Dissolved organic carbon in summer precipitation and its wet deposition flux in the Mt. Yulong region, southeastern Tibetan Plateau

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Abstract

Dissolved organic carbon (DOC) is an important organic pollutant in the air-water carbon cycle system, potentially influencing the global climate. In this study, 204 rainwater samples from five sampling stations in the Mt. Yulong region were synchronously collected from June to September in 2014. We comprehensively investigated the sources and wet deposition of DOC in summer precipitation. The average concentrations of DOC at five stations ranged from 0.74 to 1.31 mg L^{-1}. The mass absorption efficiency (MAE) of rainwater DOC evaluated at 365 nm was 0.43 ± 0.32 m^2 g^{-1}. Backward trajectory analyses indicated that the southwest advection air parcel accounting for 46% of precipitation events, while the corresponding average concentration of rainwater DOC was 1.25 ± 0.56 mg C L^{-1}. In addition to the local or regional contribution, large amount of atmospheric pollutants were transported from South Asia and Southeast Asia to the Mt. Yulong region, both of which had exerted great influence on the regional atmospheric environment. For the first time, the annual wet deposition of DOC in the Mt. Yulong region was estimated and determined to be 1.99 g C m^{-2} $year^{-1}$. This is significant because the deposition of DOC on glaciers has great influence on surface albedo of snow and glacier melt. This study can bridge the gap of rainwater DOC research between the Mt. Yulong region and the southeast of Tibetan Plateau (TP), which has significant implications for better understanding the relationship of DOC deposition and glacial shrink in the TP.

Keywords Dissolved organic carbon · Mt. Yulong · Rainfall · Wet deposition

1 Introduction

Dissolved organic carbon (DOC) plays an important role in the air-water carbon cycle, accounting for ~80% of the global rainwater dissolved carbon flux (Willey et al. 2000). It

can influence cloud albedo, increase cloud condensation nuclei (CCN) concentration, and contribute to rainwater pH, visibility impairment, photochemical process, and the nutrient enrichment in ecosystems (Seitzinger et al. 2003; Psichoudaki and Pandis 2013). Removal of carbonaceous aerosol by rainwater is an important process for carbon from the atmosphere (Willey et al. 2000; Coelho et al. 2008; Patrycja et al. 2015). Thus, it is important to investigate spatio-temporal variation and wet deposition flux of DOC in precipitation. It was estimated that the deposition flux of global rainwater DOC was 0.4 Gt C yr.$^{-1}$, which was much higher than that of nitric and sulfuric acids in the rainfall (Willey et al. 2000). DOC is often composed of a highly complex mixture of compounds covering a wide range of molecular structures, physical properties as well as reactivities, and indirectly influences the forcing of precipitation and climate (Gioda et al. 2011). It was well recoganized that DOC is emitted directly from combustion sources and is formed by gas-to-particle conversion processes (Guillermo et al. 2014; Park et al. 2015). More importantly, DOC is an important warming agent of climate system due to its strong light absorption ability (Hu et al. 2018; Li et al. 2016a; Niu et al. 2017a; Yan et al. 2016). Considering the significance of DOC in the global carbon cycling, the study of DOC in rainwater should be a high priority (Kieber et al. 2002; Niu et al. 2014).

DOC originates from multiple sources, including climatic factors (Evans et al. 2005), marine and terrestrial biogenic emissions (Kawamura and Kaplan 1986), anthropogenic emissions (e.g., primary emissions, fossil fuels) (May et al. 2013; Raymond 2005). In the past few decades, the rapid development and industrialization in East and South Asia, the extensive land use, unusual urbanization (Whelpdale and Kaiser 1997) as well as industrial expansion (Moreira-Nordemann et al. 1998), have led to severe atmospheric pollution. The air pollutants from these source regions can significantly affect the climate and environmental system of other regions, such as the Tibetan Plateau (TP) and surrounding areas (Cong et al. 2015; Ji et al. 2011; Niu et al. 2016, 2017a). Correspondingly, the recent history of an air mass is an important factor controlling the sources of DOC in precipitation. It was noted that approximately 20–30% of DOC present in atmospheric water was from combustion processes, and 4%–24% of the rainwater DOC was of fossil fuel origin (Avery Jr et al. 2006; Patrycja et al. 2015; Yan and Kim 2012). Moreover, the water-soluble fraction of OC generally dominates the water-insoluble fraction (WinOC) (Legrand et al. 2013a; Pio et al. 2007).

Water soluble organic compounds could be removed from the atmosphere by the processes of dry deposition of particulate-bound pollutants, and scavenging by rainfall (Jurado et al. 2004, 2005). The removal process of atmospheric DOC by rainwater prior to its oxidation to carbon dioxide is of great importance in evaluating the global carbon cycle. It has been estimated that the organic carbon fraction may account for 80% of the global flux of rainwater carbon (Campos et al. 2007; Willey et al. 2000). Studies on DOC in rainwater have been investigated worldwide in recent years, such as in Asia (e.g., Li et al. 2016a, 2017; Hu et al. 2018; Pan 2010; Sempére and Kawamura 1994; Yan and Kim 2012), in the USA (e.g., Hecobian et al. 2010; Raymond 2005), in Europe (e.g., Evans et al. 2005; Patrycja et al. 2015), in New Zealand (e.g., Kieber et al. 2002; Willey et al. 2000) and in South America (e.g., Coelho et al. 2008). Moreover, rainwater DOC from different environments in Northern China have also been analyzed (Pan 2010). Similarly, the spatial and temporal distributions of DOC in urban, rural, and forest areas in Poland have been comprehensively studied. Their results demonstrated that biogenic emission is a primary source of organic carbon in forest rainwater of Poland (Patrycja et al. 2015). Almost all of these studies concluded that fossil fuel and biogenic emissions are the major sources of DOC in rainwater. Moreover, the variations of other chemical components in lakes, surface streams and soil can significantly be affected by

the increasing DOC concentration, which is likely to influence the whole ecosystem of nearby areas (Evans et al. 2005).

Despite the significance of DOC in the global carbon cycle, its spatial distribution is still unclear due to relatively few studies in precipitation, especially in the southeast edge of the TP. The rainwater DOC in the Mt. Yulong region has not yet been studied. It is necessary to investigate rainwater DOC of this area, particularly due to its geographical importance. Study on the rainwater DOC in urban/rural areas and its spatial-temporal variations in the Mt. Yulong region have significant implications for the investigation of carbon deposition and carbon cycle at the high elevation areas of the TP. Moreover, the long range cross-border transport of atmospheric pollutants strongly influences the eco-environment and glacier melting and need urgent attention.

High-sensitivity measurements of DOC and inorganic ions in precipitation were conducted from the Mt. Yulong region. Rainfall samples were synchronously collected from five sampling stations in the Mt. Yulong region. The objectives of this study are (1) to clarify the variability of rainwater DOC concentrations and its spatial distribution in the Mt. Yulong region from June to September 2014; (2) to explore the emission sources and transport pathways of DOC in rainwater; and (3) to estimate the wet deposition amount of DOC in the Mt. Yulong region.

2 Study area

Mt. Yulong (26°59′-27°17′ N, 100°04′-100°15′ E) located in the southernmost of Hengduan Mountains Range, Yunnan Province, China, has a maximum length of 35 km and width of 18 km with a peak of 5596 m asl (Fig. 1). It has a complex anticline structure by Indosinian Movement; limestone is the dominate rock in this area. Approximately 19 temperate glaciers are distributed around Mt. Yulong with the total glacier area of about 11.6 km^2. These glaciers are generally influenced by the southwest monsoon climate (He et al. 2010). The largest glacier in Mt. Yulong is Baishui glacier in the eastern slope of Mt. Yulong; it is a temperate glacier in the southeast of the TP.
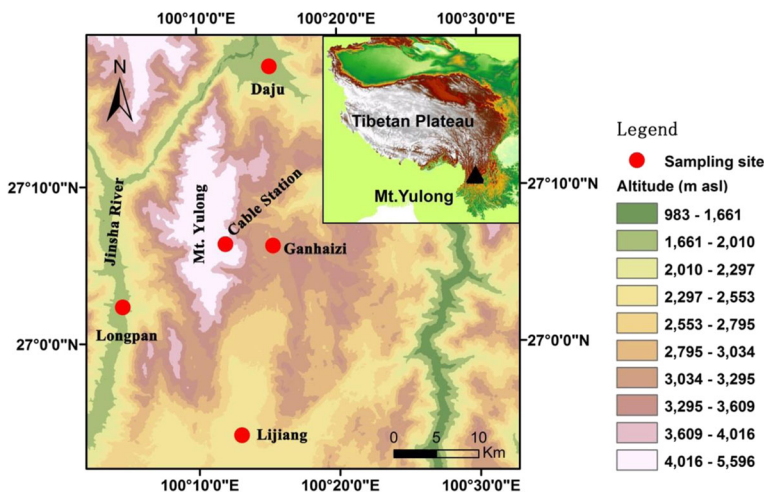

Fig. 1 Map of the study area and sampling sites in the Mt. Yulong region

Under the influence of summer monsoon and west wind circulation, the region has a distinct seasonal monsoon climate with annual average temperature of 14.15 °C and annual precipitation of 917.9 mm (Table 1). Approximately 90% of the rainfall occurs during the monsoon season, and a large amount of moisture and heat is transported northward and westward from the India and Pacific oceans by the prevailing southwest and southeast monsoons, respectively (Niu et al. 2013, 2014, 2016).

Lijiang city (LJ) (27°10′-27°40′N, 100°07′-100°10′ E) is located 25 km south of the Mt. Yulong; the total population in Lijang city is 1.24 million. Statistical sources indicate a rapid increase in tourism in this area, and excessive exploit and use of basic facilities and resources is having significant influences on the local eco-environment of this region. The amount of NO_x emission was up to 36,887 ton in Lijiang in 2014, far more than that of sulfur dioxide (22,023 ton) (Shi et al. 2017).

Ganhaizi (GHZ) Basin is located at the foot of Mt. Yulong, and is separated from the urban area (Table 2). This area has also seen an increase in tourism activity. Longpan Town (LP) and Daju Town (DJ) are located to the west and to the north of Mt. Yulong, respectively. Both of LP and DJ are close to and along the Jinsha River (Fig. 1), where the planting industry is one of the major sources of economy to the local habitants. The geomorphology of LP is a typical gorge. The climate of LP is warm and wet, whereas it is hot and dry in DJ.

The Cable Station (4510 m asl) is very close to the Baishui glacier and is an ideal field observation site for high atmospheric environment in the TP.

3 Material and methods

3.1 Rainwater sampling

Rainwater samples were synchronously collected from LJ, LP, DJ, GHZ and CS in the Mt. Yulong area from June to September, 2014. For each individual rainfall event, one rainwater sample was collected for chemical analysis at each sampling site. A rainfall sampling event is defined as the sample collected from the onset until the end of a specific rainfall period (Niu et al. 2014). The numbers of rainfall samples collected at each site were: LJ = 38; LP = 48; DJ = 21; GHZ = 37; and CS = 60. Each sampling site was carefully selected prior to installing sampling equipment. The sampling sites were located at relatively less polluted areas and away

Table 1 Monthly meteorological data of the Mt. Yulong region in 2014

Month	Precipitation (mm)	Pressure (hPa)	Wind speed(m/s)	Temperature (°C)	Relative humidity (%)
January	0.60	764.10	3.20	7.50	39.00
February	4.40	761.00	4.00	9.40	39.00
March	4.50	763.50	4.30	12.40	37.00
April	12.50	763.70	4.10	16.00	36.00
May	2.20	762.10	4.00	19.00	44.00
June	219.90	760.30	2.30	20.00	67.00
July	358.80	762.40	1.50	18.50	80.00
August	192.50	763.40	1.70	17.80	81.00
September	108.60	764.30	1.80	17.30	78.00
October	11.30	767.00	2.00	13.60	66.00
November	0.00	764.70	2.60	10.40	53.00
December	2.60	764.80	3.00	7.90	48.00

Table 2 Description of the five sampling stations

Sampling sites	Altitude (m asl)	Latitude (N)	Longitude (E)	Type of site
Cable Station (CS)	4510	27°06′16.953″	100°11′59.297″	High altitude
Ganhaizi (GHZ)	3054	27°06′08.285″	100°15′25.418″	Tourist area
Lijiang City (LJ)	2395	26°54′ 04.336″	100°12′ 55.486″	Urban
Longpan (LP)	1921	27°05′54.270″	100°04′12.491″	Suburban
Daju (DJ)	1754	27°17′36.442″	100°05′11.541″	Suburban

from the places where human activities are intense. However, besides the emissions from tourist vehicles in the Lijiang city, there are some other limited pollution sources, such as agricultural waste burning, biomass burning (open fire), and crustal aerosols (Niu et al. 2016, 2018b) near the study area. However, these five sampling sites are located on the southeast fringe of the Tibetan Plateau (TP), away from urban influences, and they can be considered as ideal observation areas for atmospheric research in the glacierization region.

The collected rainwater samples were separated into two polyethylene bottles for determination of major ions and DOC concentrations. The sampling equipment was installed 1.5 m above the ground to avoid pollutants from the ground surface. After collection, the rainwater samples were transferred to pre-cleaned polyethylene bottles. The bottles were cleaned by soaking in 20% HNO_3 for 24 h and thorough rinsing with deionized water (Al-Khashman 2005; Niu et al. 2014). All the collected samples were kept in a refrigerator at Yulong glacier and environment observation station in Lijiang city, before being transported to the State Key Laboratory of Cryospheric Science, Northwest Institute of Eco-Environment and Resources, Chinese Academy of Sciences in Lanzhou city. The whole collecting process was done manually wearing disposable gloves to avoid sample contamination at the 0.1 μeq L^{-1} level.

3.2 Analysis of major ions and DOC

Major ions including cations (Na^+, K^+, NH_4^+, Ca^{2+}, Mg^{2+}) and anions (SO_4^{2-}, Cl^-, NO_3^-) in rainfall samples are measured using the ion chromatography system DX-600 and ICS-2500. Before measurements, deionized water was injected into the instrument (while the instrument was stably running) to measure the blank value and ensure the accuracy of detection limits (0.01–0.05 ueq L^{-1}). Each rainfall sample was measured twice and the mean ion value was calculated. We determined that the measurement precision was better than 8%.

Each rainwater sample was filtered using disposable needles-type filters (MN Chromafil^R, PA-20, 0.20 μm, USA) before measuring DOC concentrations. DOC concentration was determined employing TOC-5000A (Shimadzu Crop, Kyoto, Japan) (Stubbins and Dittmar 2012) with the measured accuracy of ±5%. The measurements were conducted using the total carbon (TC) and inorganic carbon method. The inorganic carbon in the sample was defined as the carbon in carbonates and dissolved CO_2 in the sample. The TOC or DOC content was calculated by subtracting the measured inorganic carbon content from the TC content (Niu et al. 2017a, 2018a).

3.3 Methods for light absorption of DOC

The light absorption spectra of rainwater DOC samples were determined by employing an ultraviolet-visible absorption spectrophotometer (SpectraMax M5, USA), scanning wavelengths from 200 to 800 nm at an interval of 5 nm (Yan et al. 2016; Hu et al. 2018).

The mass absorption efficiency (MAE) of DOC (or MAE_{Doc}) (unit: m^2 g^{-1}) was calculated according to the Lambert-Beer Law (Kirillova et al. 2014a, b; Li et al. 2017; Niu et al. 2018a; Yan et al. 2016).

$$MAE_{Doc} = \frac{-\ln\left|\frac{I}{I_0}\right|}{C \times L} = \frac{A}{C \times L} \tag{1}$$

Where I and I_0 are the light intensity of incident light and transmitted light, respectively. C is the concentration of DOC and L is the light path length (1 cm, for the quartz cuvettes used in measurements) and A is the absorbance directly measured by the spectrophotometer.

The measurement uncertainty for the light absorption of DOC includes the precision of DOC concentration measurements, the precision of the absorbance measured by the spectrophotometer, and the interference from light-absorbing inorganic compounds such as nitrate (Cheng et al. 2011; Kirillova et al. 2014a, b). Moreover, the different spectrophotometers and the corresponding wavelength ranges employed in different studies in measuring the light absorption of DOC might cause some uncertainties. In this study, the measurement uncertainty for the light absorption of DOC is ±6%.

3.4 Backward trajectory analysis

The trajectories of air masses were traced by using the HYSPLIT4 model (HYbrid Single-Particle Lagrangian Integrated Trajectory) which was developed by the NOAA Air Resources Laboratory (http://www.arl.noaa.gov/ready/hysplit4.html). This model is widely utilized to track the transport, diffusion pathways and the deposition processes of atmospheric pollutants from the source regions.

3.5 Statistical analysis

Elements data (ion and DOC concentrations) were analyzed using analysis of variance (ANOVA) methods (Gu 2013; Gueorguieva and Krystal 2004). ANOVA is based on the variance of the observed variable, which is the variable that has significant influence on the observed variable (e.g., Niu et al. 2017a). It provides a statistical test of whether the means of several groups are equal or not, and therefore generalizes the t-test to more than two groups. Post-hoc tests are widespread hypothesis testing, they can be used to examine the mean of one or two normal population when the variance is unknown. Additionally, factor analysis and Pearson correlation analysis are also used to analyze the sources of DOC in rainwater of the Mt. Yulong area.

4 Results and discussion

4.1 Variability of DOC concentrations in the Mt. Yulong region

The average concentrations of DOC in rainwater from five sites are presented in Fig. 2. In addition, statistical tests were performed to evaluate significant differences between DOC at the five sampling stations (Table 3). The results of post-hoc test showed that significant differences of DOC concentrations existed, for example, between LP and GHZ, LP and LJ
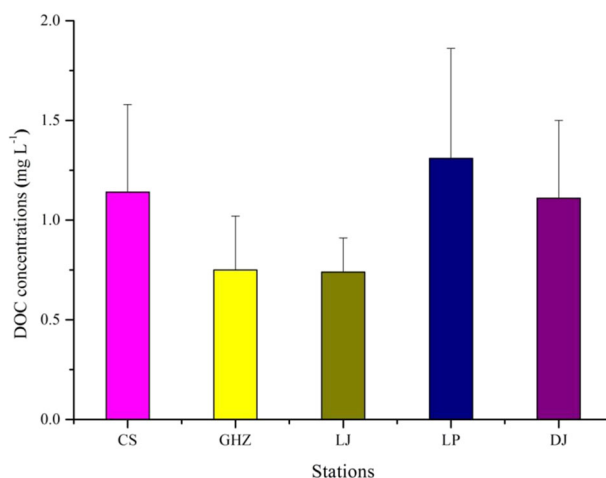
Fig. 2 Spatial variations of the average DOC contents in rainwater samples in the Mt. Yulong region (hanging bars represent standard deviation)

at the 0.05 confidence level (Table 4). Rainwater in LP had the highest DOC concentration (1.31 ± 0.55 mg L^{-1}), followed by CS and DJ (1.14 ± 0.44 and 1.11 ± 0.39 mg L^{-1}, respectively), while GHZ and LJ had the lowest values, i.e. 0.75 ± 0.27 and 0.74 ± 0.17 mg L^{-1}, respectively (Fig. 2). Among the five stations, CS has the highest frequency of precipitation (on average once a day) during the summer time, which is because the station on Mt. Yulong has the highest elevation (4510 m asl) compared with other stations. However, the long-range transport of pollutants from the source regions contributed relatively high DOC concentrations in CS rainwater (e.g., Cao et al. 2010; Cong et al. 2015; Lüthi et al. 2014). The highest DOC concentrations found in LP rainwater are mostly due to its particular topography and anthropogenic emissions in the area. Due to its gorge topography, it is very difficult for the pollutants to escape and spread outside the region. With the rapid development of tourism industry and economy in this area, highways in the Mt. Yulong region are extensive. In addition, the heavy traffic system and passenger flow (Niu et al. 2018b) have created an adverse impact on the local atmospheric environment. Agriculture industry is also thriving in LP which can affect air quality by frequent fertilizer use and straw burning (biomass or biogenic emissions) (Coelho et al. 2008; Niu et al. 2016). Additionally, air pollutants from South Asia can be easily transported and deposited over the Himalayas and the Tibetan Plateau under the monsoon circulations in monsoon season (Fig. S1) (Cao et al. 2010; Cong et al. 2015; Lüthi et al. 2014; Niu et al. 2017a, 2018b), which can significantly affect the atmosphere and environment in this area. LP is located to the west of Mt. Yulong, thus it was directly influenced by anthropogenic emissions (e.g., biomass burning, vehicle emissions) of short-haul transport from the downstream of the Jinsha River compared with other stations in the Mt. Yulong region.

Table 3 Statistical analysis for DOC concentrations in five groups of rainwater from the Mt.Yulong region

	Sum of squares	df	Mean square	F	Sig.
Between groups	5.868	4	1.467	9.063	0.000
Within groups	14.407	89	0.162		
Total	20.274	93			

DJ town is located to the north of Mt. Yulong and has the least amount of rainfall (on average 33% less) among the five stations. DOC concentrations in rainwater from DJ were relatively higher. CS is a typical high-elevation station on the Mt. Yulong. However, it has higher rainwater DOC contents than those of found in GHZ and LJ stations (Fig. 2), in addition to long-range cross-border transport of pollutants from southwest and southeast Asia, regional-emissions from Lijiang city and surrounding areas through convection transport might have contributed to the relatively higher DOC concentration in CS rainwater (e.g., Niu et al. 2018b). Generally, valley wind can easily climb along the mountain slope and transport pollutants or moist air to the higher altitude and then coagulate as precipitation falling on land (Niu et al. 2016; Orlandini and Lamberti 2000). DOC concentrations in rainwater from CS station were more likely reflecting the effects of strong wind on high-elevational air quality in the Mt. Yulong area. The content of DOC in fresh snow was nearly more than 2.0 mg L^{-1} (Niu et al. 2017a), considerably higher than that in rainwater, which might be due to massive deposition of pollutants in snow during the winter and spring seasons. The lower concentrations of DOC in GHZ and LJ rainwater were probably due to the effects of stringent environment protection measures had been taken in these areas (Niu et al. 2018b).

Moreover, we analyzed temporal variation of DOC concentrations in LP rainwater (LP has the most sampling stints during the frequent rainfall events (on average every ~1.3 days)). As shown in Fig. 3, DOC concentrations in LP rainwater demonstrated significant temporal variations during the rainy season. The decrease of DOC concentrations in rainwater was mainly due to the photolysis of DOC (Sumner and Shepson 1999; Grannas et al. 2004; Niu et al. 2017b), and wash out or scavenging by frequent rainfall events (e.g., Soyol-Erdene et al. 2011; Pan 2010; Yan and Kim 2012), although DOC can be continuously supplied during the

Table 4 Post-hoc tests for DOC concentrations in five groups of rainwater samples (CS, GHZ, LJ, LP, DJ) from the Mt. Yulong area

I	J	Mean difference (I-J)	s.d.	sig.	95% confidence interval	
					lower bounder	lower bounder
CS	GHZ	0.386	0.143	0.085	−0.027	0.799
	LJ	0.385	0.136	0.058	−0.007	0.778
	LP	−0.183	0.132	1.000	−0.562	0.196
	DJ	−0.016	0.162	1.000	−0.483	0.451
GHZ	CS	−0.386	0.143	0.085	−0.799	0.027
	LJ	−0.001	0.127	1.000	−0.365	0.364
	LP	−0.569*	0.122	0.000	−0.919	−0.219
	DJ	−0.402	0.154	0.106	−0.845	0.041
LJ	CS	−0.385	0.136	0.058	−0.778	0.007
	GHZ	0.001	0.127	1.000	−0.364	0.365
	LP	−0.569*	0.113	0.000	−0.895	−0.243
	DJ	−0.401	0.147	0.078	−0.826	0.023
LP	CS	0.183	0.132	1.000	−0.196	0.562
	GHZ	0.569*	0.122	0.000	0.219	0.919
	LJ	0.568*	0.113	0.000	0.243	0.895
	DJ	0.167	0.143	1.000	−0.245	0.579
DJ	CS	0.016	0.162	1.000	−0.451	0.483
	GHZ	0.402	0.154	0.106	−0.041	0.845
	LJ	0.401	0.147	0.078	−0.023	0.826
	LP	−0.167	0.143	1.000	−0.579	0.245

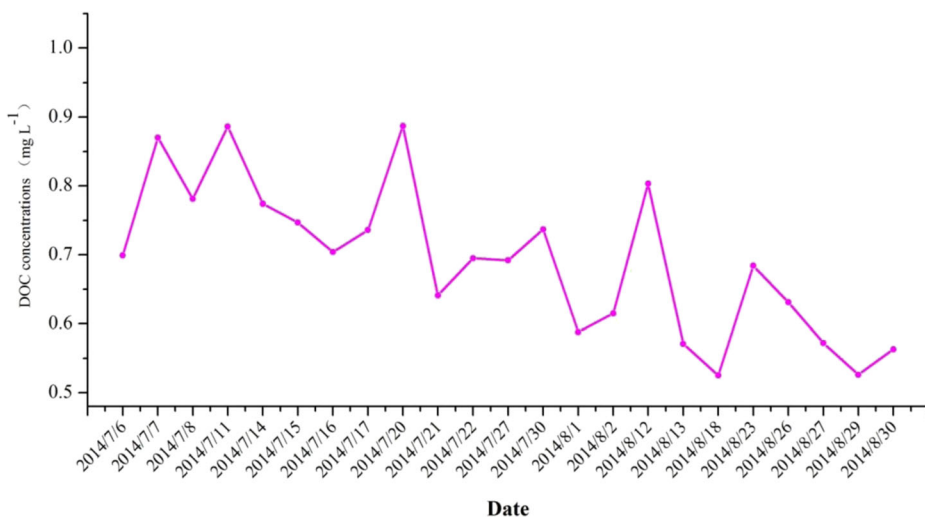*The mean difference is significant at the 0.05 level

Fig. 3 Temporal variations of DOC contents in rainwater samples in LP

rainy season (Kieber et al. 2002). Many of the oxidation products in rainfall may be more volatile than their precursors, leading to their release to the atmosphere (Anderson et al. 2008). The sporadic peaks of DOC concentration could be due to the dry period preceding the precipitation events (Yan and Kim 2012), or to frequent rainfall events (every ~1.3 days) with occasional dust from anthropogenic activities (Dong et al. 2011; Niu et al. 2014), and local emissions from tourism related activities (Niu et al. 2016, 2017b, 2018b). Additionally, it was recognized that the production of organic aerosol from biogenic precursors may have been enhanced by the change in the oxidative capacity of the atmosphere (Grannas et al. 2004; Han et al. 2012; Kanakidou et al. 2000). Several environmental factors can affect the amount of biogenic emissions, such as summer temperatures and atmospheric CO_2 levels (Guenther 1997; Niu et al. 2017a). Therefore, rainwater DOC concentrations presented a distinct temporal trend in the rainy season.

The average MAE of rainwater DOC calculated at 365 nm (MAE_{365}) using Eq. (1) was 0.43 ± 0.32 m^2 g^{-1} in rainwater, which is significantly lower than that from snow and ice on Baishui glacier in the Mt. Yulong (Niu et al. 2018a). In addition, the MAE_{DOC} in rainwater was lower than those from the glaciers in other remote regions, such as Barrow, Alaska (2.6 ± 1.1 m^2 g^{-1}) (Voisin et al. 2012) and Laohugou (LHG) glacier in the northern TP (1.4 ± 0.4 m^2 g^{-1}) (Hu et al. 2018; Yan et al. 2016). However, the MAE_{DOC} in rainwater from Mt. Yulong is comparable with that found in rainwater from Nam Co station (i.e. the Nam Co Monitoring and Research Station for Multisphere Interactions) (0.48 ± 0.47 m^2 g^{-1}) and Everest station (i.e. the Qomolangma Station for Atmospheric and Environmental Observation and Research) (0.64 ± 0.49 m^2 g^{-1}) in the Himalayas and TP (Li et al. 2017). Different with those from seriously polluted urban areas (e.g., Lhasa and Beijing), the variations of MAE_{DOC} in rainwater in the remote areas of the TP are independent of the DOC concentration (Li et al. 2017; Zhang et al. 2011). Factor analysis on the 24-h integrated filter data associated ~20 to 30% of absorption coefficient (Abs_{365}, in units m^{-1}) over 2007 with a secondary source that was highest in summer and also the main source for oxalate, suggesting that aqueous phase reactions account for the light-absorbing property of DOC observed throughout the Southeastern US in summer (Hecobian et al. 2010).

It has been reported that the MAE_{DOC} of Lhasa rainwater was 0.38 ± 0.24 m^2 g^{-1}, which was much lower than that from aerosols of 0.78 ± 0.21 m^2 g^{-1} (Li et al. 2016c, 2017). Atmospheric water-soluble organic carbon (WSOC) was about twice as absorbing per carbon as humic acids (Limbeck et al. 2005). The mean MAE_{365} of humic-like substances (HULIS) was 0.25 ± 0.12 m^2 g^{-1} in aerosols of central TP (Nam Co, 4730 m asl) during summer season (Wu et al. 2018). However, the mean MAE of elemental carbon in aerosols at 632 nm, measured for the first time at Mt. Yulong, was 6.82 ± 0.73 m^2 g^{-1} (Niu et al. 2018b), whereas the MAE_{365} of DOC in aerosols was 0.61 ± 0.97 m^2 g^{-1} measured in our previous investigation. The average MAE_{365} of water-soluble brown carbon (WS-BrC) was 0.32 ± 0.07 m^2 g^{-1} for aerosols (in summer season) over the southeastern TP (Zhu et al. 2018), it was nearly comparable with the mean MAE_{365} of BrC (0.45 ± 0.18 m^2 g^{-1}) in aerosols in the high Himalayas during monsoon season (Kirillova et al. 2016). The MAE_{DOC} of rainwater is lower than that of surface aerosols since DOC originates from the rain-scavenging of aerosol particles in atmosphere (Li et al. 2017). This is also due to (a) larger amounts of biogenic volatile organic compounds (VOCs) exist in rainwater DOC. But the biogenic VOCs had lower light absorption abilities than that of particulate-bound DOC (Li et al. 2017; Zhang et al. 2011). (b) DOC in rainwater undergoes stronger oxidation in the atmosphere than aerosolized WSOC. Previous studies showed that oxidized low light-absorption water-soluble carbonyls with low molecular masses are more easily dissolved into rainwater (Kiss et al. 2003; Ervens et al. 2011), resulting in low MAE_{DOC} values. Moreover, rainwater DOC contains more secondary organic aerosols (SOAs) that experience strong light bleaching processes (Lambe et al. 2013) and more biogenic VOCs than surface aerosols. Because of the lack of enough light absorption components, the light absorption abilities of SOAs are relatively low (Lambe et al. 2013).

4.2 Source apportionment of DOC in the Mt. Yulong region

4.2.1 Principal component analysis

Generally, rainwater DOC reflects the carbonaceous particles in atmosphere, the content of which could be greatly influenced by meteorological conditions, such as ambient temperature, relative humidity, precipitation, etc. Moreover, site characteristics, regional or long-range transport of anthropogenic (biomass or fossil fuel burning) and biogenic (plants and animals) emissions in terrestrial systems (Patrycja et al. 2015; Orlović-Leko et al. 2009) can also affect rainwater DOC contents. Principal component analysis (PCA) was performed to investigate the possible sources of DOC in rainwater. PCA allows a robust assessment of the behaviour of the nine variants (Table 5). PCA decomposition or factor loading provides objective representations of multivariate data through the analysis of the covariance structure of its variants (Meeker et al. 1995; Kang et al. 2002; Niu et al. 2014, 2016). Results showed that the total variance of the first three components (PC1) was 85.54%. K$^+$, Mg^{2+}, Ca^{2+}, SO$_4^{2-}$, NO$_3^-$ and DOC were heavily loaded on PCA1 and their total variance was 68%, indicating their similar sources in rainwater. Mg^{2+}, Ca^{2+} are generally recognized as indicators of mineral dust from natural environment (Wake et al. 1993; Yao and Thompson 1992; Kang et al. 2010), their high loadings (percents of variance: 0.96 and 0.95, respectively) are related to strong weathering of the limestone rocks (Niu et al. 2014, 2016). Besides a crustal source, K$^+$ (percent of variance: 0.69) is usually derived from biomass burning (Andreae and Merlet 2001; Niu et al. 2016) and biogenic emissions (Legrand et al. 2013b; Singer et al. 2012). This source may be relevant to

Table 5 Results of PCA carried out on rainwater samples: factor loading, and percentual explained variance

Species	PCA1	PCA2	PCA3
Na^+	0.07	0.92	0.06
NH_4^+	−0.04	0.19	0.94
K^+	0.69	0.61	0.03
Mg^{2+}	0.96	0.13	0.06
Ca^{2+}	0.95	0.10	0.16
Cl^-	0.05	0.81	0.31
SO_4^{2-}	0.51	0.13	0.76
NO_3^-	0.93	−0.01	0.04
DOC	0.68	0.37	0.25
% of variance	51.52	20.93	13.10

The numbers in the table represent the percent of variance associated with each major ion and DOC. Negative values indicate an inverse relationship

our samples since the majority of villagers in Lijiang and the surrounding villages or South Asia use wood and crop straw to heating and cooking. DOC has the same loading percent (i.e. 0.68) with that of K^+ in rainwater, largely suggesting their common sources (primary biomass burning and little biogenic emissions). High loadings of NO_3^- and SO_4^{2-} (percents of variance: 0.93 and 0.51, respectively) indicate their common anthropogenic sources, probably the enrichment of gas-phase SO_x and NO_x in atmosphere due to numerous vehicle emissions (Niu et al. 2018b; Shi et al. 2017). Furthermore, correlation analysis demonstrated that strong correlations exist between DOC and SO_4^{2-} ($R^2 =$ 0.48, $p < 0.01$), DOC and NO_3^- ($R^2 = 0.64$, $p < 0.01$) in rainwater (Fig. 4), further manifested that anthropogenic emissions (vehicle emissions) from tourism related activities in the Mt. Yulong area partly contributed to DOC concentrations in rainwater. According to statistical data, during 2012–2014 the emitted NO_x was approximately 36,887 ton, which is considerably more than that of SO_2 (22,023 ton) (Shi et al. 2017).

The second component (PC2) accounts for 21% of the total variance with Na^+, Cl^- heavily loaded (percents of variance: 0.92 and 0.81, respectively) (Table 5). It was previously recognized that a portion of Na^+ in the rainfall in the Mt. Yulong region was derived from the Na^+-rich rock weathering within the monsoon circulations (Niu et al. 2013, 2016). Strong monsoon circulation over this region accounts for the sea salt source for Cl^- and part Na^+ in rainwater (Niu et al. 2014). The total variance of PC3 was 13% with NH_4^+ and SO_4^{2-} heavily loaded (percents of variance: 0.94, 0.76, respectively). Both of these two ions indicated the contribution of fossil fuel and partly biomass burning to DOC in rainwater (Niu et al. 2016, 2017a). Under the assistance of PCA method, we have conducted a detailed investigation on DOC sources because ions in samples were also water-dissolved and have been experienced the same experimental process with that of DOC (Li et al. 2016a).

4.2.2 Backward trajectory analysis of the prevailing air mass

The abundance of DOC in rainwater is influenced by many parameters, including regional and remote transmission of pollutants. Ninety-six hour air parcel backward trajectory analysis was performed and the prevailing air masses were categorized into three groups, i.e. southwestern, southern and southeastern (Fig. 5). Those three groups of air mass are typical trajectories, and thus can provide insight into the source of DOC in the Mt. Yulong region. The air mass demonstrated in Fig. 5a was transmitted from the north of Indian Ocean, crossed over densely
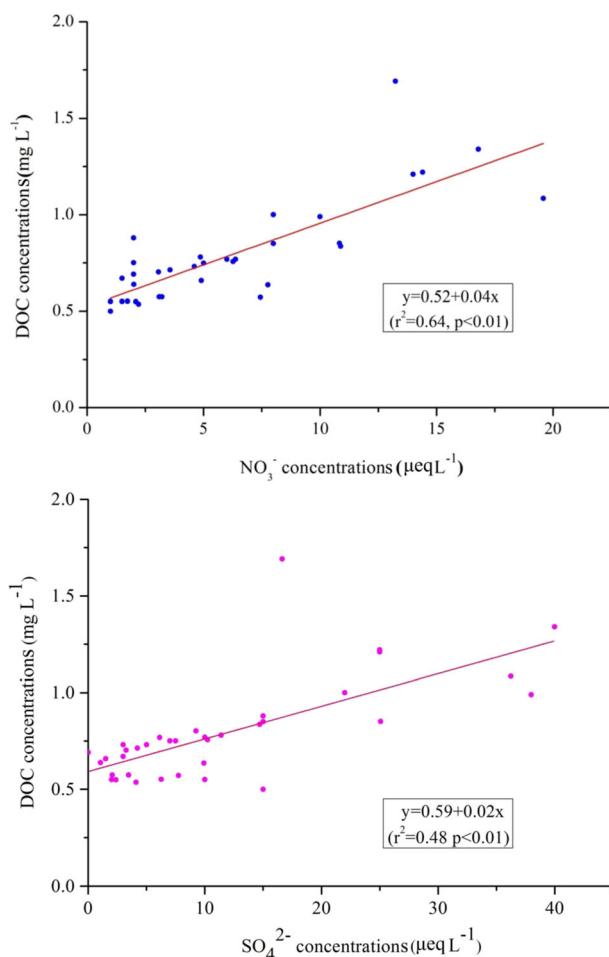
Fig. 4 Regression analyses of DOC, SO_4^{2-}, and NO_3^- concentrations in Lijiang rainwater

populated, agricultural and industrialized regions in South Asia, such as Bangladesh, north-eastern India and north Burma. The southwestern monsoon advection can easily transmit mixed fraction of gaseous mircro-particles to the southeast of the TP, which can seriously influence the air quality of the Mt. Yulong area (Niu et al. 2018b). The frequency of southwestern monsoon accounts for 46% of the total investigated monsoon events during the rainy season, and the volume-weighted mean (VWM) DOC concentration was 1.25 ± 0.56 mg C L^{-1}. Patrycja et al. (2015) noted that when the level of air masses travel decrease with time, the residence time of gaseous and particulate pollutants within the planetary boundary layer before arriving at the receptor site is longer. That means aged air mass has a strong correlation with the concentration of total organic carbon in aqueous phase (fog and cloud water) due to its high oxidability and easy solubility (Ervens et al. 2011, 2012).

The prevailing southeastern monsoon/advection in the Mt. Yulong region is mainly from the north of Thailand and Laos by cross-border transport (Fig. 5b), which accounted for 21% of the total investigated monsoon events and the VWM DOC concentration was 0.95 ± 0.40 mg C L^{-1}. The pervasive agriculture activities and

biomass/biogenic burning in the southeast of Asia probably produced much carbonaceous particles, which significantly contributed to the deposition of carbonaceous aerosol in the Mt. Yulong area in addition to the local emissions.

Figure 5c shows that air masses mainly from the southeastern Asia crossed over the natural block of the Himalayas and TP, and travelled to the southeast of Hengduan Mountain, which makes up 13% of the investigated monsoon events. The mean DOC concentration in rainwater was 0.98 ± 0.43 mg C L^{-1}, comparable to the scenario of Fig. 5b. However, it is lower than the concentration calculated for the scenario of which under the influence of southwest monsoon (Fig. 5a). Coastal cities in the southeast of China are densely populated and intensely industrialized which understandably impact air quality (Huang et al. 2008). The other fraction (21%) of wind events was the south branch of westerly, which brings little precipitation to the Mt. Yulong region and it was not presented in the current discussion.
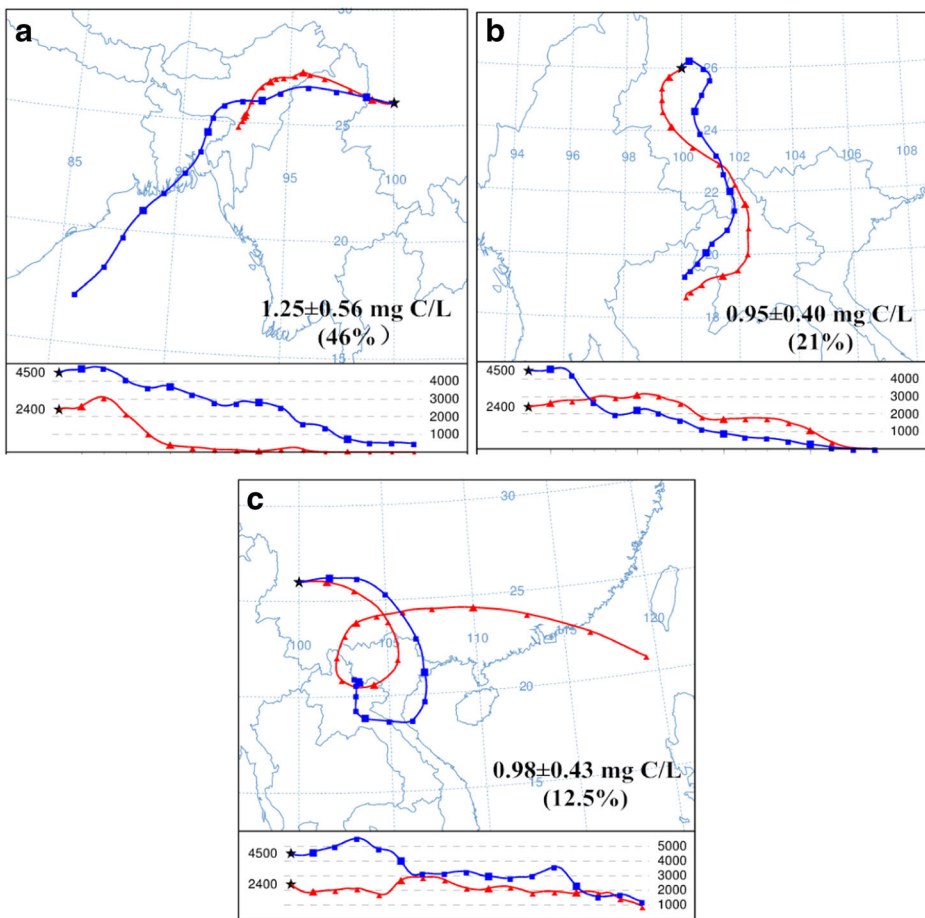

Fig. 5 Ninety-six hour backward trajectories generated using NOAA HYSPLIT_4 model for prevailing air masses in the Mt. Yulong region during June and August in 2014. Each figure represents a different category: southwestern (**a**). southern (**b**). and southeastern (**c**). The occurring frequency of each prevailing air mass in the region (expressed as percentage of the total events) and volume-weight mean concentrations of DOC (VWM ± SD) are marked in the plot

4.3 Wet deposition flux of DOC in Mt. Yulong region and its implication

The wet deposition flux of DOC in precipitation during monsoon season can be calculated as the sum of depositional amount per precipitation event using the following equation (Li et al. 2016a, 2017; Willey et al. 2000; Zhang et al. 2012):

$$F_c = 0.001 \times \sum_{i=1}^{n} C_i \times P_i$$

where F_c (g C m^{-2}) denotes the wet deposition flux of DOC in precipitation, C_i (mg L^{-1}) expresses the DOC concentration in each precipitation event i, P_i (mm) represents the depth of precipitation corresponding to the precipitation event i. DOC concentrations in winter precipitation were based on the mean concentrations measured in the snowfall (fresh snow) samples collected in Mt. Yulong in 2014. Accordingly, the wet deposition flux of DOC in the Mt. Yulong region during the monsoon season was 0.66 g C m^{-2} season^{-1}. Therefore, the annual wet deposition of DOC was estimated at 1.99 g C m^{-2} year^{-1} in the Mt. Yulong area.

Figure 6 showed the annual wet deposition of DOC in the Lijiang city and other studied areas. It is clearly evident that Amazonia has the highest wet deposition flux (4.8 g C m^{-2} year^{-1}) (Williams et al. 1997), followed by Beijing (2.7 g C m^{-2} year^{-1}) (Pan 2010), while Lhasa city (Li et al. 2016a) and Marshall Islands (Zafiriou et al. 1985) had the lowest flux values (0.59 g C m^{-2} year^{-1}, 0.63 g C m^{-2} year^{-1}, respectively). In addition, the wet deposition of DOC in Lijiang city (1.99 g C m^{-2} year^{-1}) was comparable to the flux in Seoul (1.90 g C m^{-2} year^{-1}) (Yan and Kim 2012), Wilmington (2.1 g C m^{-2} year^{-1}) (Willey et al. 2000), and Netherlands (2.0 g C m^{-2} year^{-1}) (Nguyen et al. 1990). Therefore, wet deposition flux of DOC characterized by distinct regional difference worldwide. The highest wet deposition flux of DOC (found in Amazonia) was primarily due to agriculture-related activities, especially due to the intense sugar cane burning. It was suggested that regional scale organic carbon emissions prevail over long-range transport (Coelho et al. 2008). Seoul, Wilmington and Marshall Islands are all under the strong impact of marine vapors. Air masses originated from oceans can easily influence the climate, visibility, and atmospheric environment. Willey
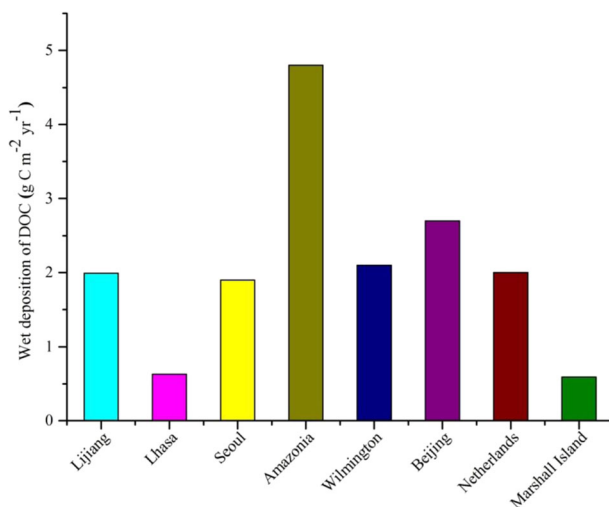

Fig. 6 Wet deposition flux of DOC in the Lijiang city and other areas

et al. (2000) found that the high DOC contents in continental rainfall (featured by cold fronts, low-pressure system, and local thunderstorms). The Marshall Islands has significantly low deposition flux of DOC (Fig. 6), because it is a remote island in the Pacific Ocean (Zafiriou et al. 1985). Tourist activities and traffic transportation somewhat have exerted influences on air quality in Mt. Yulong (Niu et al. 2016, 2018b). The annual wet deposition of DOC in Mt. Yulong was considerably higher than that in Lhasa. Compared with other cities, the highest elevation and least human activities in Lhasa city resulted in the lowest annual flux of DOC. Relatively intensive domestic coal use and combustion for house heating, less precipitation scavenging and dilution of organic carbon during winter can well account for the higher annual deposition flux of DOC in Beijing city (Pan 2010). However, there was little coal use for house heating and cooking during winter in the Mt. Yulong area, which could be the reason for good air quality of this region.

Carbonaceous aerosols affect radiative balance of the earth by absorbing and scattering sunlight radiation. It was investigated that DOC has strong light absorption property at both ultraviolet and visible wavelengths (Chen and Bond 2010; Li et al. 2016a, b; Yan et al. 2016; Hu et al. 2018). The visible light absorption is important for direct radiative forcing since 47% of solar energy is distributed within visible range from 400 to 700 nm (Cheng et al. 2011; Hecobian et al. 2010; Jacobson 1998, 2001; Kirillova et al. 2014a, b). The climate effects of carbonaceous aerosol depend on its physical and chemical properties, as well as depend on the residence time and distribution in the atmosphere (Jacobson 2001; Li et al. 2016b). Kirillova et al. (2014a) elucidated that the direct light absorption property of DOC were found in the range of 2–10% relative to that of the main light absorption elements, such as black carbon, brown carbon, mineral dust, etc. DOC in snow and ice on glacier significantly reduced surface albedo of glacier (approximately by 2~10%) (Niu et al. 2017a, b). As one of light absorption factors, DOC can absorb much sunlight radiation and affect energy fluxes of glacier, which further accelerates glacial melting and poses a serious threat to water resources supply for local habitants (e.g., Liu et al. 2016; Niu et al. 2018b). Therefore, more attention should be paid on rainfall DOC in the future studies. The estimates and preliminary analyses in this work, however, are tentative and need to be refined, so as to more valuable data are made available on the DOC concentrations in rainwater in the TP.

5 Conclusions

For the first time, a study of rainwater DOC was conducted in the Mt. Yulong region. Rainwater samples were synchronously collected during the rainy season from five study stations from the surrounding areas of Mt. Yulong.

DOC concentrations in rainwater showed distinct regional differences in the Mt. Yulong region. Rainwater in LP station had the highest DOC concentrations (1.31 ± 0.55 mg L^{-1}) due to its particular topography and some anthropogenic emissions (including agriculture and industry) in this area. GHZ and LJ rainwater had the lowest DOC concentrations (0.75 ± 0.27 and 0.74 ± 0.17 mg L^{-1}, respectively). Regional emissions and long-range convection transport of emissions contributed to the relatively high DOC concentration (1.14 ± 0.44 mg L^{-1}) in the high atmosphere (>4500 m). Temporal variations of DOC concentration in LP rainwater displayed an obvious decreasing trend during the course of our study, mainly due to the photolysis of DOC and scavenging by frequent rainfall events.

The results from PCA method revealed that anthropogenic emissions (vehicle emissions) from tourism related activities in the Mt. Yulong area partly contributed to DOC concentrations in rainwater, in addition, biomass or biogenic burning also played a role in the deposition of DOC in this area. The prevailing air masses in the Mt. Yulong area were categorized into three groups from backward trajectory analyses, they are southwestern monsoon (46%), southern monsoon (21%), and southeastern monsoon (12.5%), which significantly contributed to the abundance of rainwater DOC in this area. The MAE of rainwater DOC evaluated at 365 nm was 0.43 ± 0.32 m^2 g^{-1} in rainwater. Annual wet deposition flux of DOC in the Mt. Yulong region was estimated at 1.99 g C m^{-2} year^{-1}. As one of light absorption factors, DOC can accelerate glacial melting and further affect water resources supply for a great number of local habitants. Therefore, more attention should be paid to DOC deposition and its effects on glaciers in the future studies.

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