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Determining rainwater dissolved organic carbon to reveal atmospheric carbon deposition in China's karst city: Variations, origins, and deposition flux

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ABSTRACT

A large amount of organic carbon (OC) in the atmosphere are transferred to the Earth's surface through dry (40%) and wet (60%) deposition. Therefore, wet deposition is an important physical pathway for the removal of atmospheric OC. Identifying the variations of DOC in wet deposition (rainwater) is essential for clarifying the earth-surface C balance. The present study detected the DOC content in 96 daily rainwater samples collected over an entire year in a karst city, with abundant rainfall in Southwest China. The DOC concentrations varied between 1.03–37.7 mg C L^{-1}, while the VWM value stood at 2.76 mg C L^{-1}, which is similar to the worldwide and Asian averages. The yearly DOC wet deposition flux was calculated as 2.88 g C m^{-2} yr^{-1}. Both the VWM concentration and flux of rainwater DOC exhibit pronounced seasonal variations and regional differences, primarily controlled by precipitation and the external input of OC. The sources of rainwater DOC were multifaceted, including urban waste emission, agricultural activities, and fossil fuel combustion (especially coal combustion), while the contribution from natural sources was limited. Additionally, the C: N (2.08) ratio of rainwater is significantly lower than the Redfield ratio (6.625), indicating the importance of considering the impact of nutrient components in rainfall on the material cycling of surface water ecosystems. This work will benefit the knowledge of the present status of rainwater DOC and its deposition flux on the karst regional scale and further on a global scale, and contribute to a better understanding of the C geochemical cycle on the territorial system.

1. Introduction

The atmosphere is one of the most important reservoirs of carbon (C), and the carbon-containing components (e.g., organic carbon, OC) play an important role in the radiative forcing processes of Earth (Godoy-Silva et al., 2017). As the main chemical component of particulate matter, the increase in the concentration of carbon-containing components can lead to reduced visibility (e.g., the accumulation of $PM_{2.5}$ in the atmosphere can cause serious haze pollution) (Huang et al., 2012; Huang et al., 2014; Cui et al., 2021; Wang et al., 2022; Wei et al., 2023a; Wei et al., 2023b). Meanwhile, its light absorption characteristics can change the earth-surface balance of energy, and further indirectly influence the regional climate and eco-environment (Duan et al., 2007; Wang et al., 2023a; Zeng et al., 2024b). Because of the rapid intensification of global urbanization and highly intensive human activities, urban areas have become hotspots for OC emissions in recent years (Xu et al., 2018a). Hence, the removal process and mechanism of OC from the urban atmosphere have garnered attention of the academic community.

The wet deposition stands as the primary physical pathway for converting reactive OC into dissolved organic carbon (DOC) and removing it from the atmosphere (Iavorivska et al., 2016). A study has used models to calculate DOC deposition flux in worldwide rainwater and pointed out that 85 and 188 Gt carbon were transported to the ocean and Earth's surface annually (Safieddine and Heald, 2017). In general, rainwater DOC includes thousands of C-containing species on the molecular scale (Chen et al., 2022), which include different functional groups, such as ester, carbonyl, carboxyl, and conjugated aromatic substituents (Zeng et al., 2020b). Its physical and chemical properties indirectly affect precipitation forcing, thereby affecting global climate

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change (Gioda et al., 2011). The enrichment of DOC in precipitation can directly impact freshwater ecosystems, coastal ecosystems, and terrestrial carbon balance (Evans et al., 2005). Therefore, exploring the variations and possible origins of DOC in rainwater, and accurately quantifying its wet deposition flux is significant to reveal and clarify the atmospheric C dynamics (source and sink), which are also beneficial to the C budget evaluation and carbon neutrality (Iavorivska et al., 2016).

The rainwater DOC in originates directly from the dissolution of particulate or gaseous OC species in the atmosphere. The sources of these atmospheric OC are quite complex, including fossil fuel combustion, biomass burning, agricultural emissions, plant emissions, and soil resuspension (Kieber et al., 2002; Pantelaki et al., 2018; Zeng et al., 2020b). Some OC molecules generated by natural and human activities can transported thousands of kilometers in the air (Cao et al., 2009). For instance, isotopic analysis of ^{13}C and ^{14}C in atmospheric precipitation in northeastern United States cities revealed that marine organic carbon is transferred from the ocean to mainland with rainfall (Raymond, 2005). A study investigated DOC in glacier meltwater and snowfall in Alaska region of the United States, revealing that DOC mainly derived from human activities (particularly fossil fuel combustion) and ultimately deposited in glaciers through atmospheric circulation (Stubbins et al., 2012). This is consistent with the research results of DOC in ice core samples from Mont Blanc (the highest peak in the French Alps) (May et al., 2013). In addition, the atmospheric carbon-containing organic compounds (e.g., formic acid, acetic acid, oxalic acid, etc.) in some areas have relatively short migration distances and can be quickly washed by rainfall and deposited. This leads to an increase in the concentration of organic acids in the rainfall, which affects the degree of acidification and chemical composition of the rainwater (Brooks Avery et al., 2006; Zhang et al., 2011; Sun et al., 2016; Niu et al., 2018). In different regions, the sources contribution and controlling factors of rainwater DOC are greatly varied. A study found that biomass combustion was the principal source of rainwater DOC in two Brazilian cities, where are impacted by the burning of sugar cane foliage (Coelho et al., 2008). The source of rainwater DOC in a marginal sea area (affected by human activities and sea spray) of the Yellow Sea in China has been explored, with coal combustion as the main contributor (Xing et al., 2019). The in-site observations in the Varanasi area (India) have found that significant increase in rainwater DOC deposition flux caused by industrial emissions and biomass combustion (Pandey et al., 2015).

The rapid increase in population, coupled with rising energy consumption and transportation demand, has significantly increased the emissions of anthropogenic OC pollutants in the atmosphere, providing an important material basis for the wet deposition of organic carbon. Furthermore, ample rainfall typically efficiently purges OC from the atmosphere in a certain area (Ravan et al., 2022), allowing it to deposit on the surface in the form of DOC. However, there are still numerous uncertainties and issues in the process identification, flux estimation, and impacting factors of rainwater DOC wet deposition, due to the inadequate systematical and continuous monitoring (Iavorivska et al., 2016), especially the less observation of precipitation DOC in karst regions (southwest China, fragile ecological environments) (Zeng et al., 2020b). This study investigated the daily-based rainwater samples in Guiyang (typical karst city), an eco-civilization constructed city in Guizhou Province, from April 2022 to March 2023 to comprehend the DOC wet deposition processes. The concentrations of rainwater DOC and the typical ions were determined, and further analysis was conducted in conjunction with environmental and meteorological issues. The major objectives in this work encompass (a) examining the alterations and influencing issues in rainwater DOC, (b) exploring the prospective sources and their relative importance of DOC in wet deposition, and (c) evaluating the deposition flux of DOC in such as karst city and possible environmental effects. This research bears critical importance in comprehending the biogeochemical processes of C, which would be helpful for the environmental management in eco-civilization city construction and air systems.

2. Experimental

2.1. Environmental setting

Guiyang is located in the Yunnan-Kweichow Plateau, which is part of the hilly basin region in central Guizhou (Fig. 1a) and is an iconic karst mountainous city in Southwest China (Wang et al., 2023b; Wang et al., 2024). It has a wide distribution of carbonate rocks and developed karst landforms (Tang and Han, 2019). The predominant land use encompasses urban area, waterbody, grassland, barren land, farmland, forest, and shrubbery (Fig. 1b). The terrain in Guiyang's urban area is undulating, with no plains, primarily characterized by mountains and hills (Fig. 1c). The sample collection site is situated within the Huaxi District of Guiyang, characterized by a subtropical humid climate. Winters lack severe cold spells, and summers are devoid of excessive heat. The yearly average temperature stood at 13.3 °C, exhibiting marked seasonal fluctuations (Fig. 1d). The annual precipitation in the study area varied between 900 and 1500 mm (Han et al., 2011). The monthly average rainfall ranged from 15 to 281 mm, peaking in June and dropping to its lowest in February (Fig. 1e). The June displayed a higher monthly average relative humidity of 83%, while April recorded a lower monthly average relative humidity of 76% (Fig. 1f).

Since the 1980s, the advancement of urbanization and rapid industrial expansion has led to a highly concentrated population and a rapidly growing Gross Domestic Product (GDP) in this city. The data disclosed on the website of the Guiyang Municipal Government shows that the year-end permanent resident population of Guiyang City was 6.22 million in 2022, reflecting an increase of 1.9% in contrast to the last year. The amount of civilian vehicles in this city has exceeded 2.13 million, marking an increase of 8.9% compared to 2021. Guiyang is a city with agriculture, industry, and tourism as its industrial pillars. Due to the limitations of climate and terrain, as well as the influence of the total stationary front of Yunnan and Guizhou, it had relatively serious air pollution and was previously designated as a typical acid rain control zone (Larssen et al., 2006). As economic development and construction progressed, people gradually recognized that prioritizing ecological conservation and embracing green, low-carbon development was the right path forward. Since the establishment of an ecological civilization city in 2012, Guiyang has undergone industrial restructuring and has achieved notable results in air pollution control. The air quality excellence rate reached 100% in 2022. The concentration of inhalable particles such as $PM_{2.5}$ and PM_{10} has roughly decreased 2 times in the past decade.

2.2. Sampling and analysis

Rainwater samplers (5 L glass beaker) were placed on the roof of a building in Huaxi District, Guiyang City (26.44° N, 106.66° E) (Fig. 1b) to collect rainwater. It is an open environment with no obvious sources of pollution. The sampler was covered in non-rainy weather to avoid the influence of other substances. Turn on the sampler in advance of the onset of rainfall and collect the sample in bottles after the rain stops and store them away from light immediately. The rainwater samples were manually collected daily on rainy days (if the rainfall duration was >1d, one sample was collected per 24 h). According to the weather forecast, if the rainfall event was likely to occur in the evening, the sampler lid was opened ahead of time. Then, the sample was collected as early as possible in the next morning (if the overnight rain has ended) or collected after the rainfall event finished in the next day. After sampling, the sampler was cleaned with deionised water and let it dry. During the sampling period of April 2022 to March 2023, 96 daily- rainwater samples were collected. Followed the previous rainwater DOC study (Bao et al., 2022), the rainwater samples were immediately filtered via the GF/F glass filter membrane (Whatman, pore size = 0.7 μm, precombusted at 400 °C before use) and glass solvent filter (negative pressure filtration). All glass containers were soaked in 10% nitric acid

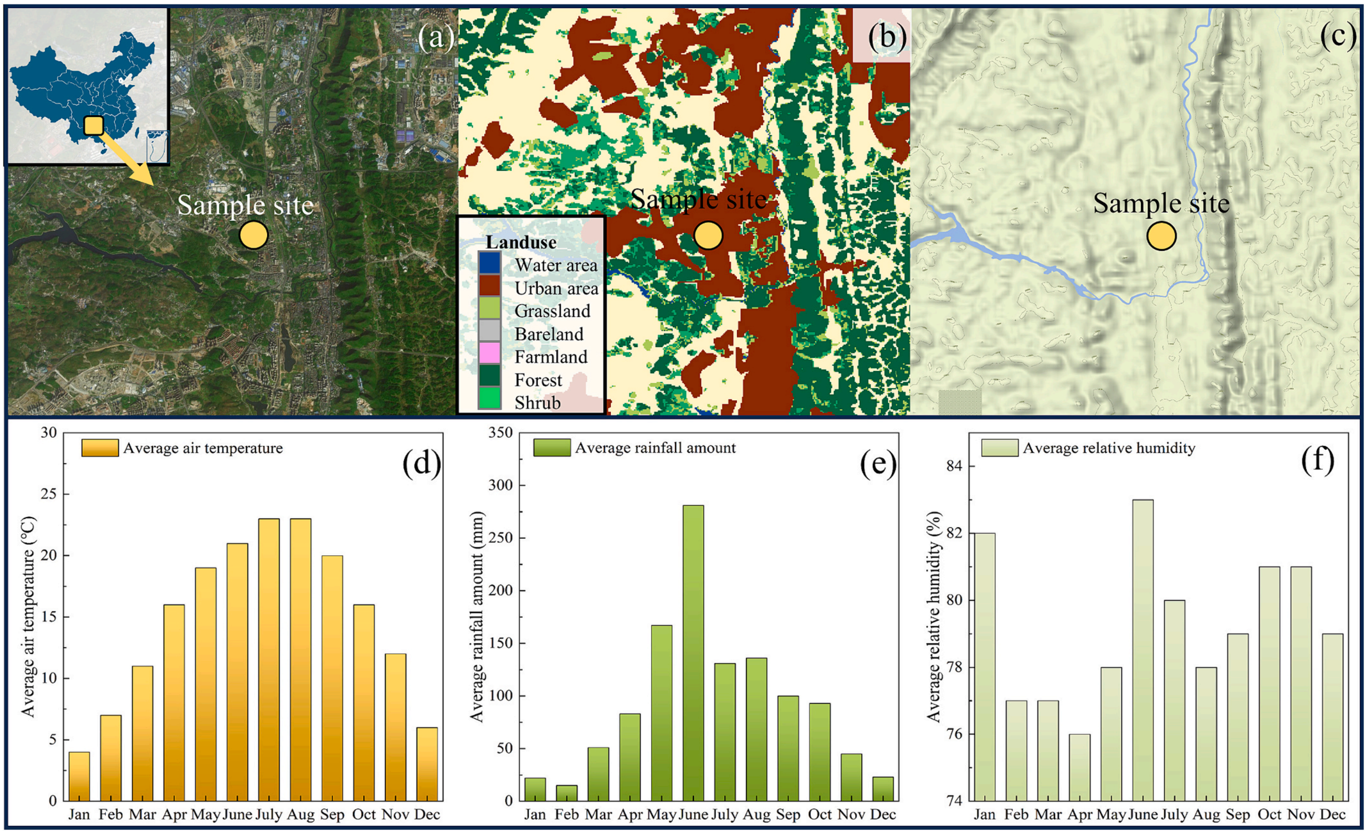

Fig. 1. (a) The study area's geographic location within China and an aerial view of the sample site, (b) land use distribution, (c) topographic distribution, (d) average monthly air temperature, (e) average monthly rainfall amount, and (f) average relative humidity.

for >24 h, rinsed repeatedly by ultrapure water and dried for use. This method aimed to prevent any potential alterations to the chemical components of rainwater. All samples were measured in the laboratory of Guizhou University. Briefly, measuring the rainwater DOC concentration in a TOC analyzer (Elementar Vario). The theory of the TOC analyzer and its measured processes can be consulted in published articles (Witkowska et al., 2016). Before measurement, the rainwater samples were pre-treated with pure phosphoric acid (pH < 2) to remove the dissolved inorganic carbon (DIC), despite its low level (Górka et al., 2011). For water samples, the direct Non-Purgeable Organic Carbon (NPOC) method is applied with burning under high temperature (850 °C). Put the water sample in a glass bottle in the autosampler with the carrier gas of O_2 (gas flow = 200 cm^3/min). 0.2 μL water sample was directly loaded into the incineration tube and further catalytically oxidized DOC to CO_2, and then the CO_2 was determined by an IR detector. The calibration curve for DOC concentration utilized standards derived from potassium hydrogen phthalate dissolved in ultrapure water. The content of major ions (NH_4^+, K^+, Na^+, Ca^{2+}, Mg^{2+}, F^-, Cl^-, SO_4^{2-}, and NO_3^-,) were measured using ionic chromatography (ICS, Dionex 1100) and reported in our previous study (Zeng et al., 2024a). During the experimental analysis and testing process, the reagent blank and procedure blank, samples, parallel samples and standard reference material (certified standard solution GBW08606 for ions) are measured simultaneously to ensure the quality of the analysis. The total dissolved nitrogen (DTN) content in rainwater samples were tested using the method described in (HJ 636–2012). The specific analysis method is outlined as follows: initially, take 10 mL of the water sample into a 25 mL ground glass colorimetric tube. Subsequently, add 5 mL of alkaline potassium persulfate solution to the tube. Then seal the tube with gauze and string to prevent bursting. All samples are processed according to the above steps and then placed in an autoclave to digestion for 30 min. After cooling, introduce 1 mL of hydrochloric acid (HCl) solution, dilute the mixture with ultrapure water up to the 25 mL mark, and thoroughly shake the contents. The absorbance is then measured at wavelengths of 220 nm and 275 nm using water as the reference on the ultraviolet spectrophotometer. Finally, the sample concentration was calculated from the linear relationship (working curve) between absorbance and standard solution concentration. Overall, the blanks were below the detection limit and the relative standard deviation of repeated measurements was ±5%, revealing the negligible impacts of possible pollution during the measurement process on concentration in rainwater. The website (http://www.weather.com.cn/) provided meteorological parameters for this study, including rainfall amount, air temperature, and relative humidity. The content data of atmospheric pollutants ($PM_{2.5}$, PM_{10}) in Guiyang City were from historydata (https://www.aqistudy.cn/historydata/).

2.3. Data calculations

The volume-weighted mean (VWM) concentration of DOC and DTN in rainwater were calculated in the following formula:

$$VWM_{concentration} = \frac{\sum C_i R_i}{\sum R_i} \quad (1)$$

where C_i and R_i represent the determined concentration of DOC or DTN (mg L^{-1}) in rainwater and corresponding rainfall (mm).

The DOC or DTN wet deposition fluxes (g $m^{-2}\cdot yr^{-1}$) were counted as below:

$$F = VWM_{concentration} \times R_t \quad (2)$$

Where F represents the monthly or yearly wet deposition fluxes of DOC or DTN, R_t refers to the total rainfall for the corresponding time (mm).

2.4. Data processing method

The relationship between rainwater DOC concentrations and other chemical components of rainwater was analyzed using Spearman rank correlation analysis, based on the results via the Kolmogorov-Smirnov test (K—S, a non-parametric statistical test used to compare whether the cumulative distribution function of a sample conforms to a particular theoretical distribution) (Cao et al., 2022), Using Origin 2023b to process data and visualize them.

3. Results and discussion

3.1. DOC concentration in wet deposition

3.1.1. Comparison of DOC concentration within the global dataset

The VWM concentrations, mean concentrations, and range of rainwater DOC in this work were presented in Table 1. Observably, the arithmetic mean concentration of rainwater DOC (6.21 mg C L^{-1}) exceeded the VWM value (2.76 mg C L^{-1}), implying the high level of rainwater DOC deposition often occurs during events with smaller rainfall, consistent with observations worldwide. Throughout the research period, rainwater DOC concentrations exhibited significant variation, the lowest DOC concentration (1.03 mg C L^{-1}) occurring on 21st October 2022 corresponding to the rainfall of 16.6 mm, and the highest concentration (37.72 mg C L^{-1}) occurred on 18th February 2023 corresponding to the rainfall of only 1 mm. The difference between the highest and lowest concentrations was nearly 37 times. These results indicated that rainfall had a significant impact on DOC concentrations. Furthermore, rainwater DOC concentrations in the sampling period did not adhere to a normal distribution based on the K—S test results and exhibited a large standard deviation (SD, 6.16 mg C L^{-1}), suggesting that the average rainwater DOC concentration was influenced by extreme values of rainwater samples. Therefore, it is more reasonable to compare VWM concentrations for rainwater DOC (Zeng et al., 2020b).

On a global scale (Table 1), the rainwater DOC VWM concentration of Guiyang (2.76 mg C L^{-1}) is close to the average concentration in Asia (2.65 mg C L^{-1}) or globally (2.64 mg C L^{-1}), but much higher than monitoring values in some remote areas with few people and far away from industrial areas (e.g., Everest, Himalayas, 0.86 mg C L^{-1}, New Zealand, 0.70 mg C L^{-1}) (Kieber et al., 2002; Iavorivska et al., 2016; Li et al., 2017). In some agricultural areas such as the karst agricultural area (Houzhai village) in southwestern China (0.63 mg C L^{-1}) and Pennsylvania in the United States (0.71 mg C L^{-1}), the rainwater DOC concentrations were much lower than the present result (Iavorivska et al., 2017; Zeng et al., 2020b). In comparison, the rainwater DOC VWM concentration in the Kofu (located in a basin) (1.15 mg C L^{-1}) (Matsumoto et al., 2022) and Seoul (densely populated) (1.13 mg C L^{-1}) (Yan and Kim, 2012) were approximately twice lower than that in this study. However, the VWM concentration in this study was close to Beijing (2.38 mg C L^{-1}), a mega-city with numerous potential sources of atmospheric organic carbon components, and close to that in Shandong (2.57 mg C L^{-1}), where the main source of DOC in rainwater and snow has been confirmed to be fossil fuels (Wang et al., 2016; Zeng et al., 2023). Additionally, it was found that the VWM concentration of rainwater DOC in Guiyang was lower than that in Jiaozhou Bay but higher than that in Xiamen, Yangma Island, and Aveiro when considering geographical location (inland and coastal) (Santos et al., 2013; Bao et al., 2018; Xing et al., 2019; Xie et al., 2022b). The comparison results of this study with annual VWM concentration values for rainwater DOC in different regions highlight the following two points: firstly, the VWM concentration of rainwater DOC in different regions exhibits different characteristics may be controlled by various factors such as geographical location, anthropogenic inputs, and meteorological conditions (Willey et al., 2000; Coelho et al., 2008; Avery et al., 2013; Siudek et al., 2015; Yang et al., 2019; Zeng et al., 2023). Secondly, the contribution of exogenous OC inputs on the concentration of rainwater DOC in the study area significant (Xu et al., 2022).

3.1.2. Temporal Variations of DOC

In the sampling period of this study, a total rainfall of 1045 mm was recorded, with a maximum monthly rainfall of 275.4 mm and a minimum of 8.7 mm, indicating significant inter-monthly variations in precipitation. The monthly VWM concentrations of rainwater DOC fluctuated between 1.54 mg C L^{-1} (August 2022) and 9.65 mg C L^{-1} (February 2023), exhibiting distinct seasonal variations (Fig. 2). The precipitation DOC concentrations (in VWM value) of spring (March to May) and winter (December to February) exhibited an inverse relationship with rainfall, with lower (higher) concentrations observed during months with higher (lower) rainfall.

To further explore the relationship between rainfall and the concentration of rainwater DOC, correlation analyses on both original and logarithmically transformed data (Fig. 3). The results revealed an

Table 1
DOC concentration and wet deposition flux in Guiyang and other areas in the world.

Location	Areas	Period	DOC concentration			DOC wet deposition flux	Annual amount rainfall	Reference
			Ranges	Mean	VWM			
			mg C L^{-1}			g C m^{-2} yr^{-1}	mm	
Guiyang (This study)	City	2022–2023	1.03–37.7	6.21	2.76	2.88	1045.1	This study
Asian average	–	1985–2015	–	2.65	–	–	–	(Iavorivska et al., 2016)
World average	–	1985–2015	–	2.64	–	3.40	–	(Iavorivska et al., 2016)
Everest, Himalayas	Background	2014–2016	–	–	0.86	0.16	–	(Li et al., 2017)
New Zealand	Background	1999–2000	0.12–4.81	–	0.70	–	–	(Kieber et al., 2002)
Puerto Rico	Background	2004–2007	–	0.40	–	–	–	(Gioda et al., 2011)
Houzhai Village, Southwest China	Rural	2016–2017	0.11–8.18	1.46	0.63	0.67	1064	(Zeng et al., 2020b)
Pennsylvania, America	Rural	2010–2015	0.11–4.98	–	0.71	0.79	1113	(Iavorivska et al., 2017)
Shandong, China	City	2014	0.34–7.39	–	2.57	2.38	710	(Wang et al., 2016)
Beijing, China	City	2021	–	2.75	2.38	1.29	542	(Zeng et al., 2023)
Kofu, Japan	City	2017–2019	–	–	1.15	1.28	1120	(Matsumoto et al., 2022)
Wuhan, China	City	2018–2019	0.89–2.19	1.45	–	–	–	(Bai et al., 2021)
Zagreb, Croatia	City	2009–2010	0.69–4.86	1.82	–	–	–	(Orlović-Leko et al., 2020)
Seoul, Korea	City	2009–2010	0.18–9.39	–	1.13	1.90	–	(Yan and Kim, 2012)
Jiaozhou Bay	Coastal city	2015–2016	1.58–20.4	5.20	3.63	3.15	866	(Xing et al., 2019)
Xiamen, China	Coastal city	2011–2012	0.10–11.18	–	1.54	2.08	1350	(Bao et al., 2018)
Aveiro, Portugal	Coastal town	2008–2009	0.15–6.75	–	0.63	0.40	–	(Santos et al., 2013, 2014)
Yangma Island	Coastal	2020–2021	0.37–7.18	–	1.52	0.95	626.9	(Xie et al., 2022b)

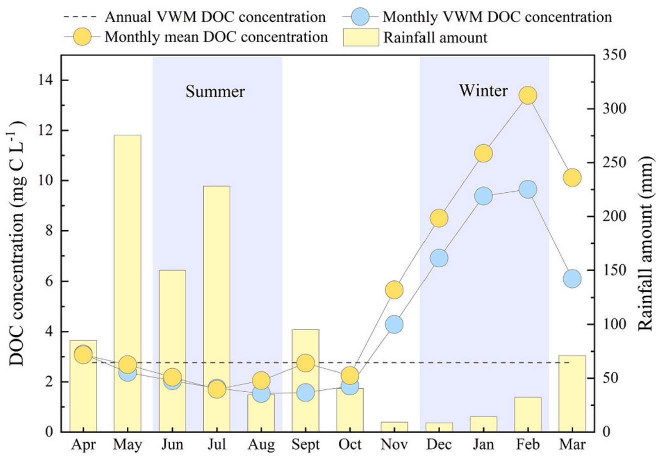

Fig. 2. Monthly variations in rainfall amount, DOC concentration, and DOC VWM concentration during the sampling period.

opposite correlation between the rainwater DOC concentration with rainfall, and the logarithmic correlation analysis further confirmed the flushing effect of rainfall on DOC ($r^2 = 0.40$, $p < 0.01$). The dilution effect of rainfall on DOC had been acknowledged in prior research studies (Bao et al., 2018; Zeng et al., 2020b; Czarnecki et al., 2023). The rainfall amount in this area among the rainy season (May–September) was 783.5 mm, accounting for 75% of the annual precipitation. During the rainy season, monthly rainwater DOC VWM concentrations were lower than the annual VWM concentration (even though the rainfall in August was relatively low, Fig. 2). This indicates that sufficient and continuous rainfall washes out aerosol particles in the air, continuously settling to the land in the form of DOC. Additionally, the rainwater DOC VWM concentration decreases continuously, which remains at a lower level for some time, consistent with previous findings on the effective removal of water-solubility OC through wet deposition (Kieber et al., 2002; Jurado et al., 2005). Total rainfall of 55.5 mm was recorded from December 2022 to February 2023, accounting for 5% of the annual precipitation. Correspondingly, higher monthly VWM concentrations of DOC were observed (Fig. 2). This phenomenon may be attributed to a reduction in winter precipitation, while human activities associated linked to coal-fired heating continuously introduce gaseous soluble OC and particulate matter into the atmosphere. This results in a scenario where a substantial amount of OC is carried away by limited rainfall (Pan et al., 2010; Zeng et al., 2020b). Interestingly, the New Zealand study had higher rainfall DOC concentrations in the warmer season in contrast with the winter season (contrary to the phenomenon observed in this study), which may be due to carbon transport from terrestrial vegetation to the atmosphere in the growing season (Kieber et al., 2002). Overall, rainwater DOC may be affected by the rainfall amount and seasonal source variations (Szidat et al., 2006).

3.2. *Sources of DOC in rainwater*

3.2.1. *Correlation analysis*

Carbon is an important component of atmospheric particulate matter, >93% of OC and EC in total suspended particulates (TSP) are concentrated in particles with a diameter < 10 μm (Chen et al., 1997). Photochemical reactions in the atmosphere are closely tied to organic carbon compounds, and their reaction processes can affect DOC concentrations. Therefore, the dissolved process of carbon in atmospheric particulate matter in the study area may to some extent affect the DOC content in rainwater. The support for this proposition stems from the clear and direct correlation established between rainwater DOC and $PM_{2.5}$ and PM_{10} of the atmospheric environment (Fig. 4). The Spearman correlation analysis (CA) results between rainwater DOC and typical chemical components (anions: F^-, Cl^-, SO_4^{2-}, NO_3^-; and cations: Na^+, K^+,

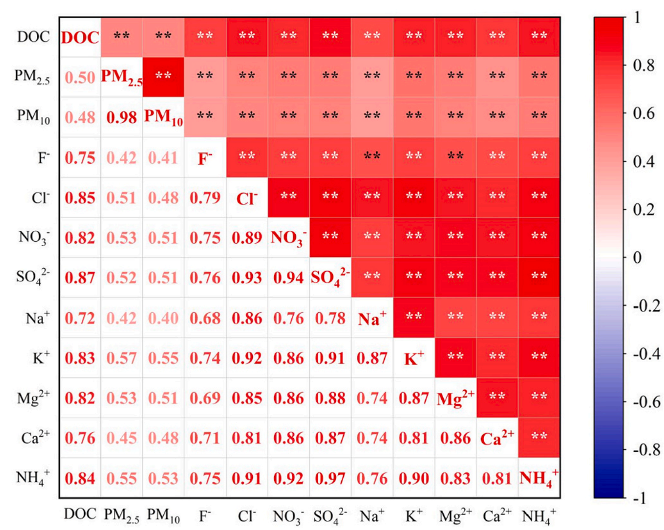

Fig. 4. Spearman rank correlation analysis of rainwater DOC and major ions concentrations in the Guiyang region. *, significance level $p < 0.05$; **, significance level $p < 0.01$.

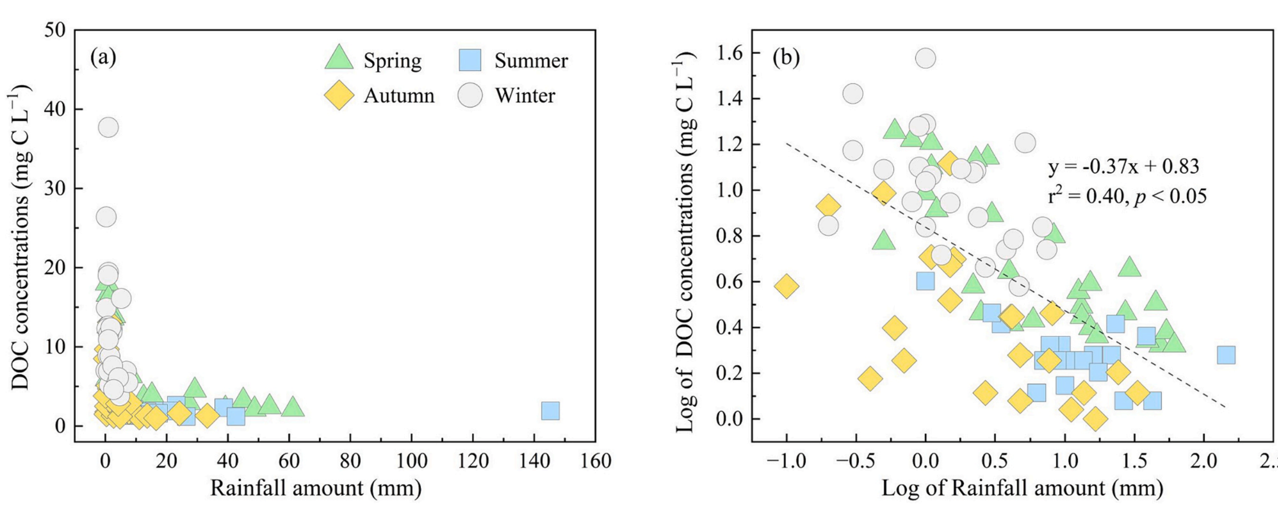

Fig. 3. Relationship between DOC concentration and rainfall for rainwater samples collected in 2022–2023. (a) Raw values; (b) Logarithmic values.

Mg^{2+}, Ca^{2+}, and NH_4^+) can determine potential co-sources of atmospheric substances (Willey et al., 2000). On the foundation of the analysis of rainwater DOC concentration and characteristic cations and anions, there is a prominent correlation between rainwater DOC and most ions ($R = 0.48$–0.87, $p < 0.05$) (Fig. 4). This implies that similar sources contribute to the ions and rainwater DOC. In addition, it was inferred from the correlation of DOC concentrations with different gaseous pollutants and meteorological factors (Table S1) that CO, NO_2, and SO_2 have the same sources as rainwater DOC.

3.2.2. Potential source identification

Previous studies have confirmed that NH_4^+ and NO_3^- are the main ions in rainfall (Yang et al., 2012; Zeng et al., 2024a). Generally speaking, it is believed that agricultural fertilization, ammonium volatilization from feces and fuel combustion are the main sources of NH_4^+ in rainwater (Wu et al., 2012; Feng et al., 2022). NO_3^- originates from the conversion of NO_X produced by fossil fuel combustion in the industrial and transportation industries (Galloway et al., 2004; Chen et al., 2011; Fu et al., 2020). The CA results clearly demonstrate a strong correlation between rainwater DOC concentration and NH_4^+ ($R = 0.84$) as well as NO_3^- ($R = 0.82$) (Fig. 4). In addition, rainwater DOC also presents a strong linear

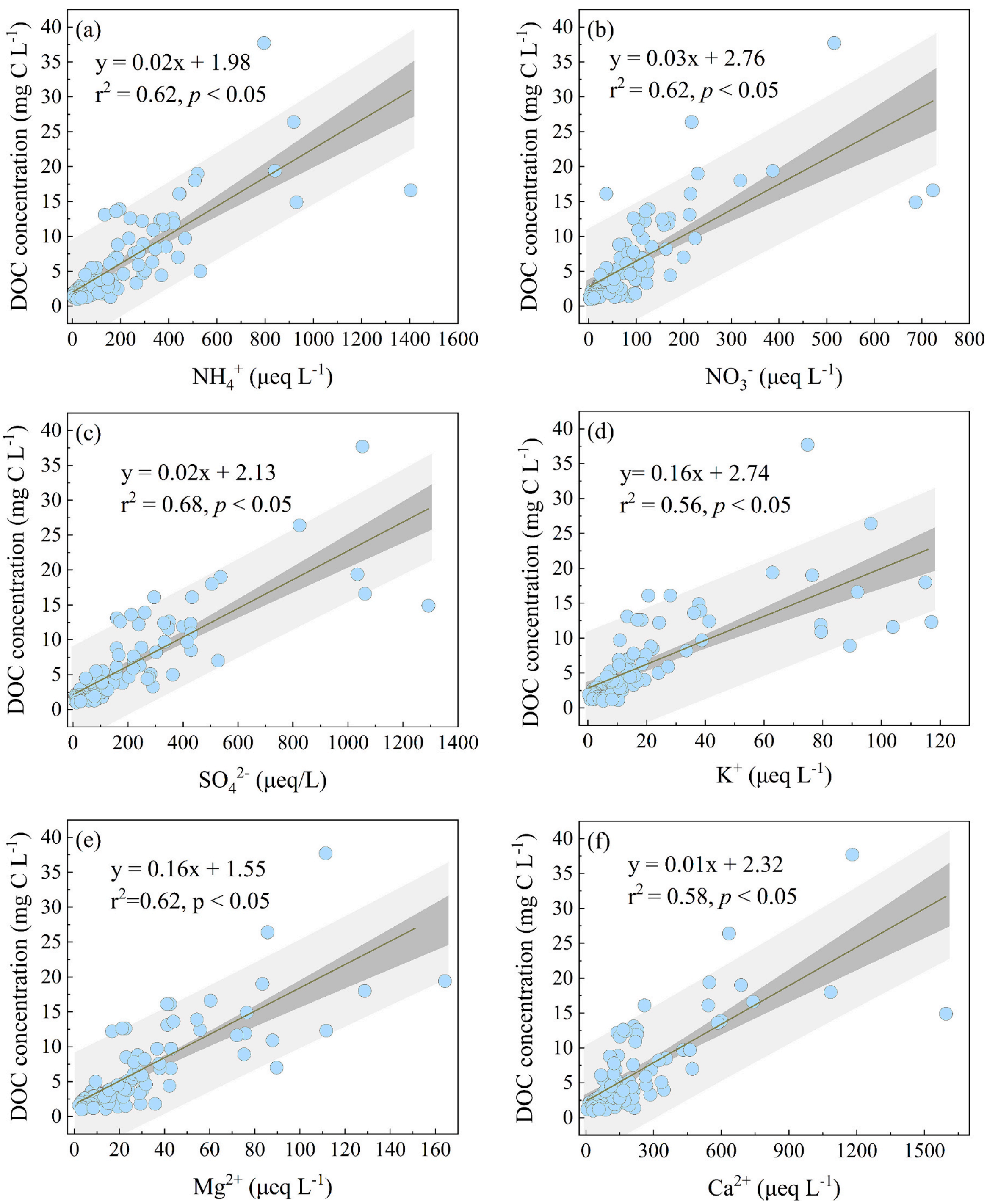

Fig. 5. Relationship between rainwater DOC concentration with major ions in Guiyang. (a) NH_4^+, (b) NO_3^-, (c) SO_4^{2-}, (d) K^+, (e) Mg^{2+}, (f) Ca^{2+}.

correlation with NH_4^+ and NO_3^- (Fig. 5a and b). This indicates that emissions related to human activities are an important source of rainwater DOC. Furthermore, based on the characteristics of NH_4^+ and NO_3^-, analyzing the ion equivalent ratio in rainwater NH_4^+/NO_3^- within a certain period can investigate the relative contributions of artificial and natural sources (Zeng et al., 2023). In areas with intense human activities, like waste emission, agricultural emissions, and fuel combustion, the NH_4^+/NO_3^- ratio in rainwater is generally >1, while in natural areas, $NH_4^+/NO_3^-$is <1. From the plot of rainwater NH_4^+/NO_3^- versus DOC concentrations (Fig. 6a), it can be observed that most of the rainwater samples in Guiyang are distributed to the right side of the $NH_4^+/NO_3^- = 1$ line, similar to the distribution patterns in Beijing and the karst agricultural area (Houzhai village), confirming that input from human sources can significantly affect the rainwater DOC.

There exists a significant positive correlation between rainwater DOC concentration with SO_4^{2-} as well as NO_3^- (Fig. 5b and c). This implies that the sources of rainwater DOC may coincide with NOx and SOx (converted to NO_3^- and SO_4^{2-}, respectively), which originated from coal combustion and fuel exhaust emissions (Han et al., 2010; Zhu et al., 2016). The contribution of stationary and mobile sources to SO_4^{2-} and NO_3^- in Guiyang rainwater can be determined by the ion equivalence ratio of SO_4^{2-}/NO_3^- (Ming et al., 2017). Most rainwater samples in Guiyang exhibited an SO_4^{2-}/NO_3^- ratio >1 (Fig. 6b), indicating a relatively higher contribution from stationary sources. This discovery is consistent with research conducted in karst agricultural region (Houzhai village) (Zeng et al., 2020b) but there is a significant difference from the results observed in Beijing (Zeng et al., 2023), probably because the contribution of urban transportation sources in this study is far less than that of the megacity Beijing (with huge vehicle ownership). Thus, the conclusion that can be drawn is that fixed emission sources are another considerable origin of rainwater DOC in Guiyang.

K^+ is commonly regarded as an indicator of biomass combustion (Pernigotti et al., 2016). Earlier research has shown the significant impact of biomass burning on global atmospheric DOC, especially in regions characterized by agricultural production and processing (Coelho et al., 2008). The K^+ is positively correlated with rainwater DOC concentration (Fig. 5d), suggesting a certain that the input of bioorganic carbon generated by biomass combustion affects the concentration of dissolved DOC in rainwater. This study also observed good correlations between rainwater DOC with Mg^{2+} as well as Ca^{2+} (Fig. 5e and f). The research area has developed carbonate rocks, which have weathered to form soil rich in calcium (Wu et al., 2012). In addition, dust generated by urban construction is considered as an input source of Mg^{2+} and Ca^{2+} in the atmosphere (Adhikari et al., 2021). herefore, it is inferred that rainwater DOC may come from carbonate weathering and urban building dust. Moreover, The PMF model-based source assessment reflected that the contribution ranking of rainwater DOC in Guiyang is as follows: long-distance transported sources (40.4%) > coal-fired sources (26.6%) > biomass combustion sources (17.2%) > secondary inorganic salt sources (12.1%) > dust sources (3.7%). This indicates that anthropogenic sources make a significant contribution to the rainwater DOC (Supplementary Information, Text S1 and Fig. S1).

3.3. DOC wet deposition flux in Guiyang

According to the monthly rainfall in Guiyang and the corresponding rainwater DOC VWM concentration, the total DOC deposition flux during the sampling period was counted as 2.88 g C m^{-2} yr^{-1}, which is lower than the global average level (3.4 g C m^{-2} yr^{-1}) (Iavorivska et al., 2016). The DOC deposition flux in Guiyang was slightly higher than in some urban areas, such as Beijing (1.29 g C m^{-2} yr^{-1}), Shandong (2.38 g C m^{-2} yr^{-1}), Japan (1.28 g C m^{-2} yr^{-1}), and South Korea (1.9 g C m^{-2} yr^{-1}) (Wang et al., 2016; Matsumoto et al., 2022; Zeng et al., 2023). In comparison to coastal areas, rainwater DOC deposition flux in this study was close to the data reported in Jiaozhou Bay (3.15 g C m^{-2} yr^{-1}) (Xing et al., 2019) and Xiamen (2.08 g C m^{-2} yr^{-1}) (Bao et al., 2018). It is worthy of remark that the DOC wet deposition flux observed in this work exceeded that in the karst agricultural areas (0.67 g C m^{-2} yr^{-1}) (Zeng et al., 2020b), Pennsylvania rural site (0.79 g C m^{-2} yr^{-1}) (Iavorivska et al., 2017), and background area (0.16 g C m^{-2} yr^{-1}) in the Himalayas (Li et al., 2017), and remote Yangma Island (0.95 g C m^{-2} yr^{-1}) (Xie et al., 2022b). The covariation trend of monthly DOC deposition flux and monthly rainfall (Fig. 7) emphasized the leading role of rainfall amount on the wet deposition of OC (Xing et al., 2019). This confirmed that rainfall is a major cleaning process for carbon pollutants in the atmosphere, and it can significantly improve the local atmospheric environment within a short period, which further resulted in a non-negligible level of DOC deposition flux.

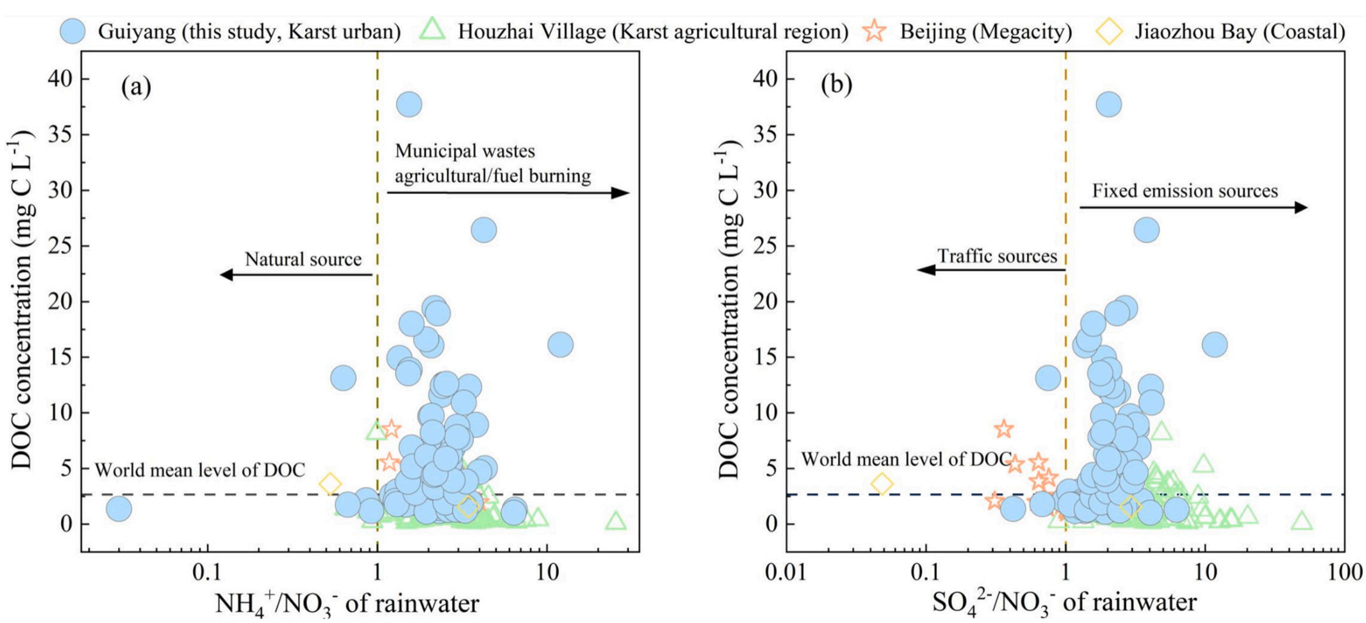

Fig.6. (a) Rainwater NH_4^+/NO_3^- ratios v.s. precipitation DOC concentration, and (b) rainwater SO_4^{2-}/NO_3^- ratios v.s. precipitation DOC concentration in Guiyang. Data of other regions are from (Xing et al., 2019; Zeng et al., 2020b; Zeng et al., 2023).

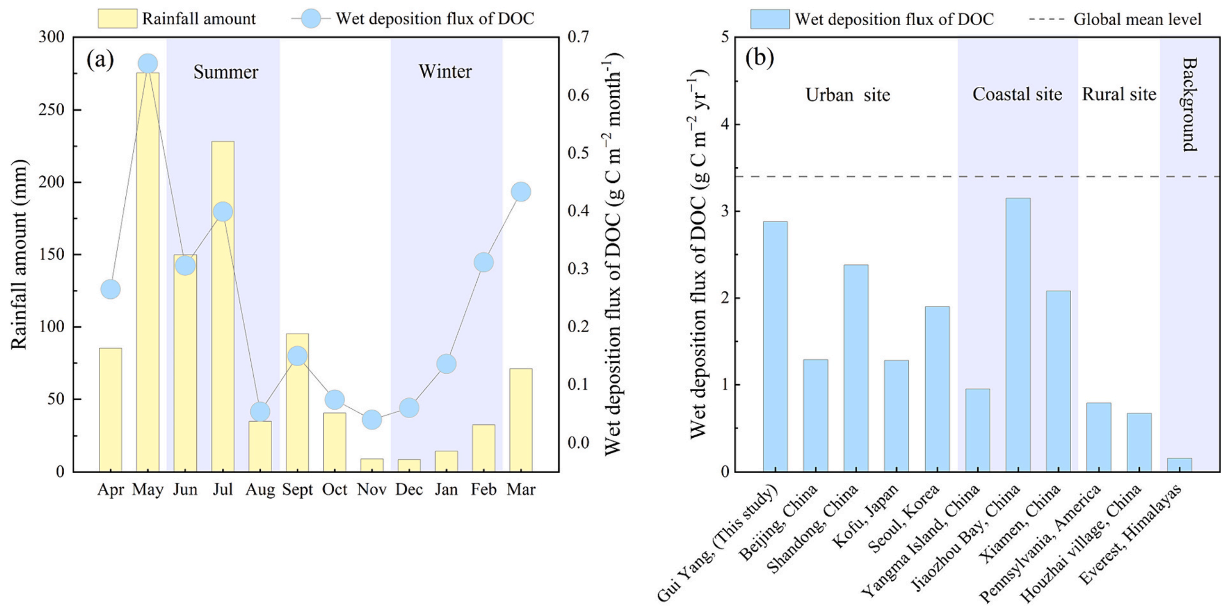

Fig. 7. (a) Monthly variations of deposition flux of rainwater DOC and (b) annual deposition flux comparisons between Guiyang and various areas. Note: data sources are same to Table 1.

3.4. *Environmental implication*

Wet deposition caused substances such as nitrogen and carbon to settle on the surface, thereby providing nutrients for plant growth (Willey et al., 2000; Bourgeois et al., 2018). Rainfall can not only directly input C and N into surface water bodies but may also transfered C and N particles from the soil into water bodies through soil erosion. This erosion effect may increase their content in water bodies, affecting the chemical composition and nutrient cycling of aquatic ecosystems (Gao et al., 2018; Li et al., 2023). For instance, DOC is one of the main transport forms of OC in the hydrosphere, which can reduce water transparency and facilitate the transfer of dissolved pollutants (Raymond and Bauer, 2001; Evans et al., 2005; Pan et al., 2010). An increase in nitrogen deposition input not only can stimulate the growth and reproduction of primary producers but also has adverse effects on the survival and reproductive ability of aquatic animals (e.g., eutrophication) (Camargo and Alonso, 2006; Gao et al., 2014b; Zhan et al., 2017). Meanwhile, carbon-related wet deposition and other nutrients (nitrogen-bearing species) can affect gross primary productivity (GPP) in the system of surface hydrosphere (Crossman and Whitehead, 2016). The GPP represents the amount of C absorbed through photosynthesis in ecosystems and plays a crucial role in the exchange of carbon dioxide (CO_2) between terrestrial ecosystems and the atmosphere (Hao et al., 2019). We generally calculate that the contribution of DOC wet deposition (2.88 g C m^{-2} yr^{-1}) to regional GPP is approximately 0.192% ~ 0.288%, based on the GPP of 1000–1500 g C m^{-2} yr^{-1} in the Guizhou province (Yao et al., 2018). Meanwhile, under the background of human-induced activities, the high level of wet nitrogen deposition was widely found, and Guiyang is no exception. The atmospheric nitrogen deposition flux in Guiyang (1.33 g N m^{-2} yr^{-1}) exceeded a dryland farming area in Wuwei (0.64 g N m^{-2} yr^{-1}) (Fu et al., 2020), but below Three Gorges Reservoir area (1.85 g N m^{-2} yr^{-1}) (Lu et al., 2022), Yangtze River Basin (2.26 g N m^{-2} yr^{-1}) (Xu et al., 2018b) and the average nitrogen deposition flux of China (1.93 g N m^{-2} yr^{-1}) (Xu et al., 2015). The stoichiometric ratios of nutrients in water can affect the growth and composition of planktonic organisms (Diez et al., 2013). The C:N (6.625:1) proposed by Redfield is a significant basis for quantifying nutrient limitation factors (Redfield et al., 1963; Li et al., 2022). Therefore, the specific carbon-nitrogen relationship (C:N) in atmospheric deposition can be a vital factor influencing aquatic organisms. In this work, the strong correlation between the concentration of rainwater DOC and DTN (Fig. 8), implying that they may have similar potential sources (e.g., agricultural activities, transport, fossil fuel combustion) (Schlesinger, 2009; Gao et al., 2020). The average value of rainwater C:N (DOC:DTN) was 2.08:1, which is significantly lower than the ratio proposed by Redfield, indicating that rainfall driven external nitrogen input has led to a state of nitrogen excess in the study area. In addition, the comparison of C:N value of rainfall in this study with other regions revealed that it were close to coastal cities such as Qingdao (C:N = 2) and Yantai (C:N = 2.76), as well as the karst agricultural area (C:N = 2.76), and slightly higher than those of the inland city of Taian (C:N = 0.62) and the oceanic area of Yangma Island (C:N = 0.82) (Xu et al., 2016; Zeng et al., 2020a; Xie et al., 2022a). The C:N values varied among regions but were all below the appropriate ratio.

Although there is uncertainty in determining whether the carbon-to-nitrogen ratio in atmospheric precipitation causes eutrophication in surface water systems, rainfall processes have become an important component of the global carbon and nitrogen cycles (Avery et al., 2006; Galloway et al., 2008; Gu et al., 2015). Furthermore, nutrients in rainfall can have a significant impact on terrestrial and marine ecosystems (Gao et al., 2014a). For instance, in nutrient-poor coastal aquaculture areas, the nitrogen and phosphorus carried in wet deposition are considered as the crucial sources of nutrient input (Xie et al., 2022a). After a long period of low nitrogen deposition, grassland plant species may decline (Clark and Tilman, 2008). Considering that atmospheric deposition is one of the crucial nutrient sources of terrestrial ecosystems (Decina et al., 2018; Wu and Gao, 2019), we will continue to focus on nutrients in atmospheric wet deposition in our future research to provide a scientific basis for sustainable water resource management and ecological environmental protection.

4. Conclusions

A systematic investigation of rainwater DOC was conducted in karst city (Guiyang) from April 2022 to March 2023 in this work, aiming to determine the variations in concentrations, interfering issues, potential sources, and deposition flux. The observations demonstrated that rainwater DOC concentration (2.76 mg C L^{-1} in VWM) was similar to the average levels in Asia and global rainwater, while the DOC wet deposition flux (2.88 g C m^{-2} yr^{-1}) was below the global average. The DOC

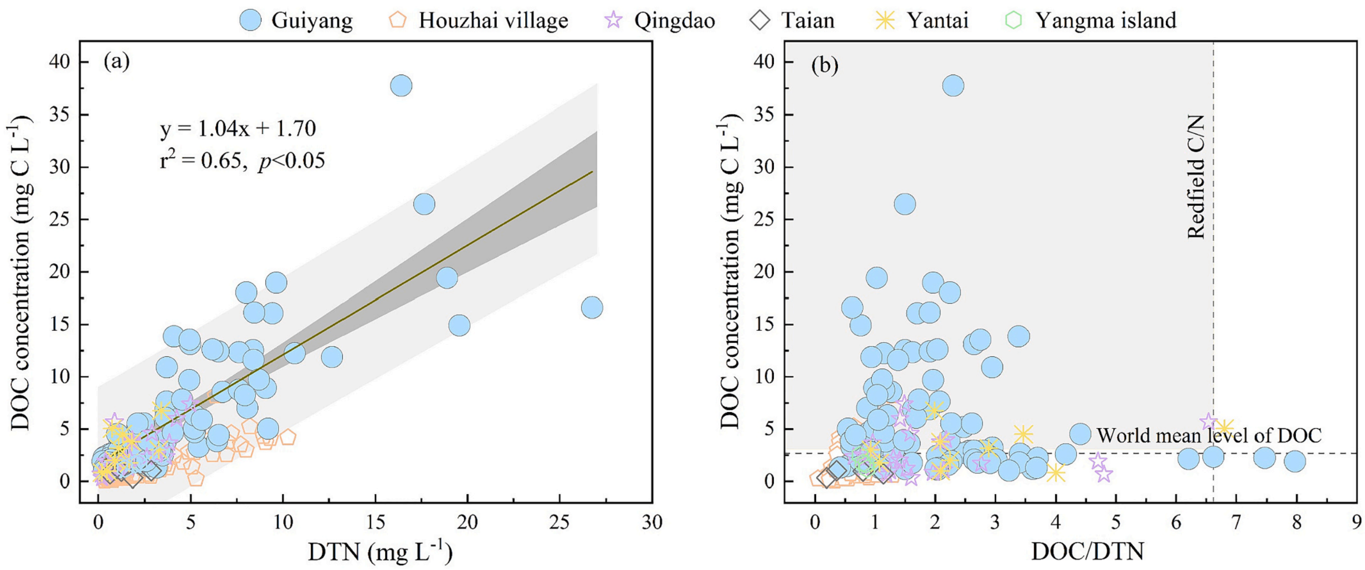

Fig. 8. (a) The relationship between the concentration of rainwater DOC and DTN (b) Presentation of DOC concentration and C/N ratio of rainwater in Guiyang with other regions. Note: the data comes from (Xu et al., 2016; Zeng et al., 2020a; Xie et al., 2022a).

concentration exhibited an overall inverse relationship with precipitation in the spring and winter, whereas the monthly DOC deposition flux showed a positive tendency to inter-monthly rainfall variations during the study period, indicating that significant influence of precipitation amount on the rainwater DOC deposition. Abundant rainfall during the rainy season continuously washed out DOC from the atmosphere, leading to an elevated efficiency in the removal of DOC below the clouds and maintaining a relatively low level of DOC concentration for a certain period. The relationship between the rainfall DOC concentration and characteristic ions (and their ratios) revealed that urban waste emission, agricultural activities, and fossil fuel combustion were the primary sources of rainfall DOC, while natural rock weathering processes contributed limited. Moreover, the N deposition flux in Guiyang was counted as 1.33 g N m^{-2} yr^{-1}, and the average C: N ratio in Guiyang rainfall was found to be 2.08, significantly lower than the Redfield ratio. The Nutrient components in rainfall may affect the material cycling of surface water ecosystems. This study was the complement to rainwater DOC in karst urban areas and dedicated to regional urban construction and air environmental governance. Additionally, in this study, we conducted an annual survey on the sources of rainwater DOC. In future work, we will further differentiate seasonal sources. Meanwhile, pay attention to the impact of special events during specific periods on the chemical composition of rainfall. This will contribute to a comprehensive understanding of how changes in environmental conditions affect the chemical composition of rainwater.

CRediT authorship contribution statement

Qing Ma: Writing – review & editing, Writing – original draft, Software, Methodology, Investigation, Data curation. **Jie Zeng:** Writing – review & editing, Writing – original draft, Supervision, Resources, Methodology, Investigation, Funding acquisition, Formal analysis, Data curation, Conceptualization. **Qixin Wu:** Writing – review & editing, Supervision, Resources, Methodology.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.atmosres.2024.107439.

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