5 to R7 due to the absence of branch inflow, which also means DOC generation and degradation reached an equilibrium.

For most rivers, the C_{DOC} varied seasonally. It has been proven that season was one of the main factors which can affect the variation of C_{DOC} in rivers (Spitzy and Leenheer, 1990; Zhang, 2008). Through one-year monitoring data, we came to the conclusion that, for the Yichun River, the highest and the second highest C_{DOC} appeared in winter with a value of about 14.3 mg/L and in summer with a value of 13.6 mg/L, respectively. For the full year, to sort high to low, the C_{DOC} was winter, summer, autumn, and spring (Tao et al., 1997). Studies on the freshwater side in the Yangtze River estuary showed that the C_{DOC} in rivers appeared the highest value in winter was about twice as much as that in spring. For the whole year, the C_{DOC} from high to low was winter, autumn, summer, and spring (Lin, 2007). Both the above two rivers had the highest C_{DOC} in winter and the lowest in spring, but in summer and autumn the results were different. The main reason was that riverine DOC came from an internal river in winter when the river runoff was the lowest with a low dilution ratio. Besides, the tidal backwater of Yangtze River estuary promoted the release of DOC from river sediment to the water bodies. As a result, the C_{DOC} was especially high in winter in Yangtze River estuary. Exogenous source played a dominant role in summer and autumn. However, the river had the highest dilution ratio in summer, so the C_{DOC} values in summer and autumn were between those in spring and winter.

On average, the C_{DOC} of the Dagu River were highest in winter and lowest in autumn, while there was no significant difference among other three seasons (Fig. 5). The spring precipitation was relatively low, but the increasing of temperature brought increased microbial activity which promotes the production of DOC (Kong et al., 2013). Also, ice and snow melts with increased temperature, which can bring a large quantity of DOC into the river. In summer, river runoff increased continuously because of high precipitation. However, the C_{DOC} was almost invariant or even had a decreasing trend due to the dilution effects of water flow. In autumn, the C_{DOC} in the Dagu River dropped to the lowest level with decreased precipitation. In winter, the C_{DOC} increased again which was due to the low precipitation and the zero flow. A study on the seasonal variation of C_{DOC} in the Xijiang River indicated that Xijiang had the highest C_{DOC} with a value of about 4.6 mg/L after the summer flood peak. In the whole year, the C_{DOC} was the highest in summer and the lowest in winter (Li et al., 2002). Thus, for different rivers, the seasonal variation was different, which was primarily resulted from temperature, precipitation, and the dynamic process of the erosion, export, and transport of organic carbon made by surface runoff. Among the four seasons, difference in temperature determined biomass and soil organic matter in each unit area, and the seasonal difference of DOC transport in rivers (Worrall et al., 2012; Bai et al., 2016).

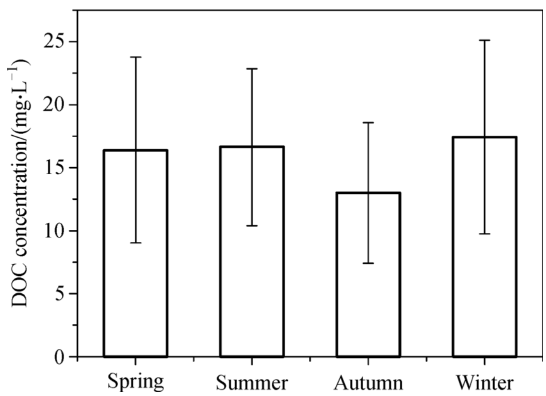

Fig. 5 Seasonal changes of DOC concentrations (mean value) in the lower Dagu River.

Generally, C_{DOC} appears to be higher in flood periods than that in dry seasons, which is mainly because of the increasing erosion of surface organic matter caused by the high rainfall amount and intensity. C_{DOC} increased with river runoff increasing (Patel et al., 1999). The highest value of C_{DOC} in flood periods appeared in the maximum flood peak discharge, which were attributed to the flushing effect of precipitation in rivers. The C_{DOC} showed an increasing trend from April to June, during which the river discharge increased continuously in the Dagu River except at R4 and R5. Additionally, the C_{DOC} showed a decreasing trend from July to August, October to November, and March to April because the river discharge decreased and even reached zero flow during these months. However, there was no significant correlation between the C_{DOC} and river runoff among all the sampling plots in the Dagu

River, which was similar to that of Niger River (Martins and Probst, 1991). This was because overland flow and lateral leaching caused by precipitation brought DOC from upper soil layers into rivers. Meanwhile, high rainfall diluted the C_{DOC} in river water (Tao et al., 1997). Though the effects on the C_{DOC} from precipitation and dilution were opposite, in most cases, especially in areas with high organic matter content and intermittent precipitation, C_{DOC} was more heavily affected by precipitation than dilution. On the other hand, it was also associated with the artificial construction of storing facilities of water in the Lower River, which changed the characteristic of natural flow in India River. For instance, site R1 had the lowest correlation coefficients which was attributed to the extend water residence time caused by the dam regulation. R3 had negative correlation coefficients between C_{DOC} and river runoff under the influence of the Jihongtan reservoir. The C_{DOC} and the composition proportion of organic carbon (DOC/POC) were both affected by man-made building facilities such as reservoir or barrage in natural rivers (Spitzy and Leenheer, 1990).

In recent decades, studies on water DOC showed that there was a good correlation between C_{DOC} and optical absorption of water samples at the low wavelength. Abs_{254}, as the characteristic index of the C_{DOC} in sewage, has been applied to water quality parameters monitoring (Moore, 1987). Through Pearson correlation analysis, the C_{DOC} showed significant positive correlations with Abs_{254} and Abs_{280}, and positive correlations with Abs_{400} (Fig. 6), while no significant relationships were found with Abs_{450} or Abs_{650} in the Dagu River ($P < 0.05$). Therefore, the absorbance at the wave length of 254 and 280 nm was suitable for forecasting C_{DOC} in the Dagu River. This indicates that the suitable ultraviolet absorption band should be selected first when the C_{DOC} was determined by UV-is spectra. DOC was a complex compound, and the characteristics of the absorption bands were distinguished among different components.

To forecast the C_{DOC} more accurately, three characteristic wavelengths (254, 400, and 545 nm) were selected with multiple linear stepwise regression and a multiple linear regression equation was established on the C_{DOC} of pore water in Zoige peatland (Lou et al., 2014). Compared with the simple linear regression in Eqs. (3), (4), and (5), the correlation of the multiple linear regression in Eq. (6) was more significant, which indicated that a multiple regression equation could calculate the C_{DOC} in the Dagu River more accurately

$$Y = 0.0122X_1 + 0.0635 \ (R = 0.45, \ n = 42), \qquad (3)$$

$$Y = 0.0099X_2 + 0.0407 \ (R = 0.429, \ n = 42), \qquad (4)$$

$$Y = 0.0028X_3 + 0.002 \ (R = 0.339, \ n = 42), \qquad (5)$$

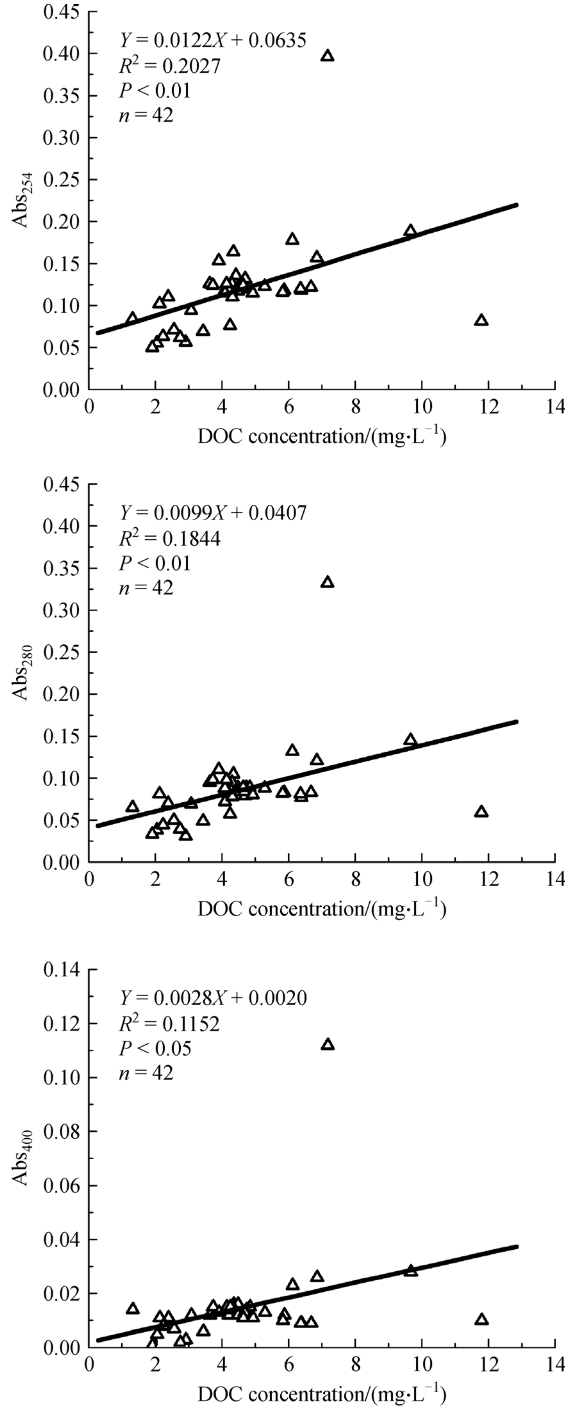

Fig. 6 Relationship between the DOC concentration and Abs_{254}, Abs_{280}, Abs_{400} in the lower Dagu River.

$$Y = 20.905X_1 + 21.227X_2 - 79.433X_3 + 1.422$$

$$(R = 0.494, \ n = 42), \qquad (6)$$

where Y was the C_{DOC} (mg/L); X_1, X_2, and X_3 were the UV-visible light absorbance at the wave length of 254, 280, and 400 nm in the Dagu River, respectively.

The highest Abs_{254}, Abs_{280}, and Abs_{400} values were all observed at site R3, partly because R3 was located at Taoyuan River which flowed through the wetland of Jihongtan reservoir and had the highest vegetation coverage. A large number of aromatic compounds were produced from the hydrophyte residues in the river water itself or from the surrounding environment after the microbiological degradation (Li et al., 2014). R1 had the lowest aromaticity in the Dagu River water due to human activities on both sides of the river. The mean value of $E4/E6$ ratio in the Dagu River ranged from 3 to 6, which was lower than that of pore water in peatland (Wilson et al., 2011; Lou et al., 2014). Pearson correlation analysis showed that the relationship between Abs_{254}, Abs_{280}, Abs_{400}, $E4/E6$ and river runoff was not significant ($P < 0.05$), suggesting that river runoff was not the main factor to affect the DOC UV absorbance. Further analysis of monthly dynamics of Abs_{254}, Abs_{280}, Abs_{400}, and $E4/E6$ revealed that the first three absorbance increased with temperature drop from August to November 2013, meaning that temperature played a key role in the variation of DOC UV absorbance.

Based on research of over 29 rivers, an empirical formula on DOC fluxes was obtained for calculation of DOC fluxes of each river. However, sometimes, for a specific river, DOC fluxes calculated by the empirical formula were quite different from the actual determination value. In this paper, the DOC export flux of the Dagu River was roughly estimated by using river runoff multiplied by the C_{DOC} during the sampling period. Certainly the estimation of DOC export flux was uncertain due to the effects of various factors including C_{DOC} and their variance along the flow path in the Dagu River. It was estimated that the DOC export flux was about 980.92 t in a complete hydrological year in the Dagu River. Based on the basin area of 6131.3 km^2 in the Dagu River, the mean value of DOC export flux was 1.6×10^5 g C/km^2/yr, much lower than that of global rivers. Therefore, in order to better compare with global rivers, the yearly DOC flux was estimated to be the highest value of 2304.4 t by using the C_{DOC} of R3 in the Dagu River. On this basis, the mean value of DOC export flux was further calculated to be 3.76×10^5 g C/km^2/yr.

5 Conclusions

The C_{DOC} and composition showed significant spatial variation in the Dagu River during the experimental period based on analysis of the results of upstream natural processes and human activities in the watershed. The construction of dams and reservoirs, riverside ecological environment changes, and non-point source or wastewater discharge were the key factors of spatial variation. The seasonal variations of C_{DOC} were mainly related to the source of water DOC, river runoff, and temperature variation, and the composition and humification degree of DOC had no obvious differences among months ($P < 0.05$). Based on monthly records of the concentration and UV absorption values of water DOC compounds, the regression equations of multiple linear regressions between C_{DOC} and the absorbance in the Dagu River were established. This approach addressed the problems in the analytical methods of DOC. The DOC export flux of the Dagu River was roughly estimated to be $(1.6–3.76)\times10^5$ g C/km^2/yr in a complete hydrological year, which was significantly lower than the average level of most rivers (2.04×10^6 g C/km^2/yr). The export flux of DOC mainly concentrated in summer due to the influence of runoff in the Dagu River. The export flux from July to August accounted for 90% of the annual flux. However, the estimation of DOC export flux was uncertain due to the effect of various factors including sampling time and site along the flow path in the Dagu River.

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