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Original Paper

Differences in Dissolved Organic Matter Between Karstic Fissured/Non-fissured Soils

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Abstracts

Dissolved organic matter (DOM) is widespread in the environment and plays a role in various ecosystems. This study aimed to explore the differences between fissured/non-fissured soil DOM. Accordingly, the differences in DOM between fissured/non-fissured soils must be clarified to assess soil quality. This study used UV-Vis absorption spectroscopy and fluorescence excitation-emission matrix parallel factor analysis (EEMs-PARAFAC) to characterize soil samples with and without fissures. The fluorescence components of DOM were determined by comparison with OpenFluor. Significance, linear regression, and redundancy analyses were used to obtain the transformation relationship between DOM components and the effect of environmental factors on DOM. This study found that (1) the non-fissured soil DOM exhibited stronger aromaticity and hydrophobicity than the fissured soil DOM. This finding, along with the results of HIX, FI, and BIX tests, suggested that non-fissured DOM is influenced by both exogenous and microbial sources, while fissured DOM is influenced by microbial and autochthonous sources. (2) Protein-like components of non-fissured soils were more abundant (35%–51%) than those of fissured soils (17%–45%), and the transformation relationship between non-fissured components (A2→A3→A1) differed more than that between fissured components (A2→A1→A3), resulting in a greater loss of DOM protein-like components from non-fissured areas. (3) Fissure width (FW) and aperture (Ape): The width and aperture of fissures can significantly affect DOM loss and alter component characteristics under the influence of different environmental factors. Fissures with larger FW and Ape were found to result in higher soil quality (DOC/SOC) compared to non-fissures, with the highest DOC/SOC found in non-fissured coppices. Note that changes in vegetation type can also impact soil quality in fissures. The structure of the karst environment has a *dichotomous effect on the component ratios and transformation direction of DOM in fissured/non-fissured soils. Non-fissured areas are more vulnerable to the loss of lighter fractions during rainfall and are also subject to anthropogenic activities. Therefore, the environment requires deeper and wider improvement.*

Keywords

Karst, fissure, DOM, fluorescence, conversion differences

1. Introduction

Of the 17 sustainable development goals set by the United Nations to be achieved by 2030, 8 are related to the soil environment (Hou et al., 2020). As one of the scarcest natural resources in the world (Cassidy et al., 2013), soil plays a critical and mediating role in ecosystems and human activities (Marzaioli et al., 2010; Nabiollahi et al., 2018). The soil crisis is perpetuated by very low soil formation rates and the frequent exposure to erosion threats (Montgomery, 2007; Gonzalez Lago et al., 2019). Soil erosion results in the loss of soil nutrients through leaching. Dissolved organic matter (DOM) is present in soil, water, atmosphere, and sediments (Tipping et al., 1999; Wang et al., 2015) and is a part of the soil carbon pool (Kaiser & Kalbitz, 2012). The migration of DOM with soil erosion is involved in various cyclic processes due to its high reactivity and transport capacity (Batjes, 2014; Lal, 2003; Zsolnay, 2003). For instance, it enhances microbial activity and facilitates the transport of water, soil nutrients, and contaminants (Abdi & Williams, 2010; Kalbitz et al., 2000b; Tong et al., 2021).

DOM is a component of natural organic matter (NOM), making up approximately 97.1% of all NOM (Post et al., 1990), and encompasses a variety of molecules with varying sizes and structures found in soils and bodies of water (Kalbitz et al., 2000a). This substance is a non-homogeneous mixture of aliphatic and aromatic polymers (Ishii & Boyer, 2012). Approximately 25%–50% of the mixture is composed of humic and xanthic acids, while the remaining portion consists of proteins, polysaccharides, and hydrophilic organic acids (Grasso et al., 1990). The composition of DOM, on the other hand, varies depending on environmental factors. For instance, Fouché et al. (2020) reported on the characteristics of DOM in active layer (1–4.5 L mgC^{-1} m^{-1}) and permafrost in the Canadian Arctic, where the proportions of low molecular weight proteins in the organic and mineral layers (0.6–1.2 L mgC^{-1} m^{-1}) of permafrost were 58.4% and 20.8%, respectively. In contrast, the active layer had a high proportion of high molecular weight aromatic fluorophores of terrestrial origin, and the proportion of protein-like proteins in both its organic and mineral layers was 5.3%. The organic active layer exhibited higher aromaticity than the mineral tundra due to the different sources of organic matter. The characteristics of the DOM in oceanic regions near the Getz and Dotson ice shelves in the Amundsen Sea, West Antarctica, that are melted by sea ice or glaciers behave differently (Son et al., 2024). The humus-like contributions were greater (72.9±13.2%) than the protein-like contributions (27.1 ± 13.2%), and the aromaticity ranged from 0.51 m^2g^{C-1} to 3.38 m^2g^{C-1}. DOM changes are affected not only by natural environmental factors but also by anthropogenic activities. For instance, in their 2017 study, Gao et al. reported on the characteristics of DOM fractions of agricultural soils in different regions of China. The aromatic and hydrophobic components of DOM were highest in Chestnut soil, Wheat-Maize in Inner Mongolia (1.37±0.05, 1.29±0.05 L mgC^{-1} m^{-1}) and lowest in Krasnozem soil, Wheat in Jiangxi (0.26±0.07, 0.25±0.07 L mgC^{-1} m^{-1}). The highest DOC content was found in Wushan soil, Rice in Jiangsu (86.01 $mg·L^{-1}$), while the smallest was found in Krasnozem soil, Wheat Maize in Hunan (24.11 $mg·L^{-1}$). The protein-like (tyrosine) fractions of DOM accounted for the highest percentage in Yellow brown soil, Wheat Maize in Anhui (31.97%) and the lowest in Moisture soil (25.78%), Wheat Maize in Shandong. The revegetation of the Maowusu Sandy Land in Yulin City, Shaanxi, China, also altered DOM characteristics (Wang et al., 2023). The DOC content was highest in tree forests (83.72-151.01 $mg·kg^{-1}$), followed by scrub forests (56.03-111.65 $mg·kg^{-1}$), and control sands (42.33-75.20 $mg·kg^{-1}$). The hydrophobic and aromatic fractions of DOM increased with silvicultural age. Scrub forests exhibited stronger hydrophobic and aromatic properties than tree forests. Additionally, the humus-like fractions of DOM increased with afforestation age in both scrub and tree forests. The proportion of protein-like fractions gradually decreased, indicating that more soil nutrients were sequestered after afforestation. Anthropogenic activities not only alter soil nutrient content but also affect DOM characteristics.

The migration of DOM and its changes are more complex in the dual-structure environment of karst. For instance, Shi et al. (2023) reported on the migration process of DOM in rainwater (RW)-drip water (DW)-dip water (PW) in a karst spring basin in southern China. The degree of humification of RW DOM is significantly higher in the dry season than in the wet season, and the intensity of rainfall directly affects the fluorescence component of RW DOM. The characteristics of RW DOM, which include weak humus, can affect DW DOM. However, DW DOM is also influenced by various factors, such as the residence time of groundwater in the upper infiltration zone, the degree of new and old water occupancy, the physical structure, the intensity of soil plant rooting and microbial activity, the mode of groundwater recharge and groundwater flow paths, groundwater seepage rate, and other hydrological processes. The humification degree of PW DOM is the highest due to its extended residence time, which is significantly influenced by microbial activity. As a result, the characteristics of RW DOM and DW DOM are comparable when the preferential surface flow path is activated during the rainy season. When converted to groundwater runoff, old water discharge from the unsaturated zone leads to an increase in DOM humification. This vertical migration has implications for karst groundwater and watershed environments. The hydrological processes in karst areas are unique, allowing shallow karst fissures in the epikarst to act as conduits for soil deposition and leakage (Dai et al., 2015; Wang et al., 2004; Yang et al., 2011). This condition differs from the soil environment of the non-fissured karst zone. Hartmann et al. (2009) demonstrated that soil <20 cm only accounts for 35% of the total soil microbial biomass. The hydrodynamic and gravitropic nature of the plant root system in the fissure zone forces the root system to extend deeper into the soil, absorbing more water and nutrients to grow (Nie et al., 2019). This depth is not present in karst non-fissured soils. It is not surprising that surface root systems in non-fissured soils are more active and decrease with soil depth compared to fissures. This outcome is consistent with the decrease in plant root density along with soil depth, as noted by Pries et al. (2018). Conversely, fissures provide a more favorable environment for plant growth due to deeper soil and increased water availability, as reported by Yan et al. (2019a). However, soil erosion and sedimentation can also transport DOM through nutrient transport and redistribution, and this transport can contaminate groundwater. For instance, Sun et al. (2020) demonstrated that high molecular weight polycyclic aromatic hydrocarbons (PAHs) were transported as DOM in soil leachate in a karst region of southwest China. When water was transported vertically downstream, the PAHs continued to be dissolved in leachate, increasing the risk of groundwater contamination.

However, the most significant issue in the karst region is the phenomenon of rocky desertification, which is caused by the unique karst environment and extensive human activities. Severe soil erosion and degradation in the region, particularly in southwest China, have been caused by rocky desertification. Therefore, the reasons for the difference in DOM between karst fissured/non-fissured soils need to be identified. This will provide a theoretical basis for soil management and rocky desertification control.

The spectral characteristics of soil DOM in typical fissured/non-fissured zones in the karst rocky desertification region of southern China were investigated using UV-Vis, fluorescence spectroscopy, and excitation-emission matrix parallel factor analysis (EEMs-PARAFAC). The relationship between the main factors and the transformations between components of the differences between karst fissured/non-fissured DOM was obtained by linear regression analysis and redundancy analysis (RDA). The aim was to evaluate the impact of environmental factors on the DOM of fissured/non-fissured soils.

2. Materials and Methods

2.1 Study Area

The mountainous areas of the Guizhou Plateau were selected as the study area, as they can represent the general structure of karst ecological environment types in southern China. This area includes the mountainous canyon with no–potential rocky desertification Shibin-Heichong (108°01′36″~108°10′52″E, 27°13′56″~27°04′51″N), the plateau mountainous area with potential–mild rocky desertification Bijie-Salaxi (105°02′01″~105°08′09″E, 27°11′36″~27°16′51″N), and the plateau canyon with moderate–intense rocky desertification Zhenfeng-Huajiang (105°36′30″~105°46′30″E, 25°39′13″~25°41′00″N), all of which are within the demonstration area of rocky desertification control (Xiong et al., 2012). Zhenfeng-Huajiang has a subtropical dry and hot river valley climate, with uneven seasonal rainfall mainly concentrated in May–October. It is characterized by severe soil erosion, high rock exposure rate, and a thin and discontinuous soil layer mostly concentrated in depressions, karst cracks, or crevices. Shibing-Heichong has a subtropical humid monsoon climate characterized by high temperatures in summer and rainfall, and winters with low temperature and less precipitation. It area features primarily undeveloped underground karst landforms. Bijie-Saraxi has a subtropical monsoon climate with high and humid rainfall in summer and low and dry temperatures in winter. It has a rich variety of geomorphological types and an extensive development of karst-negative landforms, which make the surface more fragmented and the soil layer shallower and thinner. For more detailed information on the three study areas, please refer to Cai (2021).

2.2 Sample Collection and Processing

After a field survey of the three study areas was conducted, Huajiang (HJ) in Zhenfeng was selected as the main study area, with Heichong (HC) in Shibing and Salaxi (BJ) in Bijie chosen as auxiliary study areas. This decision was based on the fact that Huajiang has a more severe degree of rock desertification, a higher rock exposure rate, a more complex environment, and a longer history of implementing control measures (Xiong et al., 2012). Therefore, the study selected the three most typical karst binary hydrological structure fissures in each of the three study areas: HJ1–HJ3, HC1–HC3, and BJ1–BJ3. Non-fissured soils were collected from the Huajiang study area, including abandoned land (AL), grassland (GL), forest (FS), peanut cultivated land (PCL), and Zanthoxylum bungeanum land (ZBL). Soil samples were collected between August and October 2020 after rainfall in each study area. Soil samples were classified as either fissured or non-fissured. Fissured soils were sampled at 10 cm intervals, with a few samples taken within 20, 40, 80, 120, 160, and 200 cm of the soil moisture sensor placement. Non-fissured soils were collected in two layers from 0 to 30 cm. In each layer, all samples were collected and 3 parallel samples were mixed, resulting in a total of 247 samples. These samples were then returned to the laboratory for air drying. The environmental and soil characteristics of the sampling sites in the three study areas were determined through field surveys and experimental analyses, as shown in Tables S1 and S2, respectively (Wang et al., 2022).

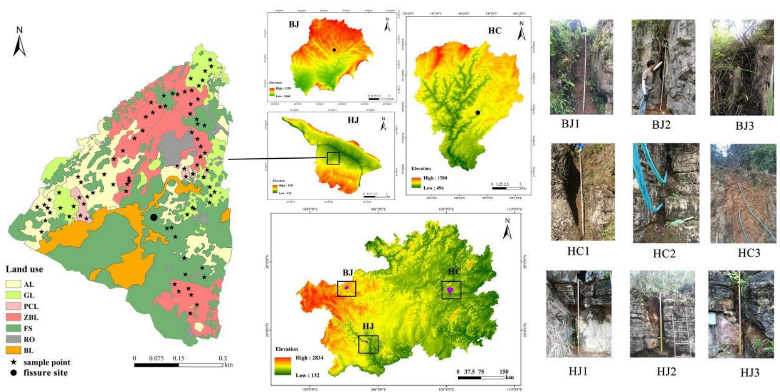

Figure 1. Study area and location of fissured/non-fissured soil sampling sites. Abandoned land (AL), grassland (GL), peanut cultivated land (PCL), Zanthoxylum bungeanum land (ZBL), forest (FS); rock outcrop (RO), building land (BL), Hua jiang (HJ), Hei chong (HC) and Bi jie (BJ)

The soil was air-dried, ground, and sieved through a 60 mesh sieve. Then, 5 g of the sieved soil was weighed and mixed with ultrapure water at a ratio of 1:5. After shock centrifugation, the supernatant was filtered through a 0.22 μm PES filter membrane to reduce microbial influence. The resulting solution was used to measure the soil DOM. The concentration of dissolved organic carbon (DOC) was measured using a TOC analyzer (Multi N/C 3100, Analytik Jena, Germany). To reduce the effect of internal filtration in the fluorescence scan (Huang et al. 2017), the DOC concentration of the samples was diluted to less than 10 mg· L^{-1}, ensuring that the absorbance at UV254 nm was less than 0.3. The UV-visible absorption spectra of the samples were obtained using a UV-visible spectrophotometer (SPECORD Plus 200, Analytik Jena, Germany) by scanning the samples at 1 nm intervals in the range of 200–800 nm with deionized water as the blank group. The fluorescence spectra of the samples were recorded using a Shimadzu RF-5301PC fluorescence spectrophotometer. The excitation wavelength (Ex) was scanned from 220 nm to 500 nm at 5 nm intervals, and the emission wavelength (Em) was scanned from 250 nm to 600 nm at 1 nm intervals. Ultrapure water was used as a blank to eliminate scatter. The fluorescence data were normalized to Raman units (R.U.). Additional information can be found in the following references: Lawaetz and Stedmon (2009) and He et al. (2021).

2.3 Optical Parameters

Table 1. Definition and Significance of DOM Optical Indices and Parameters Used in the Present Study

DOM quality index	Definition and significance
$SVUA_{254}$ and $SUVA_{260}$ absorbance: $SUVA_{254/260}$=a(λ)/c(DOC)	$SVUA_{254}$ and $SUVA_{260}$ characterise the aromatic and hydrophobic components of DOM, respectively (ElBishlawi and Jaffe, 2015).
E2/E3: a(254)/a(365)	E2/E3 is an indication of the degree of organic matter humification, with low values indicating low humification (Wang et al., 2009; Jaffé et al., 2004).
Humification index (HIX) :Em(∑I435–480)/(∑I300–345), Ex(254)	Reflects the degree of DOM humification. HIX < 4: biological or aquatic bacterial sources; 4 < HIX < 6: weakly humified features and important recent autotrophic sources; 6 < HIX < 10: stronger humified features and weak neoautotrophic source components (Ohno, 2002; Huguet et al., 2010).
Fluorescence index (FI): Em(470/520), Ex(370)	Reflects the source of the DOM. 1.7 < FI < 2.0: microbial activity is the main source of DOM; 1.2 < FI < 1.5: the contribution of organisms is small (Mcknight et al., 2001).
Biological index (BIX): Em(380/430),	Reflects the ratio of albumin to bio-component. Low

Ex(310)	biological sources (0.6 < BIX < 0.7), DOM of biological or aquatic bacterial origin (BIX > 1) (Huguet et al., 2010; Wilson and Xenopoulos, 2009).

Note. a(λ) is the UV–Vis absorbance at wavelength 254, 260(mm) and r is the path-length of the optical (0.01 m), c(DOC) is the concentration of extractable DOM ($mg \cdot L^{-1}$).

2.4 Statistical Analyses

The study analyzed 247 soil samples using MATLAB 2022a (MathWorks Inc., Natick, MA, USA) and the DOMFluor 1.7 toolbox to obtain information on the group fractions, types, and fluorescence intensities of chromophoric DOM. Statistical analyses, including one-way ANOVA, significance tests, linear regression analyses, and graphs, were performed using Origin 2021 (OriginLab Inc., Northampton, MA, USA) and IBM SPSS Statistics 26 (IBM Inc., Chicago, USA). RDA was used to analyze the relationships between the spectral parameters, components, and environmental factors of DOM using Canoco 5 (Ithaca, NY, USA).

3. Results

3.1 Differences in Soil Quality and DOM Spectral Signatures

Overall, the mean values of DOC/SOC (‰) of fissured soils (1.26±0.21~2.14±0.26) were higher than those of non-fissured soils (0.66±0.17~0.99±0.48) (Table 2), but the SOC concentration was significantly higher in the latter (Table S2). Additionally, the SOC and DOC contents of HC3 were significantly lower than those of HC1 and HC2 in the same area. The $SUVA_{254}$ and $SUVA_{260}$ values of non-fissured DOM were higher than those of fissured soils. Fissured SUVA254 and SUVA260 were concentrated in the range of 0.2–0.6 L mg C^{-1} m^{-1} (Figs. 2a, b), while non-fissured $SUVA_{254}$ and $SUVA_{260}$ were concentrated in the range of 0.5–1.0 mg C^{-1} m^{-1} (Figs. 3a, b). This result indicates that the aromatic, hydrophobic, and hydrophobic fractions of non-fissured DOM were stronger than those of fissured soil. The E2/E3 differences between them were not significant, as they were all concentrated in the 3–7 range (Figs. 2c and 3c). The HIX of non-fissured soils was only similar to that of fissured HJ1–HJ3 in the same area, and HIX<4 (Figs. 2d and 3d) was of biological and aquatic bacterial origin. The fluorescence index (FI) was also greater in rifts than in non-rifts, with rifts (FI>1.8) dominated by autochthonous and microbial sources, and only HC3 in rifts was clearly influenced by terrestrial and, to a lesser extent, microbial sources (Fig. 2f). The fractal FI was mainly influenced by a combination of microbial and terrestrial sources (Fig. 3f). The BIX of fissures was similar to that of non-fissures, but fissures had more autochthonous source components than non-fissures (Figs. 2e and 3e).

Table 2. Characteristic Parameters of DOM in Karst Soils

Type		DOC/SOC	$SUVA_{254}$	$SUVA_{260}$	E2/E3	HIX	BIX	FI
Fissured soil	HJ1	1.28±0.68	0.34±0.08	0.31±0.08	5.08±1.31	1.46±0.56	0.82±0.13	1.99±0.42
	HJ2	1.26±0.21	0.36±0.1	0.34±0.1	4.25±1.16	1.49±0.5	0.79±0.12	2.03±0.36
	HJ3	1.27±0.49	0.34±0.07	0.32±0.06	4.40±0.60	1.39±0.38	0.8±0.14	2.04±0.23
	BJ1	1.43±0.09	0.78±0.25	0.74±0.23	3.88±0.28	2.38±0.53	0.65±0.04	1.75±0.02
	BJ2	1.60±0.24	0.69±0.17	0.64±0.16	3.85±0.8	2.9±1.82	0.65±0.09	1.90±0.10
	BJ3	1.30±0.34	0.44±0.19	0.42±0.18	4.33±0.22	2.65±0.73	0.66±0.05	1.89±0.11
	HC1	2.14±0.26	0.43±0.14	0.41±0.13	5.6±0.59	4.33±1.65	0.62±0.05	1.87±0.11
	HC2	1.60±0.13	0.43±0.10	0.4±0.10	5.76±0.30	5.10±1.80	0.61±0.06	1.82±0.07
	HC3	2.06±1.01	0.36±0.11	0.31±0.12	7.91±3.03	1.12±0.52	0.75±0.08	1.63±0.18
Non-fissured soil	ZBL	0.9±0.35	0.82±0.25	0.69±0.22	5.06±1.12	1.97±0.56	0.63±0.16	1.73±0.08
	PCL	0.66±0.17	0.87±0.18	0.73±0.12	4.82±0.66	2.21±0.59	0.72±0.10	1.74±0.07
	GL	0.84±0.20	0.95±0.26	0.78±0.20	4.85±0.70	1.65±0.4	0.70±0.08	1.77±0.09
	AL	0.63±0.14	1.03±0.20	0.84±0.16	4.78±0.73	1.88±0.49	0.71±0.04	1.70±0.03
	FS	0.99±0.48	0.71±0.27	0.60±0.25	5.23±1.69	1.61±0.57	0.76±0.16	1.86±0.26

Note. $SUVA_{254}$ 与 $SUVA_{260}$ are expressed in L mg C^{-1} m^{-1}. Values are mean ± SD.

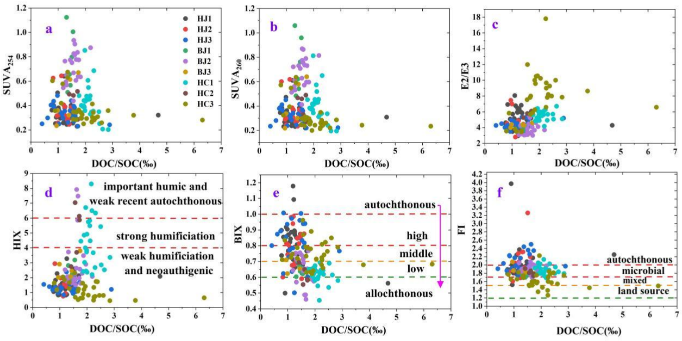

Figure 2. Distribution of $SUVA_{254}$, $SUVA_{260}$, E2/E3, FI, HIX and BIX along DOC/SOC for Fissred Soils. $SUVA_{254}$ and $SUVA_{260}$ in $L{\cdot}mgC^{-1}{\cdot}m^{-1}$

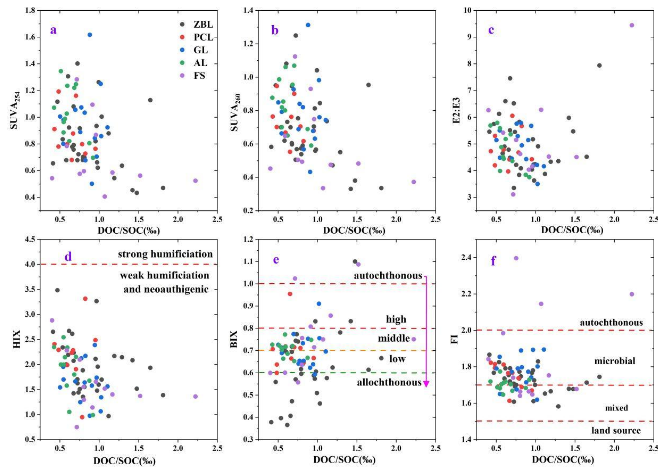

Figure 3. Distribution of $SUVA_{254}$, $SUVA_{260}$, E2/E3, FI, HIX and BIX along DOC/SOC for non-fissred Soils. $SUVA_{254}$ and $SUVA_{260}$ in $L{\cdot}mgC^{-1}{\cdot}m^{-1}$

3.2 Characterisation of DOM Components

All soil samples exhibited three fluorescence peaks (Figs. S1–S4) after the successful fitting of EEMs-PARAFAC using MATLAB. Comparative analyses in the OpenFluor database yielded six different fluorescence peaks (Table 3). Fractions C1, C3, and C5 are associated with high molecular weight humic or fulvic acids, which are A/C peaks and most abundant in forest and wetland environments (Fellman et al., 2010; Yamashit et al., 2010). Component C2 is associated with low molecular weight humic or fulvic acids and is commonly found in biologically active marine environments, as well as in wastewater, wetland, and agricultural environments (Coble et al., 1996; Fellman et al., 2010). The C4 and C6 components are present in both terrestrial and aquatic environments as tryptophan-like (C4, T peak) and tyrosine-like (C6, B peak) fractions, respectively. These components are primarily produced by microbial activities that generate amino acids, peptides, and free or bound proteins. C4 may indicate intact proteins or less degraded peptide material, while C6 indicates more degraded peptides (Fellman et al., 2010; Fouché et al., 2020).

The analysis of all soil DOM fractions yielded different Fmax values and occupancies between fractions (Figure 4). Component A1 had the highest Fmax value, followed by A2, and A3 had the lowest in the fissured soils. In the non-fissured soils, component A2 had the largest Fmax, followed by A1, and A3 had the smallest. This finding suggests a significant difference in the percentage of protein-like and humus-like substances between the fissured/non-fissured soils. The humus-like substances in the fissured DOM ranged from 59% to 79%, while the protein-like substances ranged from 21% to 41%. In the non-fissured DOM, the humus-like substances ranged from 48% to 66%, and the protein-like substances ranged from 34% to 52%. These results suggest that the fissured soil has a higher proportion of humus-like substances compared to non-fissured soil, where the proportion of protein-like substances is similar to that of humus-like substances.

Table 3. Types of DOM Fluorescence Components in Karst Soils

Component	Ex max (nm)	Em max (nm)	Cory and McKnight (2005)	Fellman et al. (2010)	Stedmon and Markager (2005)	Openfluor Comparisona(TCC >0.95)	Possible sources	Source
1 (C peak)	<260	440-460	C2	C7	C1	34	High molecular weight and aromatic humic, widely distributed, especially highest in wetlands and forested environments.	Terrestrial
2 (M peak)	280	420–460	C3	C4	C5	11	Low molecular weight, associated with biological activity in the marine environment, but also found in wastewater, wetlands and agricultural environments.	Terrestrial/anthropogenic
3 (A/C peak)	320	420–460	C1	C10	--	7	High-molecular-weight humic, widespread, especially highest in wetlands and forested environment.	Autochthonous/anthropogenic
4 (T peak)	220/255	365/397	C8	C2	C7	11	Amino acids, free or bound in proteins, fluorescence resembles free tryptophan, may indicate intact proteins or less degraded peptide material.	Terrestrial /autochthonous
5 (A peak)	260-275	480-511	C5	C5	C2	38	High molecular weight, aromatic. Fluorescence similar to fulvic acid,	Terrestrial/autocht

							widespread.	onous
6 (B peak)	280	307-319	C13	C1	C8	2	Amino acids, free or bound in proteins, fluorescence resembles free tyrosine, may indicate more degraded peptide material.	Terrestrial/autochthonous

Notes. All component data has been compared and analysed in the OpenFlour database. The Tucker Congruence Coefficient (TCC) for excitation and emcitation is greater than 0.95.

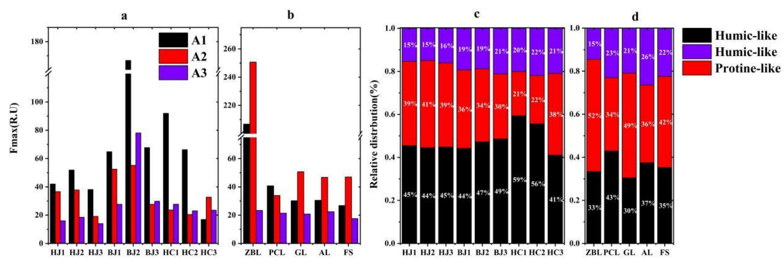

Figure 4. Fluorescence Intensities (a, b) and Percentages (c, d) of the three DOM Components in Fissured/non-fissured Soils

3.3 Environmental Factors Causing DOM Differences

Several environmental factors influence DOM variation, including soil quality, vegetation, and environment. Previous studies have reported on the factors controlling soil DOM in karst subwatersheds and the transport factors of DOM in epikarst fissured soils (Cheng et al., 2023; Wang et al., 2022). Therefore, we selected environmental factors, such as near-surface vegetation type (NSV), rock outcrop rate (ROR), vegetation cover (VC), altitude (Al), fissure width (FW), fissure dip angle (DA), depth (De), and fissure openness (Ape), as well as soil environmental factors, including pH, volumetric weight (VW), and total porosity (TPs). The factors used to assess soil quality were total N (TN), SOC, organic carbon isotopes (Is), and DOC/SOC. To better understand the influence of DOM differences between fissures and non-fissures under different environmental conditions, we used Spearman correlation coefficients to analyze and identify the factors affecting DOM in different environments (Fig. 5). The study found that the conversion relationship between the components of DOM in fissured/non-fissured DOM differed (Figs. 5a, c). All A1–A3 of fissured DOM showed extremely significant correlations ($P<0.001$), while A2 and A3 of non-fissured DOM were not significantly related. The correlations of DOC, $SUVA_{254}$, and $SUVA_{260}$ were also shown to differ significantly between fissured/non-fissured DOM. The presence of DOM in fissured soils was affected by several factors, with FW, Ape, ROR, Al, NSV, VW, and pH having the greatest impacts. All spectral parameters of DOM were found to be strongly correlated with soil quality (as shown in Figs. 5b and d, $P<0.05$).

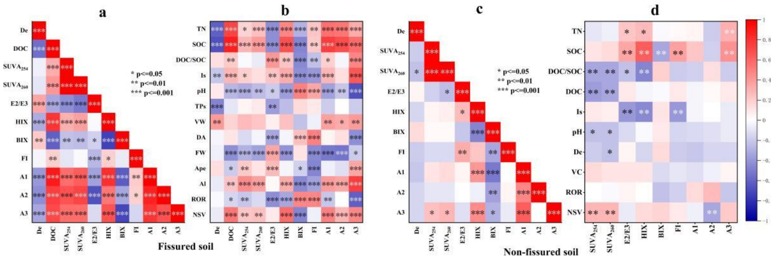

Figure 5. Spearman's Correlation Coefficients between Fissured/non-fissured soil DOM Parameters and Environment

4. Discussion

4.1 DOM Transformation and Soil Quality

Fissured/non-fissured soils in karst areas typically exhibit high SOC and low DOC contents (Table S2). This finding is in line with previous studies on SOC and DOM contents in karst areas (Bai & Zhou, 2020; Huang et al., 2021; Pang et al.) but differs from findings in non-karst areas (Han et al., 2010; Jia et al., 2017; Zhang et al., 2019a). Soil organic carbon pools have a significant impact on the carbon cycle and climate as they are the largest organic carbon pool in terrestrial ecosystems (Batlle-Bayer et al., 2010; Stockmann et al., 2013). DOM is also the main energy pool in soil (Marschner & Bredow, 2002) and the most active fraction, which can directly influence the organic carbon pool. Thus, we observed a significant decrease in the SOC and DOC of fissures with increasing soil depth (Figs. 5a, b). Note that surface SOM is primarily influenced by factors such as vegetation and climate and less by geological matrix type (Jiménez-González et al., 2020). Therefore, it cannot be used as a reference for comparing organic carbon pools of fissured/non-fissured soils. Consequently, we chose DOC/SOC (‰) as the soil quality indicator for evaluation (Lan, 2020). Table 2 shows that the DOC/SOC of fissured soil was significantly higher than that of non-fissured soil. This outcome suggests that the quality of fissured soil in the karst region is better than that of non-fissured soil and more suitable for a vegetation growth environment.

Linear regression analyses were performed on the components of DOM. The results showed that for non-fissured soils, the linear relationship between DOM components A1 and A2 (R2 = 0.85) was stronger than that between A1 and A3 (R2 = 0.10), whereas for fissured soils, the linear relationship between components A1 and A3 (R2 = 0.88) was stronger than that between A1 and A2 (R2 = 0.35). The correlations between components (Figs. 5a and c) suggest a translational relationship between them (Kida et al., 2019). Additionally, a difference exists between fissured/non-fissured soil (Fig. 6). Our hypothesis is that the non-fissured soil DOM component A2 will be preferentially converted to A1 (molecular weight > A2) and then to A3 (molecular weight > A1), which is more stable with a larger molecular weight. In contrast, the fissured DOM component A2 of the soil will preferentially convert to A3 (molecular weight > A2) and then to A1 (molecular weight ≥ A1). This is due to the decomposition of SOM proteins by microorganisms into monomers, which are later condensed and polymerized by microbial activities into humic substances (Bunting and Lundberg, 1987). Soil microorganisms preferentially utilize unstable components, such as tryptophan and tyrosine. Only when the unstable components C4 and C6 are low do microorganisms utilize the more stable components C1, C2, C3, and C5 (Kleber, 2010). For both conversion efficiencies, we propose that the non-fissured component is converted faster because the molecular weight of component A2 converted to non-fissured A1 is lower than the molecular weight of component A3 converted to fissured component A3, which is less consumed by microbial activity (Cammack et al., 2004). The HC3 component A1 (M peak) and ZBL component A1 (A/C peak), as shown in Figs. S1 and S4, were likewise found to undergo changes that impact the conversion direction.

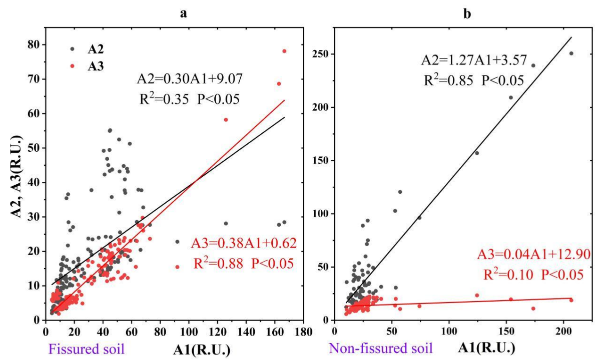

Figure 6. Relationships between C1 and C2 and between C1 and C3

4.2 Factors Altering DOM in Fissured/non-fissured Soils

The highly heterogeneous environment and complex dichotomous hydrological structure of the karst region have resulted in severe surface fragmentation and extensive subsurface development of negative landforms (Yuan et al., 2016). Various factors in this complex environment affect the performance of DOM. We selected the environmental factors with $P<0.05$ as response variables in Section 3.3 and obtained the explanation of each factor's influence on DOM through RDA (Fig. 7). Based on the correlation performance of each factor in Fig. 5, several factors contribute to the difference in DOM between fissured/non-fissured soils. The main factors include the morphology of the fissures (FW and Ape), NSV, Al, and ROR.

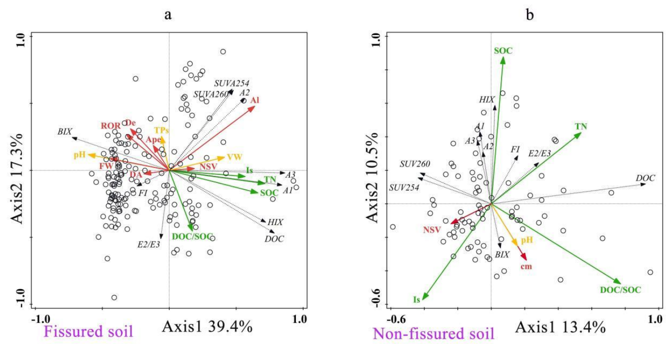

Figure 7. RDA ranking plots of DOM control factors (solid line) and optical properties (dashed

line) in fissure and non-fissure soil. The red, yellow and green solid lines represent environmental factors (AL, Ape, De, FW, NSV, ROR), soil environmental factors (VW, TPs, pH), and soil quality factors (TN, SOC, DOC/SOC, Is), respectively

Larger Ape and FW lead to the loss of soil fissure nutrients by leaching with water transport. In particular, as the most active component of the soil, DOM is lost in large quantities, which in severe cases may alter its component properties. The fissure (in the epikarst) serves as a transition zone connecting the karstic dichotomous hydrological structure, so its morphology significantly affects its vertical seepage hydrological processes (Li et al., 2020). The development of fissures is affected by the altitudinal gradient. At higher altitudes, the volume of slope water is low, resulting in less developed fissures. At middle altitudes, the convergence of water flow enhances dissolution and erosion capacity, leading to the development of wide and deep fissures with large Ape. At low altitudes, although fissures are developed in large quantities, they are small in Ape and narrow in FW due to the weakening of dissolution and erosion capacity (Cai, 2021). The soil nutrient content of HC3 is very low due to the loss of a large amount of DOM, as shown in Table S2. This loss caused a change in the proportion of DOM components in HC3, with a decrease in the proportion of humus-like substances and an increase in the proportion of protein-like fractions (Figs. 4a, c). DOM components are lost in large quantities during water transport, but the transported water also carries more proteins (lighter components), which are more susceptible to transport and loss (Fellman et al., 2009; Hood et al., 2009; Wang et al., 2021). If the extent of this loss exceeds the accumulation in the soil, it will result in a change in the DOM fraction of the soil. This is a plausible explanation of why the HC3 component differs from other fissure components in the same area. Fissure morphology, rainfall intensity, and vegetation type are key factors in this event, which makes it difficult to occur in both fissured/non-fissured soil depths (Peng et al., 2017).

The sources of DOM in non-fissured soils are formed by a combination of exogenous and autochthonous influences. This is due to the shallow soil layers of non-fissured soils in karst areas and the high influence of factors such as rainfall intensity, exogenous water, exogenous materials, and vegetation types on SOM. The non-fissured DOM is mainly derived from biological or aquatic bacteria ($HIX<4$). The DOM sources are mixed, including autochthonous and exogenous sources ($0.6 < BIX < 0.8$), terrestrial sources, and microorganisms ($1.6 < FI < 1.9$), as well as more aromatic, hydrophobic, and hydrophobic fractions ($SUVA_{254}$, $SUVA_{260}$) (Table 2 and Fig. 3). The spectral parameters of fissured soil DOM (Table 2, Fig. 2) differ significantly from those of other sources, indicating a greater influence of autochthonous and microbial sources. The exposure of irregular carbonate rock in karst areas causes surface tilting, which in turn leads to differences in rainfall infiltration at various rock–soil interfaces (Li et al., 2020; Li et al., 2014). A larger ROR also reduces the accumulation of aromatic and hydrophobic organic compounds in the soil (Lan, 2020). Changes in vegetation type can further complicate the alteration of DOM in soil. The rate of nutrient uptake in fissured soils is significantly increased by the presence of vegetation owing to the physiological and biochemical effects of the root system. As a result, nutrient levels are significantly higher in fissured soils compared to non-fissured soils (Yan et al., 2019b). Furthermore, the transition from herbaceous to arboreal vegetation in the fissure zone resulted in an increase in SOM and TN (Yan et al., 2020). Combined with the vegetation types listed in Table S1 and the dissolved organic carbon/soil organic carbon of fissured/non-fissured soils in this study, the non-fissured zone experiences a greater loss of protein-like substances from soils during the soil hydrological process in karst regions compared to the fissured zone. As a result, the quality of non-fissured soils is inferior to that of the fissured zone.

The DOM components of non-fissured ZBL soils are controlled by anthropogenic factors. While vegetation restoration in karst areas can enhance soil quality and environmental management, economic development and environmental restoration are challenging in severe rocky desertification environments. The decision to plant ZBL in the Huajiang study area aligns with the goals of sustainable economic development and environmental restoration in the region, as noted by Xiong et al. (2011, 2012). The main industry in the ZBL region is based on compound fertilizers containing N, P, and K, as well as the application of organic fertilizers (Li et al., 2022). This, combined with the long-term use of water for agricultural irrigation and changes to the soil environment (Liu et al., 2021), results in a different type and percentage of fluorescence fractions of DOM compared to other non-fissured soils (Fig. S4) (Yan et al., 2019c).

In summary, the differences between fissured/non-fissured DOM in karst areas primarily stem from the degree of soil disturbance by external elements, which is caused by a combination of factors. The role of DOM in soil and water is crucial as it can influence various variables, including the complex and variable environmental behavior of DOM as well as the impact of binding with heavy metal organic and inorganic pollutants on biogeochemical cycles (Aiken et al., 2011; Bolan et al., 2011; Deb and Shukla, 2011; Kalbitz et al., 2000b; Ren et al., 2015). Therefore, it should be included in the system of indicators for assessing rock desertification management. Hydrological stress is considered one of the drivers of DOM (Shi et al., 2023), particularly in areas with high rates of rock exposure in karst. This impact is not reflected in this study, but it should not be ignored. Rainfall and its rainwater DOM have a significant impact on soil hydrological processes and soil microbial response to DOM changes. Therefore, they should be given more attention.

The management of rocky desertification remains a challenge. To achieve the coordinated development of ecological benefits, regional economic development, and social harmony and stability, diversified measures and objectives are required (Xiong et al., 2016).

5. Conclusion

This study revealed noticeable differences in the DOM between fissured/non-fissured soils in the karst region. Non-fissured soils exhibited higher levels of SUVA254 and SUVA260 of DOM, indicating greater aromatic, hydrophobic, and hydrophilic components than fissured soils. Additionally, the sources of DOM in non-fissured soils were primarily exogenous and microbial, while those in fissured soils were mainly microbial and autochthonous. The proportion of soil DOM in the fissured area was dominated by stable humus-like substances with a larger molecular weight. The transformation between the components was from A2→A3→A1. In contrast, the non-fissured area had comparable proportions of protein-like and humus-like substances with smaller molecular weights that were easily lost. The transformation between the components was from A2→A1→A3. Therefore, the direction of transformation of DOM differed between the fissured/non-fissured soils.

External environmental factors, particularly NSV, Al, FW, Ape, and ROR, dominate the difference in DOM. The development of fissure morphology is greatly influenced by the degree of rock exposure and altitude. Large values of FW and Ape directly impact the type of DOM components and increase the proportion of protein-like substances. The type of vegetation and intervention have a direct impact on soil quality. The quality of fissured soil is higher than that of non-fissured soil, indicating that non-fissured soil in karst areas is at a higher risk of losing its lightweight component than fissured soil. Anthropogenic activities, such as tillage and fertilization, complicate the changes in DOM fractions and are key factors in altering environmental conditions.

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