

Article

Migration of Dissolved Organic Matter in the Epikarst Fissured Soil of South China Karst

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Abstract: The efficient reactivity and mobility of dissolved organic matter (DOM) affect biogeochemical processes. As important components that link aboveground and belowground vertical systems under the binary 3D structure of karst, fissures provide soil–water–nutrient leakage channels and storage spaces. However, reports on DOM properties and drivers in fissured soil are extremely rare. This study characterizes DOM in the fissured soil of different vegetation types under medium-intensity rocky desertification conditions. Soil samples were characterized via ultraviolet (UV)–visible absorption spectroscopy and fluorescence excitation–emission matrix–parallel factor analysis. Five fluorescent fractions were identified. The controlling factors for the optical properties of soil DOM were determined via the redundancy analysis method. Results showed the following: (1) Dissolved organic C/soil organic C < 4.68 + 0.49‰, specific UV absorbance (SUVA)₂₅₄ and SUVA₂₆₀ exhibited low overall performance with the vast majority of the humification index (HIX) < 4, most of the fluorescence index (FI) ≥ 1.7, most of the biological index (BIX) in 0.6 < BIX < 1 and 31.67–41.67% of protein-like fractions. These data indicate that cleaved soil, except for topsoil, has low DOM content, weak aromaticity, and low humification; (2) Rainfall intensity, aperture, and near-surface vegetation type are the major causes of DOM transport and loss; and (3) Most DOM losses are likely to be protein-like and enhance the loss of soil P. In summary, environmental factors and the characteristics of fissures determine DOM content and migration, particularly rainfall intensity and vegetation type. The loss of lighter DOM components will be greater in an area with high karst desertification grade, strong fissure development, weaker soil aromaticity, and lower humification. These results provide a clearer basis for optimizing the fissure nutrient element migration scheme in karst areas.

Keywords: DOM; UV; fluorescence; migration; karst; fissure



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1. Introduction

Amongst the 17 sustainable development projects set by the United Nations to be achieved by 2030, 8 are related to the soil environment [1]. Soil plays a mediating and critical role in ecosystems and human society [2] with extremely low production rates [3]. DOM is the most dynamic and effective component of soil organic matter (SOM), and its strong reactivity and migration capacity play important roles in soil C cycling [4–6]. DOM can bind to soil particles to become part of the soil’s organic carbon (SOC) pool [7]; it also promotes soil microbial activity, organic matter decomposition, nutrient transport and transformation in soil, weathering of minerals, soil-forming processes, and contaminant transport [8–13]. All these processes are related to DOM’s properties and the characteristics of the environment.

DOM belongs to natural organic matter, accounting for about 97.1% [14]. It refers to C-based organic compounds [15] in soil and water bodies that consist of a range of molecules with different sizes and structures [16] that can pass through 0.1–0.7 µm filter membranes.

DOM is widely present in soil, water, the atmosphere, and sediments [17,18]. Studies have shown that DOM is a nonhomogeneous mixture of aliphatic and aromatic polymers whose composition varies in time and space depending on the source and the exposure to degradation processes [19–21]. In terrestrial environmental systems, most DOM in the soil is derived from plants, exogenous organic matter, and microbial components [9,22,23]. Studies have shown that the source of DOM determines its chemical properties and persistence in soil [5,24]. Thus, the characteristics of DOM and its sources in soil are particularly critical for determining DOM's environmental impact.

As an important part of the Earth's critical zone, the karst critical zone accounts for 12% of the total land area [25]. Amongst the karst critical zones, the epikarst is the product of intense karstification of the surface in the karst area, it is the first karst development layer below the surface, a transitional zone connecting the karst dual hydrological structure, the main space for the storage and migration of surface soil and water, and an important factor for controlling the development of karst geomorphology and eco-hydrological function [26]. In the context of karst desertification, the special binary three-dimensional spatial structure of karst areas [27] forms a special erosion mode as subsurface leakage. Subsurface leakage is the migration of surface soil to subsurface space through karst channels, such as dissolution fissures and waterfall holes, under the action of hydraulic transport and chemical dissolution in karst areas [28]. This phenomenon is the primary means of soil erosion under karst desertification conditions [29–31], making fissures an integral part of the vertical system that links aboveground and belowground in key karst zones, becoming one of the soil–water–nutrient loss channels and storage spaces. Water transport and nutrient transport in fractures are of considerable interest. Studies have concluded that the size of soil and water leakage along the pore (fissure) space depends on the development of the pore (fissure) space and the connectivity of the lower part of the fissure [31]. The connectivity of shallow karst fissures and soil differences exert a strong influence on the permeability of the surface karst zone [32,33], and the presence of preferential flow in fissured soil enhances nutrient loss [34]. Researchers [35] have conducted experiments under different subsurface fissure degrees and rainfall intensities by simulating artificial rainfall, and they have concluded that overall nutrient loss from sloping farmlands, such as N, P, and K, is not significantly related to fractality; moreover, rainfall intensity is a key factor, indicating that subsurface runoff is the primary nutrient loss mode on karst slopes [36]. DOM can be used as a tracer for understanding the hydrological pathways of soil nutrient transport [37]; it fully participates in the C cycle and enhances soil nutrient transport to the surrounding surface and groundwater environment [9,38,39]. In addition, subsurface migration and loss of DOM pose a greater threat to environmental quality and can considerably affect the transport and toxicity of organic and inorganic contaminants [40,41]. As reported in Sun [42], high-molecular-weight polycyclic aromatic hydrocarbons (PAHs) are used as carriers in soil seepage with DOM in the southwestern karst region, and PAHs continue to dissolve into seepage water when water is transported vertically downward along the profile, increasing the risk of groundwater contamination. By contrast, the surface of karst areas is fragmented and heterogeneous, and the distribution and migration factors of DOM in fractured soil are more variable. Therefore, the spectral information of chromophoric dissolved organic matter (CDOM) in DOM is used to reveal the characteristics and migration factors of DOM in karst fractured soils and provide a theoretical basis for improving the ecological environment of karst desertification.

We studied the content and spectral characteristics of DOM in typical fractured soils in the desertification areas in South China Karst, obtained the spectral factors of DOM by using ultraviolet–visible (UV–Vis) absorption and fluorescence spectroscopy, compared optical indices, performed parallel factor analysis (PARAFAC) and three-dimensional fluorescence excitation–emission matrices (3D-EEMs) to analyze the source and characteristics [43–47] of DOM and explore its migration control factors. The objectives of this study were to: (1) determine the distribution characteristics of DOM in fissured soils in karst areas; (2)

identify the drivers of DOM in fissured soil; and (3) assess the environmental impact of DOM transport in fissured soil.

2. Materials and Methods

2.1. Characteristics of the Study Area

In the mountainous plateau of Guizhou, which represents the general structure of the karst ecosystem in southern China, the Zhenfeng–Huajiang karst desertification demonstration area was selected as the study area (105°36′30″–105°46′30″ E, 25°39′13″–25°41′00″ N) [26,48]. The terrain is undulating, with an altitude of 600–1400 m. The study area (Figure 1) is a subtropical dry-hot valley climate, with a mean annual precipitation of 1052 mm and a mean annual temperature of 18.4 °C. Lithology is mostly limestone, with serious soil fragmentation, high rock exposure rate, and serious soil erosion, belonging to medium-intensity karst desertification [49]. Vegetation is largely broad-leaved forests, mixed coniferous forests, and shrubs. The primary vegetation has been severely damaged, and secondary vegetation is dominant at present. For details of the study area, refer to [34].

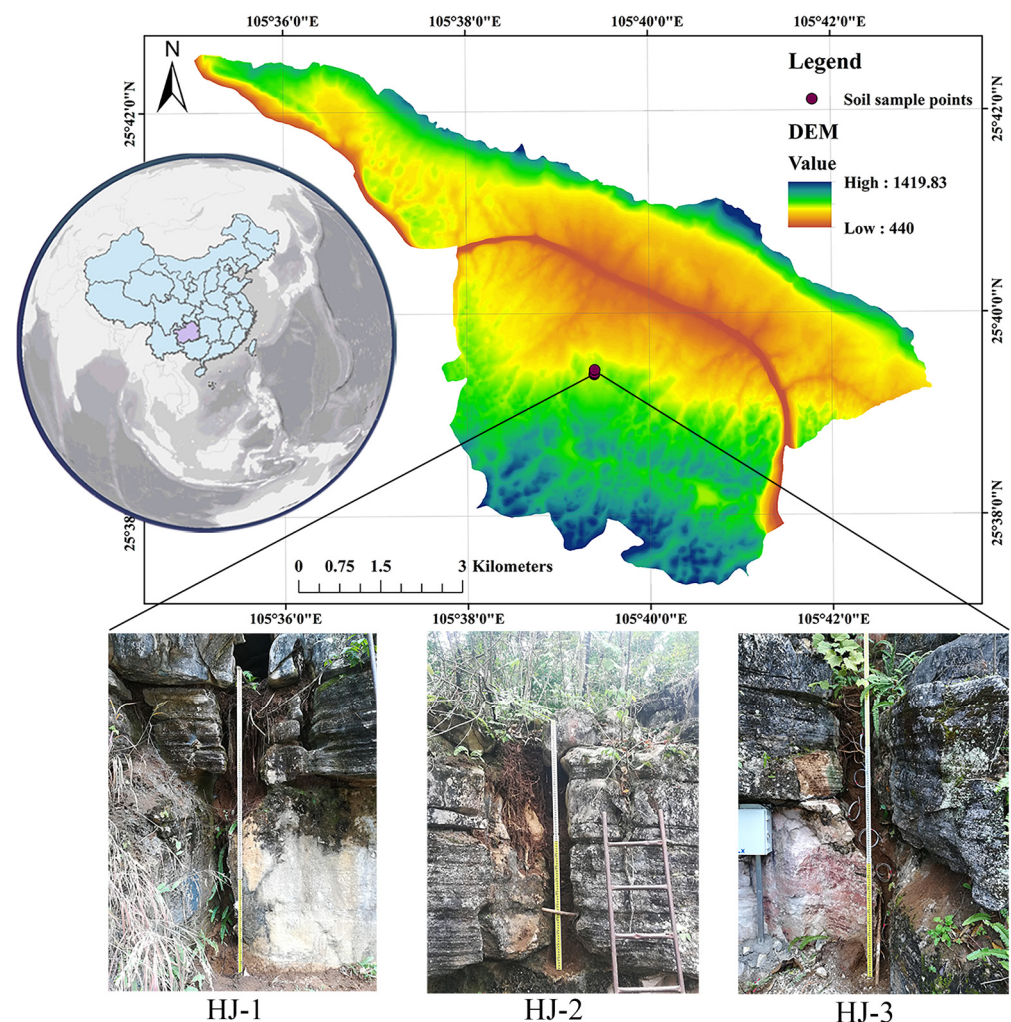


Figure 1. Locations of the study area and fissure soil sampling sites.

2.2. Sample Collection and Processing

The number of fissures, aperture, width, depth, dip angle, and near-surface vegetation were recorded through a survey of fissures in the study area. The characteristics of fissure development were clarified under varying topography and environment, and 3 typical fissures, proximity, and similar development were selected from amongst 65 fissures

(Table 1). Soil samples were collected in late August 2020 to remove loose soil, roots, and branches from the fissured soil. The soil was planed away from the outer 15 cm of the vertical profile and 1–2 cm away from the fissured rock wall. The ring knife was collected laterally from the in situ soil to measure its physical properties. Soil samples of organic matter to be measured are collected from 0–50 cm below the surface of the soil, once every 5 cm, and once every 10 cm after more than 50 cm. Sampling was performed at each layer, and 3 parallel soil samples were mixed for a total of 90 samples. The collected soil samples were stored in polyethylene (PE) self-sealing bags, transported back to the laboratory, cooled, and underwent ventilation air-drying.

Table 1. Overview of sampling sites and fissure structure characteristic parameters in the study area.

Type	Longitude and Latitude	Altitude (m)	Depth (cm)	Aperture (cm)	Average Width (cm)	Dip Angle (°)	Near-Surface Vegetation
HJ-1	25°39′23.70″ N, 105°39′23.70″ E	739	290	42	37	82	Celtis sinensis and Cipadessa baccifera
HJ-2	25°39′24.56″ N, 105°39′23.82″ E	739	190	31	25	87	Eriobotrya japonica and Zanthoxylum bungeanum
HJ-3	25°39′26.42″ N, 105°39′23.96″ E	739	285	39	32	80	Celtis sinensis and Lonicera japonica

For details of the physical properties (e.g., volume weight and total porosity) and mechanical composition of the soil, refer to [34]. The air-dried soil samples were ground and passed through a 60-mesh sieve. Then, 5 g of soil passed through the 60-mesh sieve was weighed, and 25 mL of ultra-pure water was added, shaken, and centrifuged to obtain the supernatant. The supernatant was filtered through a 0.22 µm polyethersulfone membrane (reducing the role of microbes on the DOM) to obtain the solution to be tested. Dissolved organic carbon (DOC) concentrations were determined using a total organic carbon (TOC) analyzer (multi N/C 3100, Analytik Jena, Jena, Germany). All dissolutions to be measured were uniformly diluted to a DOC concentration of less than 10 mg·L⁻¹ to ensure that absorbance at ultraviolet 254 nm was less than 0.3, reducing the internal filtering effect during fluorescence scanning [50]. The UV–Vis absorption spectra of the soil samples were obtained using a UV–Vis spectrophotometer (SPECORD Plus 200, Analytik Jena, Germany) with ultra-pure water as the blank set and scanning at 1 nm intervals from 200–800 nm. Fluorescence data from the soil samples were collected using a fluorescence spectrophotometer (RF-5301PC, Shimadzu, Kyoto, Japan). The excitation wavelengths (Ex) ranged from 220–500 nm at 5 nm intervals and the emission wavelengths (Em) ranged from 250–600 nm at 1 nm intervals, minus ultra-pure water as a control to eliminate scattering. Additional information is found in Lawaetz and Stedmon [51] and He [44].

2.3. Optical Factor

As shown in Table 2 for the DOM optical indicators used in this study.

2.4. Statistical Analysis

The number of components, type, and fluorescence intensity of CDOM for 90 soil samples were obtained by MATLAB 2020a (MathWorks Inc., Natick, MA, USA) and DOM-Fluor 1.7 toolbox analysis. Data were counted using Office (2016 enhanced version) and one-way ANOVA, significance analysis, and graphical plotting were carried out using Origin 2021 (OriginLab Inc., Northampton, MA, USA). Relationships between spectral parameters (Table 2), components, and influencing factors of DOM were analyzed using Canoco5's (Ithaca, NY, USA) redundancy analysis (RDA).

Table 2. 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: $SUVA_{254/260} = a(\lambda)/c(\text{DOC})$	$a(\lambda)$ is the UV–Vis absorbance at wavelength 254, 260 (nm) and r is the path-length of the optical (0.01 m), $c(\text{DOC})$ is the concentration of extractable DOM ($\text{mg}\cdot\text{L}^{-1}$) [52].
E2/E3: $a(254)/a(365)$ or $a(250)/a(365)$ E2/E4: $a(240)/a(420)$ or $a(250)/a(436)$	$a(240, 250, 254, 365, 420, \text{ and } 436)$ is the UV–Vis absorbance at wavelength $\lambda(\text{nm})$. E2/E3 is an indication of the degree of organic matter humification, with low values indicating low humification. E2/E4 indicates the source of organic matter, with higher values being endogenous and lower values being exogenous [53,54].
Slope ratio: $a(\lambda) = a(\lambda_{400})\exp[S(\lambda_{400} - \lambda)] + K$ $SR = S_{(275-295)}/S_{(350-400)}$	$S_{(275-295)}$ and $S_{(350-400)}$ are the spectral slope S values in each range, respectively, and λ_{400} is the reference wavelength [55–57].
Humification index: $HIX = (\sum I_{435-480})/(\sum I_{300-345})$	Ex at 254 nm, the ratio of the integral values of the fluorescence intensity of Em in the range 435–480 and 300–345 nm, reflects the degree of humification of DOM. $HIX < 4$ belongs to biological or aquatic bacterial sources, $4 < HIX < 6$ belong to weakly humified features and important recent autotrophic sources [58,59].
Fluorescence index: $FI = Em(470/520)$	Ex at 370 nm, the ratio of the fluorescence intensity of Em at 470 and 520 nm reflects the source of the DOM. Microbial activity is the main source of DOM for $1.7 < FI < 2.0$, and the contribution of organisms is lower when $1.2 < FI < 1.5$ [60].
Biological index: $BIX = Em(380/430)$	Ex at 310 nm, the ratio of fluorescence intensity at 380 and 520 nm for Em. BIX value reflects the ratio of albuminoid and biological components. BIX value reflects the ratio of albuminoid and biological components. Low biological fraction ($0.6 < BIX < 0.7$), DOM of biological or aquatic bacterial origin ($BIX > 1$) [59,61].

3. Results

3.1. DOM Overall Feature Parameters

As indicated in Table 3, the average SOC and DOC contents of fissured soil were $17.26 \pm 2.7 \text{ g}\cdot\text{kg}^{-1}$ and $16.72 \pm 8.50 \text{ mg}\cdot\text{L}^{-1}$, respectively, indicating that the average contents of HJ-1 and HJ-3 were significantly lower than those of HJ-2. The trends of specific UV absorbance ($SUVA_{254}$ and $SUVA_{260}$) were consistent, and the aromatic and hydrophobic components of DOM in each fissure did not vary considerably, with the average maximum value at HJ-2. By contrast, E2/E3 and E2/E4 exhibited higher HJ-1 humification than the others and were more endogenous. S_R characterizes molecular weight size and aromatization [55], indicating that the average molecular weight and aromatization of the three cleavages were similar, with HJ-1 being slightly higher than the others. The average FI, HIX, and BIX of the three fissures were less different, with all three fissures showing $FI \geq 1.9$, $0.7 < HIX < 1$, and $BIX < 4$, indicating that DOM was a strong autogenous source feature.

Table 3. Overall mean values of DOM characteristic parameters in fissured soils.

Type	SOC (g·kg ⁻¹)	DOC (mg·L ⁻¹)	SUVA ₂₅₄	SUVA ₂₆₀	E2/E3	E2/E4	SR	FI	BIX	HIX
HJ-1	14.85 ± 6.8	15.34 ± 10.39	0.33 ± 0.08	0.31 ± 0.08	5.08 ± 1.21	12.9 ± 2.62	1.06 ± 0.22	1.99 ± 0.40	0.82 ± 0.13	1.59 ± 0.68
HJ-2	19.35 ± 8.6	18.94 ± 6.92	0.37 ± 0.12	0.35 ± 0.11	4.25 ± 1.09	11.51 ± 1.99	0.90 ± 0.16	2.03 ± 0.36	0.77 ± 0.12	1.63 ± 0.74
HJ-3	17.57 ± 8.2	16.50 ± 6.97	0.34 ± 0.07	0.32 ± 0.07	4.38 ± 0.60	12.06 ± 1.89	0.96 ± 0.08	2.03 ± 0.21	0.77 ± 0.15	1.56 ± 0.60
Mean	17.26 ± 2.7	16.72 ± 8.50	0.34 ± 0.09	0.33 ± 0.09	4.62 ± 1.07	12.23 ± 2.28	0.98 ± 0.18	2.02 ± 0.33	0.79 ± 0.14	1.59 ± 0.67

Note: The unit for SUVA₂₅₄ and SUVA₂₆₀ is L·mg C⁻¹·m⁻¹. Values are presented as mean ± SD.

3.2. Characteristics of DOC Content and Optical Factors of DOM in Fissured Soils

The DOC content of the upper layer fluctuated significantly, whilst that of the lower layer gradually decreased and stabilized (Figure 2b). However, the variation of SUVA₂₅₄ and SUVA₂₆₀ in HJ-1 and HJ-2 (Figure 2c,d) exhibited significant fluctuations at 35–40 cm and 50–60 cm, respectively, indicating that the aromaticity, humification, and hydrophobic components of soil in this layer were stronger than those of the surrounding (in response to the S_R value of this layer in Figure 3a), and the middle and lower layers were more stable. HJ-3 demonstrated a strong response to the trend of its DOM, whilst the responses of HJ-1 and HJ-2 were poorer. The S_R values of HJ-1 and HJ-2 were more different than that of HJ-3 in shallow and deep soils, whilst both tended to be relatively stable and more aromatic with the higher molecular weight of DOM in the middle layer. The variations of E2/E3 and E2/E4 (Figure 3b,c) were more consistent, but more differences were found in deep soil, indicating that the bottom DOM of HJ-1 and HJ-2 was less humified and more endogenous. HIX < 4 (Figure 4a) constitutes the vast majority, and the vast majority of the lower and middle DOM are of biogenic origin (endogenous and low humification). BIX is higher within the range of 0.7–1 (Figure 4b), indicating an extremely low authigenic source of DOM in the surface layer, and the middle and lower layers belong to the medium-intensity authigenic feature. FI ≥ 1.9 was the majority (Figure 4c), indicating that DOM was mostly of microbial origin with minimal influence from terrestrial sources (FI < 1.4).

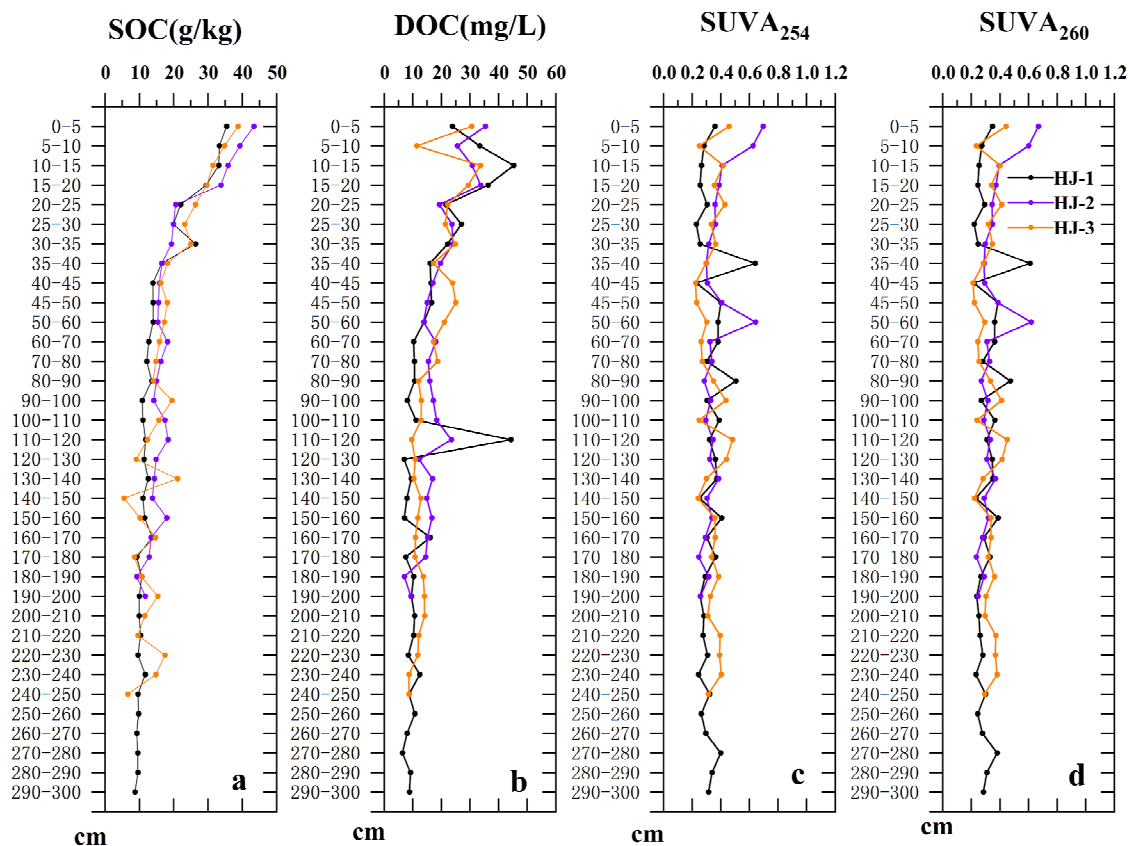


Figure 2. The contents of SOC (a), DOC (b), SUVA₂₅₄ (c), and SUVA₂₆₀ (d) in each layer of fissure soil. SUVA₂₅₄, SUVA₂₆₀ (L·mg C⁻¹·m⁻¹).

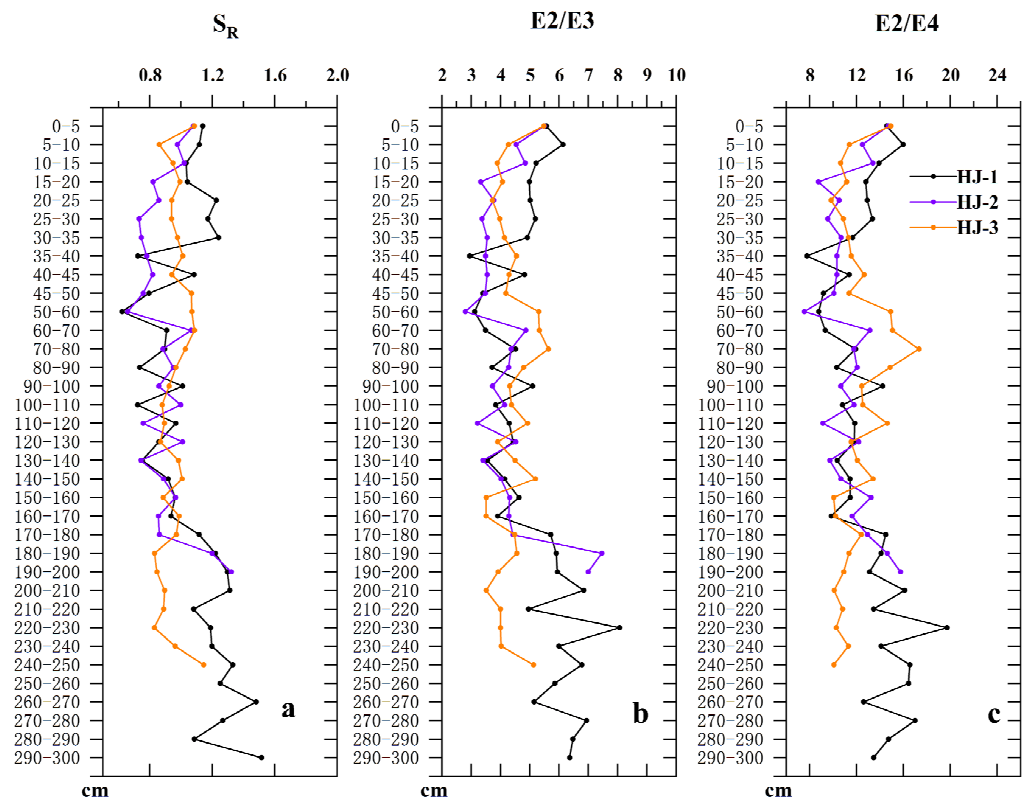


Figure 3. The content of E2/E3 (b), E3/E4 (c), and S_R (a) in each layer of fissure soil.

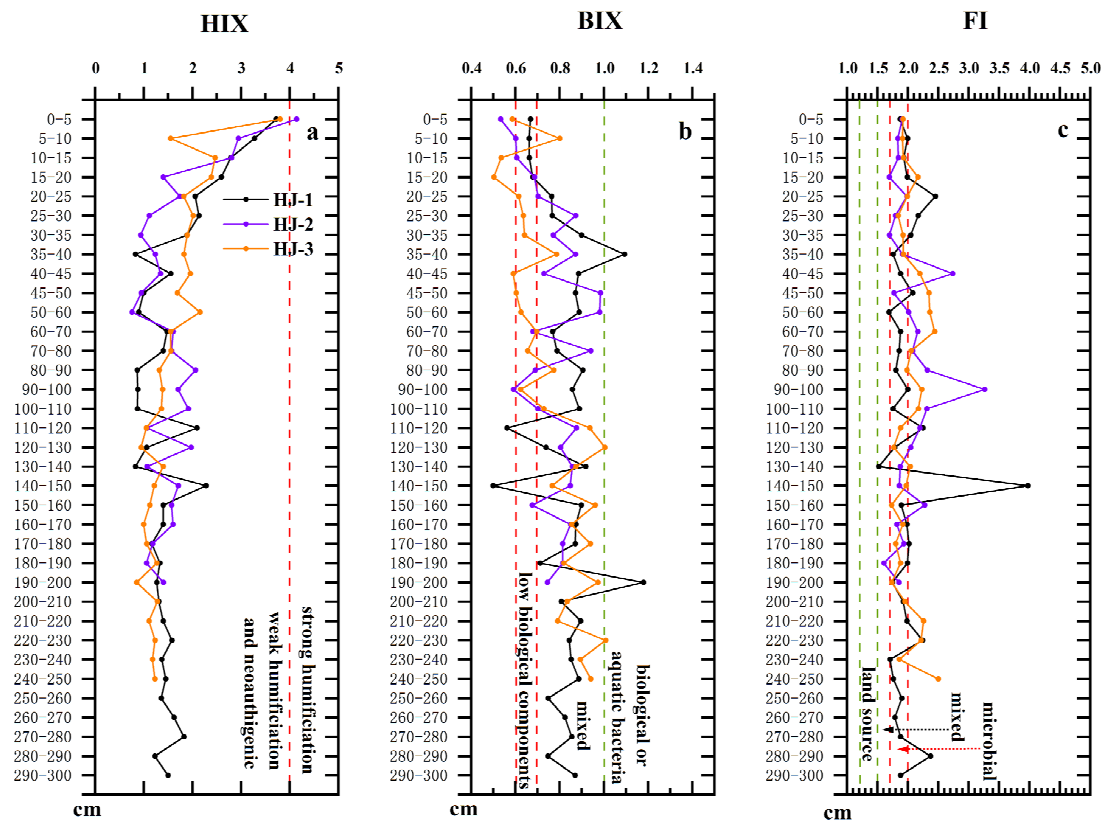


Figure 4. The content of HIX (a), BIX (b), and FI (c) in each layer of fissure soil.

3.3. Component Differences of DOM

Five fluorescent fractions (Figure A2) were derived for DOM in all three fissured soil samples through the EEMs–PARAFAC method. The maximum wavelengths of their fluorescence peaks were identified (Table 4), yielding C1, C2, and C5 as humic acid-like, and C3 and C4 as protein-like. Selection and comparison revealed that C1 and C5 were similar to the traditional fulvic acid A peaks (Ex: 237–260/275; Em: 400–500/<500 nm) [62,63]. C2 was identified as the traditional humic-like M peak (Ex: 290–325; Em: 370–430) [62,64]. C3 and C4 are similar to protein-like peaks (Ex: <240/275; Em: 330–368/340) [64], and C3, C4, and C5 are more evidently redshifted, implying an increase in molecular weight. As shown in Figure 5, all three clefts exhibit greater humic-like than protein-like peaks, with the largest proportion of the C1 component and the smallest proportion of the C5 component. The fluorescence intensity of all the peaks of HJ-2 is stronger than those of the others.

Table 4. Types of DOM fluorescent fractions in fissured soil.

Type	Maximum Wavelength	HJ-1	HJ-2	HJ-3	Description of the Source
C1	Ex _{max}	255	255	255	A peak, terrestrial humic [62]. High molecular weight and aromatic humus, widely distributed, highest in wetland and forest environments [65].
	Em _{max}	461	471	452	
C2	Ex _{max}	305	305	305	M peak, marine humic [64], Low molecular weight, similar in marine, wastewater, wetlands, and farmland [63,66].
	Em _{max}	415	428	403	
C3	Ex _{max}	255	245	250	T peak, protein-like peaks, and microbial by-product-like substances are related [64,67,68].
	Em _{max}	369	366	369	
C4	Ex _{max}	280	285	280	B peak, protein-like Complexine [64], leachate production mainly by microorganisms, phytoplankton, and higher plants [20,63].
	Em _{max}	336	334	328	
C5	Ex _{max}	290	290	285	A and C peak, terrestrial humus [63].
	Em _{max}	521	521	521	

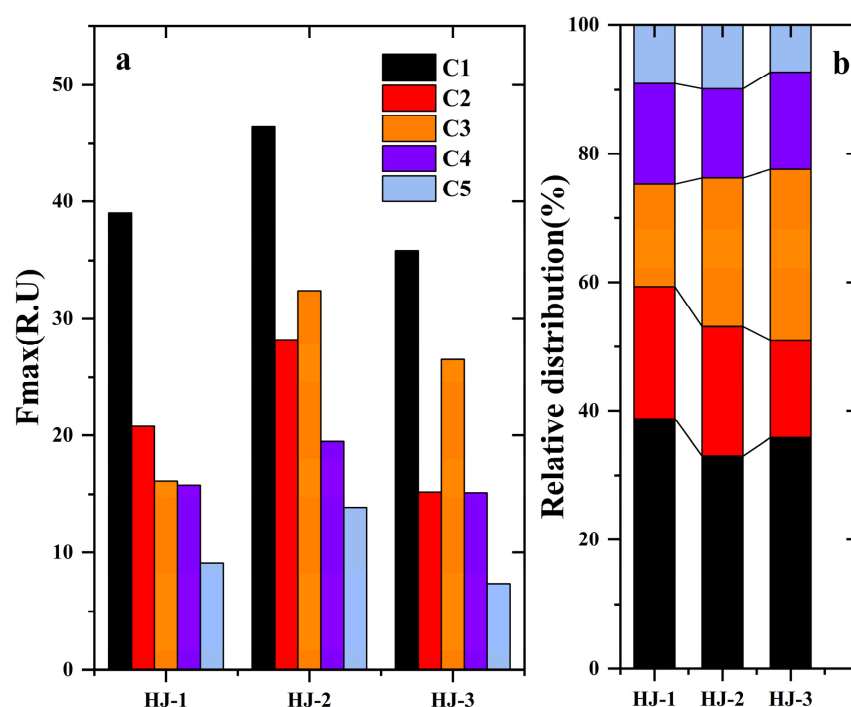


Figure 5. Intensity (a) and percentage (b) of fluorescence 5 components of DOM in fissured soils.

3.4. Factors That Affect DOM Migration

To highlight the effect of each factor on DOM migration in fissured soil, Conoco's RDA and Pearson correlation coefficients were calculated amongst parameters of interest. Environmental factors included near-surface vegetation (NSV), fracture width (FW), fracture dip angle (DA), depth (De), and aperture (Ape). Soil environmental factors were pH, volumetric weight (VW), total porosity (TPs), and electrical conductivity (EC). Soil quality factors were total P (TP), total N (TN), SOC isotope (Is), and DOC/SOC. As a soil quality standard, DOC/SOC measures the total variability of soil C pools in karst systems [69]. A conclusion could be drawn from Figure 6 that environmental factors exerted a significant effect on DOM characteristics in fissured soil, particularly De, NSV, and Ape. pH had minimal effect, whilst a significant correlation was observed between nutrient elements (TP, TN, and Is) and DOM characteristic indicators. SUVA₂₅₄ was positively correlated with the aromaticity and hydrophobicity of DOM [4,70], whilst SUVA₂₆₀ was positively correlated with the concentration of hydrophobic components of DOM [71]. SUVA₂₅₄, SUVA₂₆₀, and DOC were highly correlated with all five components (Figure 6a), allowing better characterization of DOM. De was significantly and negatively correlated with the five components (Figure 6a). NSV significantly affected the protein-like and low-humic fractions of DOM with a positive correlation ($p \leq 0.05$) and a significant negative correlation with E2/E3 ($p \leq 0.01$) and S_R ($p \leq 0.05$). As shown in Figure 7, RDA in Axis 1 was 80.9% and in Axis 2 was 11.31%.

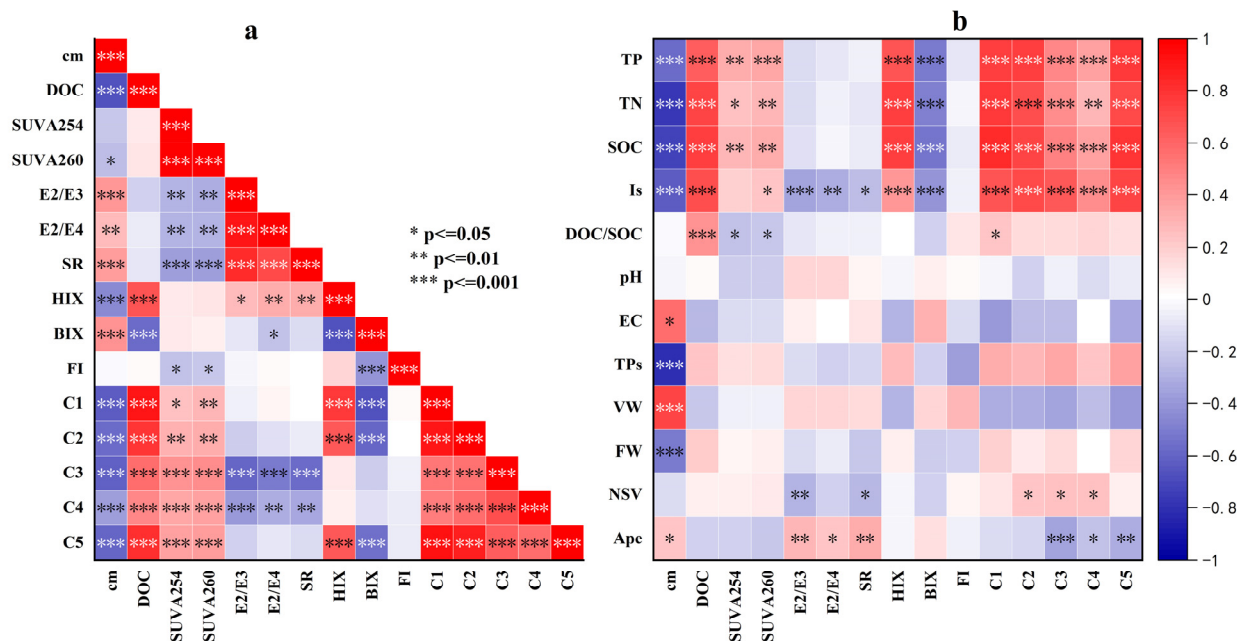


Figure 6. Pearson correlation coefficients between DOM parameters (a) and environment (b) for fissured soil.

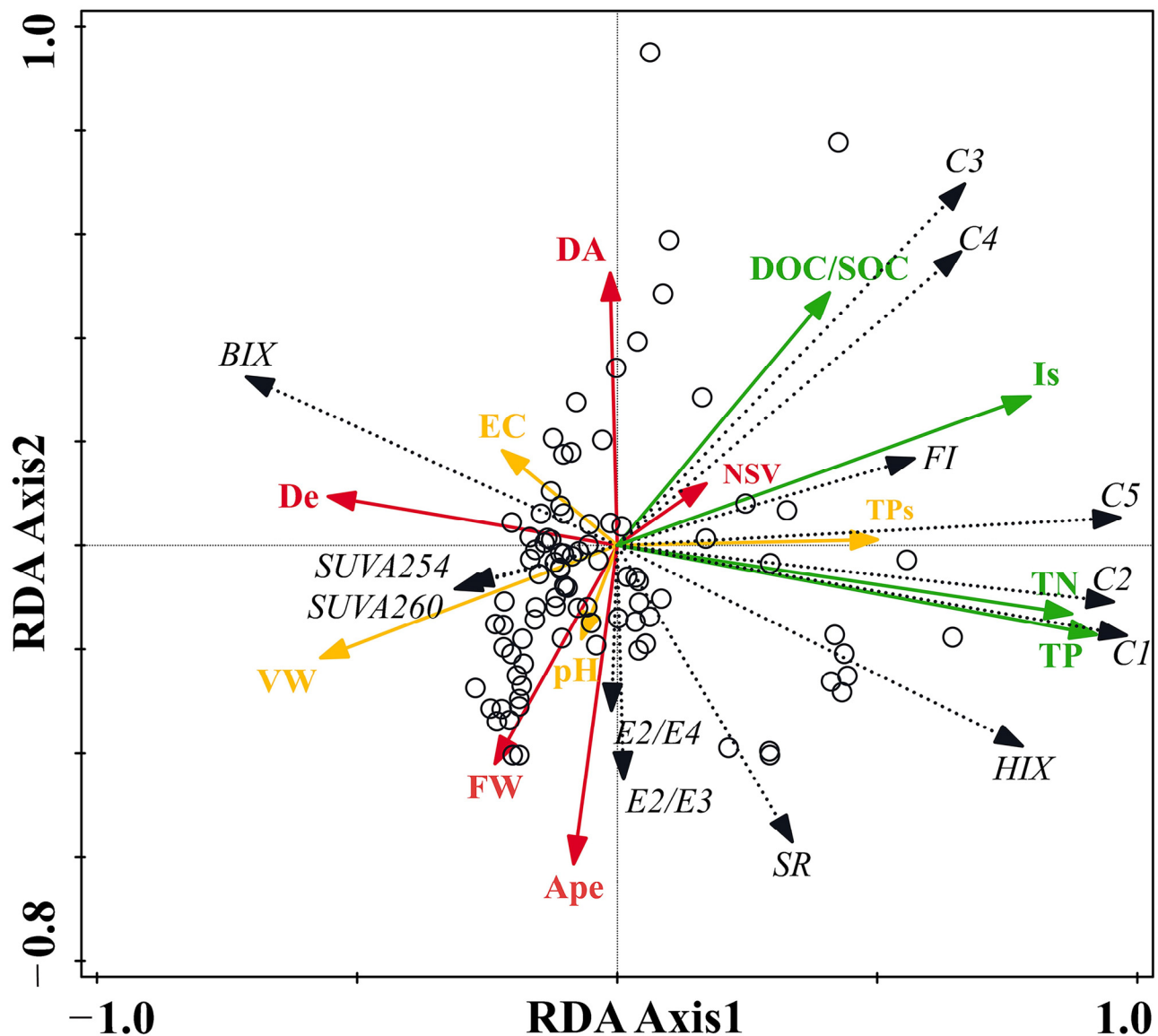


Figure 7. RDA ranking plots of DOM control factors (solid line) and Spectral factor properties (dashed line) in fractured soil. The red, yellow, and green solid lines represent environmental factors (NSV, FW, De, and Ape), soil physical factors (VW, TPs, EC, and pH), and soil chemistry factors (TP, TN, DOC/SOC, and Is), respectively.

4. Discussion

4.1. Characterization of SOC and DOM Content in Fissured Soil

DOM, as the most active part of SOM, is the major energy substrate of soil and it exerts an important effect on the organic C pool [72]. The shallow SOC and DOC contents of fissured soil in the study area (Figure 2a,b) were generally consistent with those of other studies of the same type [73,74], although SOC was significantly higher in the study area than in non-karst areas [47,75,76], whilst DOC was significantly lower in the study area than in non-karst areas [77]. With deeper depth, SOC and DOC contents gradually decreased and stabilized [78,79]. Therefore, a large amount of SOC storage is found in the study area, but the special binary 3D structure of the karst region has large DOM mobility and low storage capacity.

A significant correlation (Figure 6, $p < 0.001$) and a linear relationship (Figure 8) was observed between C3, C4, and C1, C2, C5, and the linear relationship between C1, C2, and C5 ($R_1^2 = 0.85$, $R_2^2 = 0.76$) was significantly stronger than that between C3, C4, and

C5 ($R_3^2 = 0.38$, $R_4^2 = 0.32$). This finding suggests a transformative relationship between the DOM components of fissured soil. Proteins in soil organic matter are easily broken down by microorganisms into monomers, which, in turn, collect in the soil to form humus through microbial activity [80]. Therefore, C3 and C4 may be converted into C2 (medium molecular weight, Table 4) and then into C1 and C5 (larger molecular weight, more stable), because soil microorganisms preferentially utilize unstable components (e.g., tryptophan and tyrosine); when the content of unstable components (C3 and C4) is low, microorganisms may utilize the more stable C1, C2, and C5 [81]. The average protein content of fissured soil in the study area was $36.78\% \pm 0.05\%$ (Figure 6), which was 115–143% higher than that of the surface layer of agricultural soil in Gao [77], including Heilongjiang, Jilin, Liaoning, Shaanxi, Shanxi, Hebei, Tianjin, Henan, Shandong, Chongqing, Hunan, Anhui, Jiangsu, Jiangxi, Gansu, Xinjiang, Inner Mongolia, and Yunnan Province. This finding indicates that amino acids or degraded peptides are more abundant in the fissured soil DOM in the study area, which may be attributed to humus in a subtropical environment contributing to the enrichment of protein substances [82]. Thus, the decomposition rate of protein-like substances or the content of incompletely degraded peptides was relatively high in the fissured soil of the study area [77].

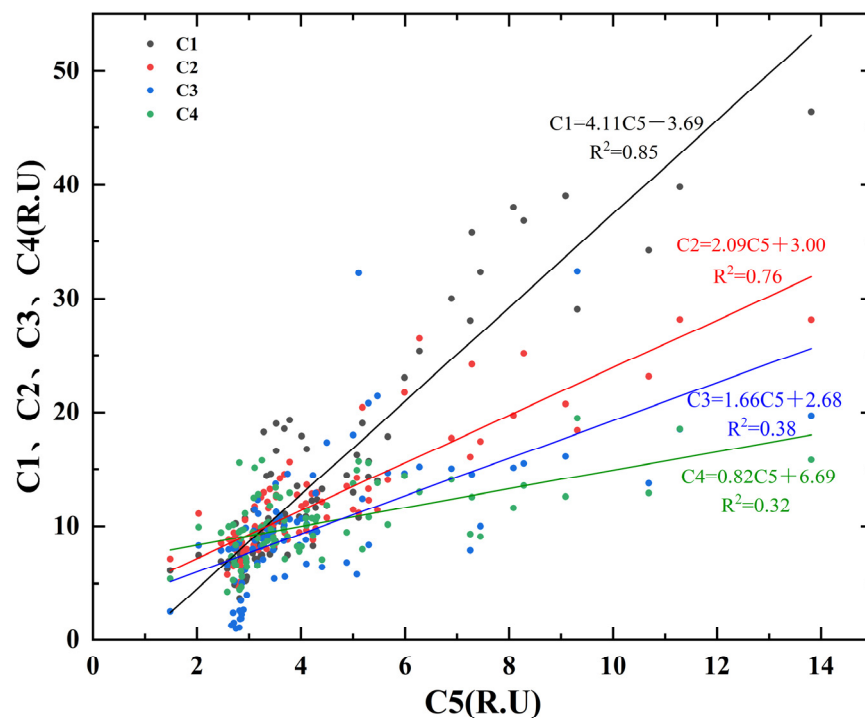


Figure 8. Relation of C5 to C1, C2, C3, and C4.

As shown in Figures 4 and A1, the surface soil exhibits a low authigenic phenomenon via external influence, whilst the middle and lower soil DOM are overwhelming from authigenic or microbial sources with a low degree of humification [58]. The higher content of DOM-like proteins in fissured soil is due to the higher material circulation capacity and reduced conversion of protein-like substances into humus during the rainy season. The low DOM content of karst areas reduces microbial activity [23], slows down the effective utilization of protein-like substances, and weakens the mineralization and utilization of low-molecular-weight organic matter [47] by the soil, making losing these nutrients through fissures easier.

4.2. Drivers That Influence Changes in DOM Components in Fissured Soil

In the study area, the DOM of fissured soils is likely to be strongly influenced by environmental and vegetation factors. The overview of the study area noted that its

average annual rainfall is 1052 mm, which will seriously affect the distribution of DOM [83]. Rainfall intensity affects the migration of DOM in fissured soils. A previous study [34] showed that DOC distribution in fissured soil in the study area was significantly influenced by hydrological transport: (1) The performance of δD and $\delta^{18}O$ enrichment in the study area indicates that rainfall to soil water undergoes the transport process of rainfall $\rightarrow$ penetrating rainfall $\rightarrow$ rock wall flow $\rightarrow$ apoplastic material $\rightarrow$ soil water when rainfall intensity is moderate (24 h rainfall: 10.0–24.9 mm). In excess of 35 mm rainfall (heavy rainfall), only the lower and middle layers of fissured soil will respond; and (2) Changes occur in DOC before the rainy season (January–May) and after the rainy season (June–September) with an average reduction rate of 21.14%. As important water-conducting channels in karst areas, fissures provide the link between atmospheric precipitation, surface water, soil water, and surface and underground rivers, playing an important role in water transport in karst areas [84]. It can lead to aggravated DOM loss.

Through previous studies [49] and field surveys [34,85,86], the study area is heavily karst desertification and is of medium intensity (up to 70% rock exposure). This is not conducive to DOM accumulation. The higher the rate of rock exposure, the more easily soil is washed away; this condition is not conducive to the accumulation of aromatic and hydrophobic substances in soil [86]. Although exposed rocks will enrich the water and nutrients of nearby soil, excessive water input during heavy rainfall leads to severe erosion and soil seepage, reducing the bearing capacity of soil [87]. As the degree of fissure opening, the Ape directly influences the infiltration and transport of soil water and nutrients, affecting the accumulation rate of the soil, gravel, and other fillers. This explains the greater loss of the lighter components of its DOM as the Ape increases (Figure 6).

In accordance with Figure 6, NSV significantly affected the C2, C3, and C4 fractions of DOM. This result related to the physiological and biochemical effects of vegetation roots and soil microbial activity, because the intervention of vegetation significantly promotes fast-acting nutrients in the cleaved area, making the fast-acting nutrient content of the soil in the cleaved area significantly higher than that in the non-cleaved area [88]. Consequently, the percentage of protein-like substances in the DOM of cleaved soil in the study area was higher. Vegetation within fissures changed from herbaceous to tree; hence, differences in their soil nutrient status were found. Organic matter tended to increase and gradually decreased significantly with an increase in soil depth. The organic matter and TN content of the soil surface layer were significantly higher than those of the lower layer [89]. The differences in DOM characteristics [90,91] were caused by differences in organic matter input and root secretions from different plant sources. The reasons for the differences in the DOM fraction content of cleaved soil caused by different overlying plants were explained.

4.3. Indicative Significance of DOM Distribution in Fractured Soil

The migration of the DOM has caused a change in the environment. A correlation exists between DOC and various nutrients, such as N, P, and K in soil (Figure 6), particularly P. DOC increases the mobility of P to occur as Ca–Mg–P rather than as the more insoluble hydroxyapatite [92]. DOC can increase the use of P by plants (crops), and the increased mobility of P makes leaching easier [88]. The higher Ca^{2+} and Mg^{2+} contents in karst areas enhance the mobility of P more easily, possibly increasing damage to surface water and groundwater.

Soil properties can alter the extent of DOM loss. Numerous studies [93,94] have shown that conductivity can determine the concentration of nutrients, salt-based ions, and other solutes in soil, along with the content and migration processes of solutes. Soil EC in the study area was significantly higher during the rainy season than during the non-rainy season [34]. VW was significantly higher in deeper soil than in the surface layer, and soil porosity decreased with depth (Figure 6), which might be the result of rainfall migrating water-carrying nutrients and other salt-based ions from fissured soil. This finding is also in line with the fact that low bulk weight, high porosity, and sand and powder content improve the permeability of the soil and facilitate soil water transport [34]. If fissure flow is

present in the soil, it can increase the loss of soluble nutrients in the soil [37]. In addition, the irregularity of rocks in karst areas causes differentiation in the infiltration of rainfall at different rock–soil interfaces [95], resulting in inconsistent nutrient migration and degree of loss in different fissures; this finding is related to soil properties and water transport effects.

In summary, DOM plays an important role in the soil–water system as a major source of C and nutrients [96,97]. The risk of loss of fissured soil DOM is greater in the study area. This finding is largely related to rainfall intensity, near-surface plant type, degree of fissure development, and soil condition. Research on the effects of vegetation types and soil microorganisms on DOM should be deepened, and more DOM characteristics in fissured soils of karst areas should be analyzed to improve the karst desertification environment. The transport distribution of DOM not only exerts an important effect on the C cycle but also on the transport of nutrients. The biogeochemical cycling and transport of DOM with heavy metals and persistent organic pollutants cannot be disregarded [98–102]. Considering that fissures are amongst the leakage channels and storage spaces of soil–water–nutrients in karst areas, DOM should be the focus of research.

5. Conclusions

The source, distribution, and influencing factors of DOM in karstic fissured soils were obtained in this study, leading to three conclusions: (1) The DOM of the fissured soils in the study area, with the exception of the surface layer, which is subject to higher values of external environmental influences, has a lower DOM content of the middle and lower layers, and is less aromatic and less humified than the surface layer; (2) Rainfall intensity in karst areas severely controls the distribution and loss of DOM in rift soil. Under the synergistic influences of higher rock exposure rates and NSV, more protein-like fractions may be preferentially lost. In addition, fissure morphology and soil properties affect DOM loss to some extent; and (3) DOM loss in fissured soil not only affects soil nutrient loss but also increases soil P mobility, particularly in karst areas.

Therefore, areas with high karst desertification intensity, strong fissure development, weak aromaticity, and low humification of DOM in fissured soil, along with the preferential loss of low-molecular-weight components of DOM and the downward migration of other nutrients and solutes, severely affect soil quality and water ecosystems, providing a basis for understanding the optical properties of DOM in karstic fissured soil and influencing factors.

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Appendix A

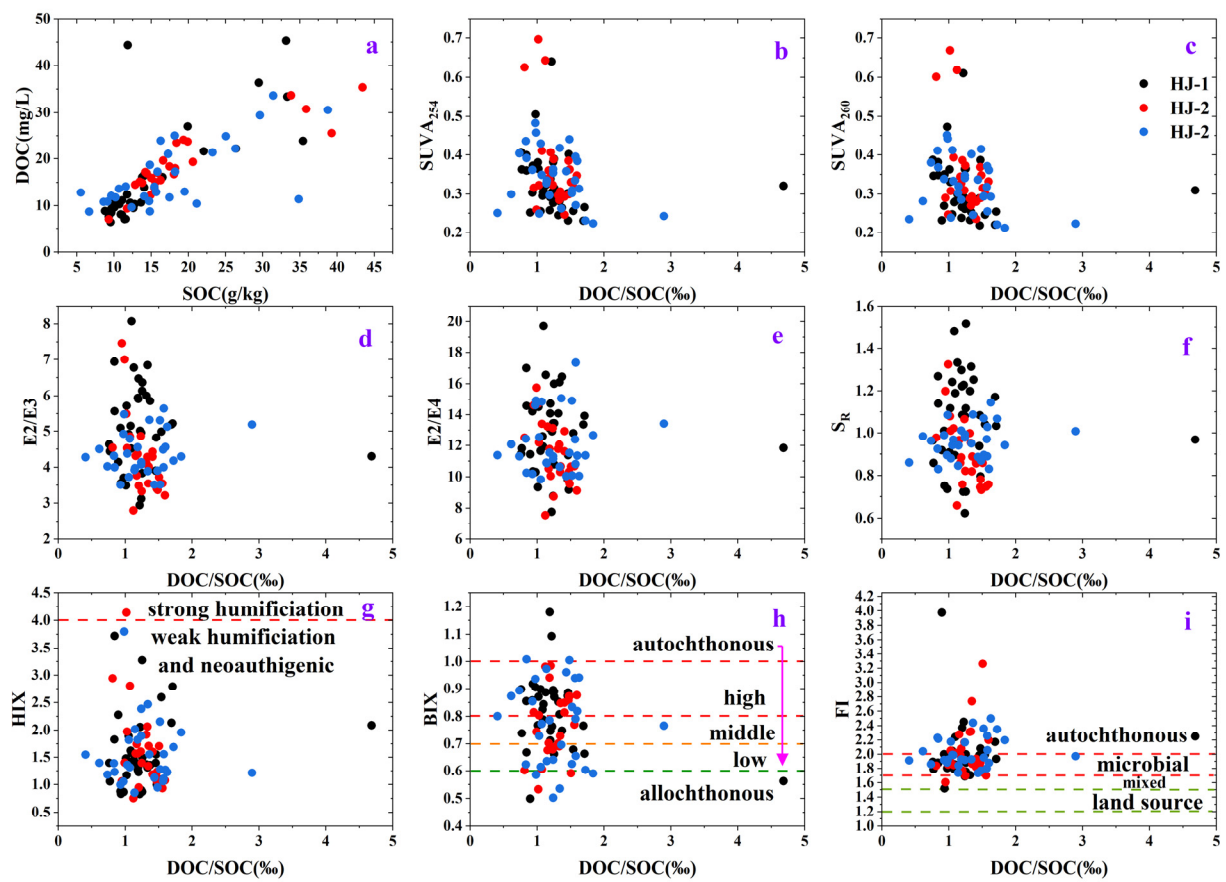


Figure A1. Scatter plots of SUVA₂₅₄ (b), SUVA₂₆₀ (c), E2/E3 (d), E2/E4 (e), FI (i), S_R (f), HIX (g), and BIX (h) with DOC/SOC (‰) as the x-axis, and DOC (a) along SOC. SUVA₂₅₄ and SUVA₂₆₀ in L·mg C⁻¹·m⁻¹.

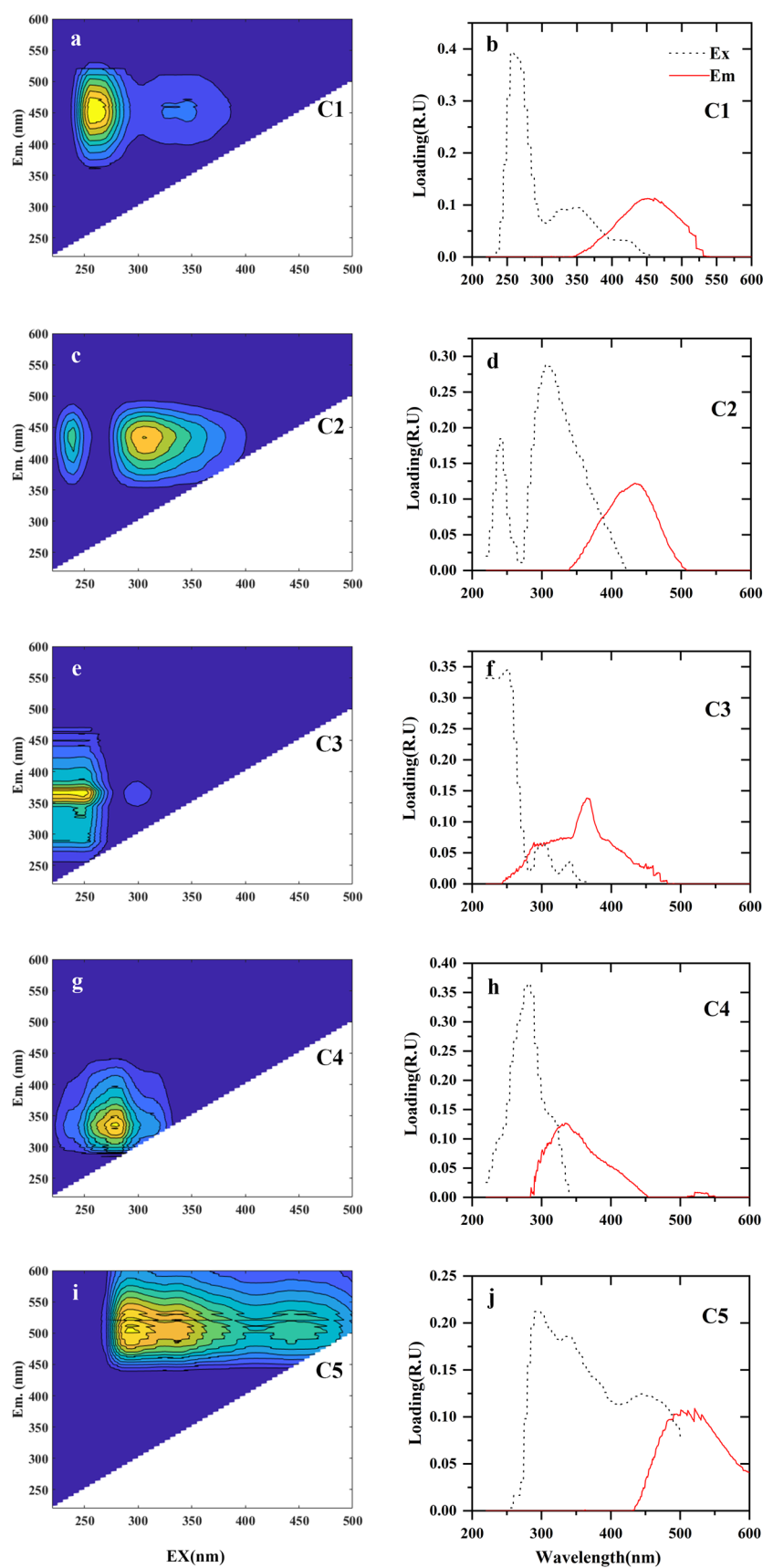


Figure A2. Contour plots of the five fluorescent components of DOM in soil samples derived using EEMs-PARAFAC, where C1 (a,b), C2 (c,d), C3 (e,f), C4 (g,h), C5 (i,j).

References

- Hou, D.; O'Connor, D.; Igalavithana, A.D.; Alessi, D.S.; Luo, J.; Tsang, D.C.; Ok, Y.S. Metal contamination and bioremediation of agricultural soils for food safety and sustainability. *Nat. Rev. Earth Environ.* **2020**, *1*, 366–381. [\[CrossRef\]](#)
- Cassidy, E.S.; West, P.C.; Gerber, J.S.; Foley, J.A. Redefining agricultural yields: From tonnes to people nourished per hectare. *Environ. Res. Lett.* **2013**, *8*, 034015. [\[CrossRef\]](#)
- Montgomery, D.R. Soil erosion and agricultural sustainability. *Proc. Natl. Acad. Sci. USA* **2007**, *104*, 13268–13272. [\[CrossRef\]](#) [\[PubMed\]](#)
- Zsolnay, A. Dissolved organic matter: Artefacts, definitions, and functions. *Geoderma* **2003**, *113*, 187–209. [\[CrossRef\]](#)
- Lal, R. Soil erosion and the global carbon budget. *Environ. Int.* **2003**, *29*, 437–450. [\[CrossRef\]](#) [\[PubMed\]](#)
- Batjes, N.H. Total carbon and nitrogen in the soils of the world (EJSS Land Mark Paper No. 3). *Eur. J. Soil Sci.* **2014**, *47*, 151–163. [\[CrossRef\]](#)
- Kaiser, K.; Kalbitz, K. Cycling downwards—dissolved organic matter in soils. *Soil Biol. Biochem.* **2012**, *52*, 29–32. [\[CrossRef\]](#)
- Kuzyakov, Y.; Cheng, W. Photosynthesis controls of rhizosphere respiration and organic matter decomposition. *Soil Biol. Biochem.* **2001**, *33*, 1915–1925. [\[CrossRef\]](#)
- Tong, H.; Simpson, A.J.; Paul, E.A.; Simpson, M.J. Land-Use Change and Environmental Properties Alter the Quantity and Molecular Composition of Soil-Derived Dissolved Organic Matter. *ACS Earth Sp. Chem.* **2021**, *5*, 1395–1406. [\[CrossRef\]](#)
- Kaiser, K.; Zech, W. Rates of dissolved organic matter release and sorption in forest soils. *Soil Sci.* **1998**, *163*, 714–725. [\[CrossRef\]](#)
- Raulund-Rasmussen, K.; Borggaard, O.K.; Hansen, H.C.B.; Olsson, M. Effect of natural organic soil solutes on weathering rates of soil minerals. *Eur. J. Soil Sci.* **1998**, *49*, 397–406. [\[CrossRef\]](#)
- Dawson, H.J.; Ugolini, F.C.; Hrutfiord, B.F.; Zachara, J. Role of soluble organics in the soil processes of a podzol, Central Cascades, Washington. *Soil Sci.* **1978**, *126*, 290–296. [\[CrossRef\]](#)
- Temminghoff, E.J.; Van der Zee, S.E.; de Haan, F.A. Copper mobility in a copper-contaminated sandy soil as affected by pH and solid and dissolved organic matter. *Environ. Sci. Technol.* **1997**, *31*, 1109–1115. [\[CrossRef\]](#)
- Post, W.M.; Peng, T.H.; Emanuel, W.R.; King, A.W.; Dale, V.H.; DeAngelis, D.L. The global carbon cycle. *Am. Sci.* **1990**, *78*, 310–326.
- He, W.; Bai, Z.L.; Li, Y.L.; Liu, W.X.; He, Q.S.; Yang, C.; Xu, F.L. Advances in the characteristics analysis and source identification of the dissolved organic matter. *Acta Sci. Circums* **2016**, *36*, 359–372.
- Kalbitz, K.; Geyer, S.; Geyer, W. A comparative characterization of dissolved organic matter by means of original aqueous samples and isolated humic substances. *Chemosphere* **2000**, *40*, 1305–1312. [\[CrossRef\]](#) [\[PubMed\]](#)
- Tipping, E.; Woof, C.; Rigg, E. Climatic influences on the leaching of dissolved organic matter from upland UK moorland soils, investigated by a field manipulation experiment. *Environ. Int.* **1999**, *25*, 83–96. [\[CrossRef\]](#)
- Wang, Y.; Yang, C.; Zou, L.; Cui, H. Optical Characteristics and Chemical Composition of Dissolved Organic Matter (DOM) from Riparian Soil by Using Excitation-Emission Matrix (EEM) Fluorescence Spectroscopy and Mass Spectrometry. *Appl. Soil Ecol.* **2015**, *69*, 623–634. [\[CrossRef\]](#)
- Kalbitz, K.; Schmerwitz, J.; Schwesig, D.; Matzner, E. Biodegradation of soil-derived dissolved organic matter as related to its properties. *Geoderma* **2003**, *113*, 273–291. [\[CrossRef\]](#)
- Stedmon, C.A.; Markager, S.; Bro, R. Tracing dissolved organic matter in aquatic environments using a new approach to fluorescence spectroscopy. *Mar. Chem.* **2003**, *82*, 239–254. [\[CrossRef\]](#)
- Wickland, K.P.; Neff, J.C.; Aiken, G.R. Dissolved organic carbon in Alaskan boreal forest: Sources, chemical characteristics, and biodegradability. *Ecosystems* **2007**, *10*, 1323–1340. [\[CrossRef\]](#)
- McDowell, W.H. Dissolved organic matter in soils—future directions and unanswered questions. *Geoderma* **2003**, *113*, 179–186. [\[CrossRef\]](#)
- Qiu, Q.; Wu, L.; Ouyang, Z.; Li, B.; Xu, Y.; Wu, S.; Gregorich, E.G. Effects of plant-derived dissolved organic matter (DOM) on soil CO₂ and N₂O emissions and soil carbon and nitrogen sequestrations. *Appl. Soil Ecol.* **2015**, *96*, 122–130. [\[CrossRef\]](#)
- Liu, C.; Li, Z.; Chang, X.; Nie, X.; Liu, L.; Xiao, H.; Zeng, G. Apportioning source of erosion-induced organic matter in the hilly-gully region of loess plateau in China: Insight from lipid biomarker and isotopic signature analysis. *Sci. Total Environ.* **2018**, *621*, 1310–1319. [\[CrossRef\]](#) [\[PubMed\]](#)
- Yuan, D.X. World Correlation of karst ecosystem: Objectives and implementation plan. *Adv. Ear. Sci.* **2001**, *16*, 461–466.
- Li, Y.; Liu, Z.; Liu, G.; Xiong, K.; Cai, L. Dynamic Variations in Soil Moisture in an Epikarst Fissure in the Karst Rocky Desertification Area. *J. Hydrol.* **2020**, *591*, 125587. [\[CrossRef\]](#)
- Yang, M.D. The geomorphological regularities of karst water occurrences in Guizhou plateau. *Cars Sin.* **1982**, *2*, 81–87. (In Chinese)
- Jiang, Z.C.; Luo, W.Q.; Deng, Y.; Cao, J.H.; Tan, X.M.; Li, Y.Q.; Yang, Q.Y. The Leakage of Water and Soil in the Karst Peak Cluster Depression and Its Prevention and Treatment. *Acta Geos. Sin.* **2014**, *5*, 535–542. (In Chinese)
- Yang, P.; Tang, Y.Q.; Zhou, N.Q.; Wang, J.X.; She, T.Y.; Zhang, X.H. Characteristics of red clay creep in karst caves and loss leakage of soil in the karst rocky desertification area of Puding County, Guizhou, China. *Environ. Earth Sci.* **2011**, *63*, 543–549. [\[CrossRef\]](#)
- Zhang, X.B.; Bai, X.Y.; He, X.B. Soil creeping in the weathering crust of carbonate rocks and underground soil losses in the karst mountain areas of southwest China. *Carbonates Evaporites* **2011**, *26*, 149–153. [\[CrossRef\]](#)
- Dai, Q.; Peng, X.; Zhao, L.; Shao, H.; Yang, Z. Effects of underground pore fissures on soil erosion and sediment yield on karst slopes. *Land Degrad. Dev.* **2017**, *28*, 1922–1932. [\[CrossRef\]](#)
- Lin, H. Linking principles of soil formation and flow regimes. *J. Hydrol.* **2010**, *393*, 3–19. [\[CrossRef\]](#)

33. Youjin, Y.; Quanhong, D.; Li, J.; Wang, X. Geometric morphology and soil properties of shallow karst fissures in an area of karst rocky desertification in SW China. *Catena* **2019**, *174*, 48–58.
34. Cai, L.L. Study on Soil Moisture and Nutrient Transport in Typical Karst Fractures. Master's Thesis, Guizhou Normal University, Guizhou, China, 2021. (In Chinese).
35. Li, C.L.; Dai, Q.H.; Peng, X.D.; Yuan, Y.F. Characteristics of nutrients loss in runoff of underground pore fissure on the karst bare slope. *J. Soil Water Conserv.* **2016**, *30*, 19–23+114. (In Chinese)
36. Peng, X.D.; Dai, Q.H.; Li, C.L.; Yuan, Y.F.; Zhao, L.S. Effect of simulated rainfall intensities and underground pore fissure degrees on soil nutrient loss from slope farmlands in Karst Region. *Trans. Chin. Soci. Agri. Engi.* **2017**, *2*, 131–140. (In Chinese)
37. Xian, Q.; Li, P.; Liu, C.; Cui, J.; Guan, Z.; Tang, X. Concentration and spectroscopic characteristics of DOM in surface runoff and fracture flow in a cropland plot of a loamy soil. *Sci. Total Environ.* **2018**, *622*, 385–393. [[CrossRef](#)] [[PubMed](#)]
38. Akagi, J.; Zsolnay, A.; Bastida, F. Quantity and spectroscopic properties of soil dissolved organic matter (DOM) as a function of soil sample treatments: Air-drying and pre-incubation. *Chemosphere* **2007**, *69*, 1040–1046. [[CrossRef](#)]
39. Aufdenkampe, A.K.; Mayorga, E.; Raymond, P.A.; Melack, J.M.; Doney, S.C.; Alin, S.R.; Aalto, R.E.; Yoo, K. Riverine coupling of biogeochemical cycles between land, oceans, and atmosphere. *Front. Ecol. Environ.* **2011**, *9*, 53–60. [[CrossRef](#)]
40. Barriuso, E.; Baer, U.; Calvet, R. Dissolved organic matter and adsorption-desorption of dimefuron, atrazine, and carbetamide by soils. *J. Environ. Qual.* **1992**, *21*, 359–367. [[CrossRef](#)]
41. Hu, S.; Lu, C.; Zhang, C.; Zhang, Y.; Yao, H.; Wu, Y. Effects of fresh and degraded dissolved organic matter derived from maize straw on copper sorption onto farmland loess. *J. Soils Sediments* **2016**, *16*, 327–338. [[CrossRef](#)]
42. Sun, Y.; Zhang, S.; Xie, Z.; Lan, J.; Li, T.; Yuan, D.; Xing, B. Characteristics and ecological risk assessment of polycyclic aromatic hydrocarbons in soil seepage water in karst terrains, southwest China. *Ecotox. Environ. Safe* **2020**, *190*, 110122. [[CrossRef](#)] [[PubMed](#)]
43. Baker, A.; Tipping, E.; Thacker, S.A.; Gondar, D. Relating dissolved organic matter fluorescence and functional properties. *Chemosphere* **2008**, *73*, 1765–1772. [[CrossRef](#)]
44. He, Q.; Xiao, Q.; Fan, J.; Zhao, H.; Cao, M.; Zhang, C.; Jiang, Y. Excitation-emission matrix fluorescence spectra of chromophoric dissolved organic matter reflected the composition and origination of dissolved organic carbon in Lijiang River, Southwest China. *J. Hydrol.* **2021**, *598*, 126–240. [[CrossRef](#)]
45. Liu, C.; Li, Z.; Asefaw, B.A.; Xiao, H.; Liu, L.; Wang, D.; Peng, H.; Zeng, G. Characterizing dissolved organic matter in eroded sediments from a loess hilly catchment using fluorescence EEM-PARAFAC and UV-Visible absorption: Insights from source identification and carbon cycling. *Geoderma* **2019**, *334*, 37–48. [[CrossRef](#)]
46. Liu, C.; Hu, B.X.; Li, Z.; Yu, L.; Peng, H.; Wang, D.; Huang, X. Linking soils and streams: Chemical composition and sources of eroded organic matter during rainfall events in a Loess hilly-gully region of China. *J. Hydrol.* **2021**, *600*, 126518. [[CrossRef](#)]
47. Zhang, X.; Li, Z.; Nie, X.; Huang, M.; Wang, D.; Xiao, H.; Liu, C.; Peng, H.; Jiang, J.; Zeng, G. The role of dissolved organic matter in soil organic carbon stability under water erosion. *Ecol. Indic* **2019**, *102*, 724–733. [[CrossRef](#)]
48. Xiong, K.N.; Zhu, D.Y.; Peng, T.; Yu, L.F.; Xue, J.H.; Li, P. Study on Ecological industry technology and demonstration for Karst rocky desertification control of the Karst Plateau-Gorge. *Acta Ecol. Sin.* **2016**, *36*, 7109–7113. (In Chinese)
49. Xiong, K.; Li, J.; Long, M. Characteristics and key problems of soil erosion in typical karst rocky desertification control area. *Acta Geogr. Sin.* **2012**, *67*, 878–888. (In Chinese)
50. Huang, M.; Li, Z.; Huang, B.; Luo, N.; Zhang, Q.; Zhai, X.; Zeng, G. Investigating binding characteristics of cadmium and copper to DOM derived from compost and rice straw using EEM-PARAFAC combined with two-dimensional FTIR correlation analyses. *J. Hazard. Mater* **2017**, *344*, 539–548. [[CrossRef](#)]
51. Lawaetz, A.J.; Stedmon, C.A. Fluorescence Intensity Calibration Using the Raman Scatter Peak of Water. *Appl. Spectrosc.* **2009**, *63*, 936–940. [[CrossRef](#)]
52. ElBishlawi, H.; Jaffe, P.R. Characterization of dissolved organic matter from a restored urban marsh and its role in the mobilization of trace metals. *Chemosphere* **2015**, *127*, 144–151. [[CrossRef](#)] [[PubMed](#)]
53. Wang, L.Y.; Fengchang, W.; Zhang, R.; Wen, L.I.; Liao, H.Q. Characterization of dissolved organic matter fractions from Lake Hongfeng, Southwestern China Plateau. *J. Environ. Sci.* **2009**, *21*, 581–588. [[CrossRef](#)]
54. Jaffé, R.; Boyer, J.N.; Lu, X.; Maie, N.; Yang, C.; Scully, N.M.; Mock, S. Source characterization of dissolved organic matter in a subtropical mangrove-dominated estuary by fluorescence analysis. *Mar. Chem.* **2004**, *84*, 195–210. [[CrossRef](#)]
55. Spencer, R.G.; Pellerin, B.A.; Bergamaschi, B.A.; Downing, B.D.; Kraus, T.E.; Smart, D.R.; Hernes, P.J. Diurnal variability in riverine dissolved organic matter composition determined by in situ optical measurement in the San Joaquin River (California, USA). *Hydrol. Process* **2007**, *21*, 3181–3189. [[CrossRef](#)]
56. Santos, P.S.; Otero, M.; Duarte, R.M.; Duarte, A.C. Spectroscopic characterization of dissolved organic matter isolated from rainwater. *Chemosphere* **2009**, *74*, 1053–1061. [[CrossRef](#)]
57. Helms, J.R.; Stubbins, A.; Ritchie, J.D.; Minor, E.C.; Kieber, D.J.; Mopper, K. Absorption spectral slopes and slope ratios as indicators of molecular weight, source, and photobleaching of chromophoric dissolved organic matter. *Limnol. Oceanogr.* **2008**, *53*, 955–969. [[CrossRef](#)]
58. Ohno, T. Fluorescence inner-filtering correction for determining the humification index of dissolved organic matter. *Environ. Sci. Technol.* **2002**, *36*, 742–746. [[CrossRef](#)]

59. Huguet, A.; Vacher, L.; Saubusse, S.; Etcheber, H.; Abril, G.; Relexans, S.; Ibalot, F.; Parlanti, E. New insights into the size distribution of fluorescent dissolved organic matter in estuarine waters. *Org. Geochem.* **2010**, *41*, 595–610. [\[CrossRef\]](#)
60. Mcknight, D.M.; Boyer, E.W.; Westerhoff, P.K.; Doran, P.T.; Kulbe, T.; Andersen, D.T. Spectrofluorometric characterization of dissolved organic matter for indication of precursor organic material and aromaticity. *Limnol. Oceanogr.* **2001**, *46*, 38–48. [\[CrossRef\]](#)
61. Wilson, H.F.; Xenopoulos, M.A. Effects of agricultural land use on the composition of fluvial dissolved organic matter. *Nat. Geosci.* **2009**, *2*, 37–41. [\[CrossRef\]](#)
62. Yamashita, Y.; Maie, M.; Briceño, H.; Jaffe, R. Optical characterization of dissolved organic matter in tropical rivers of the Guayana Shield. *Venezuela. J. Geophys. Res.* **2010**, *115*, G00F10. [\[CrossRef\]](#)
63. Yamashita, Y.; Scinto, L.J.; Maie, N.; Liu, Y.; Zhang, Y.; Zhang, Y.; Gu, W. Dissolved Organic Matter Characteristics across a Subtropical Wetland's Landscape: Application of Optical Properties in the Assessment of Environmental Dynamics. *Ecosystems* **2010**, *13*, 1006–1019. [\[CrossRef\]](#)
64. Coble, P.G. Characterization of marine and terrestrial DOM in seawater using excitation–emission matrix spectroscopy. *Mar. Chem.* **1996**, *51*, 325–346. [\[CrossRef\]](#)
65. Fellman, J.B.; Hood, E.; Spencer, R.G. Fluorescence spectroscopy opens new windows into dissolved organic matter dynamics in freshwater ecosystems: A review. *Limnol. Oceanogr.* **2010**, *55*, 2452–2462. [\[CrossRef\]](#)
66. Gao, Z.; Guéguen, C. Size distribution of absorbing and fluorescing DOM in Beaufort Sea, Canada Basin. *Deep-Sea Res. Part I-Oceanogr. Res. Pap.* **2017**, *121*, 30–37. [\[CrossRef\]](#)
67. Ahmad, S.R.; Reynolds, D.M. Monitoring of water quality using fluorescence technique: Prospect of on-line process control. *Water Res.* **1999**, *33*, 2069–2074. [\[CrossRef\]](#)
68. Ismaili, M.M.; Belin, C.; Lamotte, M.; Texier, H. Distribution and characterisation by fluorescence of the dissolved organic matter within the central Channel waters. *Ocea. Acta* **1998**, *5*, 645–676. [\[CrossRef\]](#)
69. Zhu, M.; Feng, Q.; Qin, Y.; Cao, J.; Zhang, M.; Liu, W.; Deo, R.C.; Zhang, C.; Li, R.; Li, B. The role of topography in shaping the spatial patterns of soil organic carbon. *Catena* **2019**, *176*, 296–305. [\[CrossRef\]](#)
70. Dilling, J.; Kaiser, K. Estimation of the hydrophobic fraction of dissolved organic matter in water samples using UV photometry. *Water Res.* **2002**, *36*, 5037–5044. [\[CrossRef\]](#)
71. Weishaar, J.L.; Aiken, G.R.; Bergamaschi, B.A.; Fram, M.S.; Fujii, R.; Mopper, K. Evaluation of specific ultraviolet absorbance as an indicator of the chemical composition and reactivity of dissolved organic carbon. *Environ. Sci. Technol.* **2003**, *37*, 4702–47028. [\[CrossRef\]](#)
72. Marschner, B.; Bredow, A. Temperature effects on release and ecologically relevant properties of dissolved organic carbon in sterilized and biologically active soil samples. *Soil Biol. Biochem.* **2002**, *34*, 459–466. [\[CrossRef\]](#)
73. Bai, Y.; Zhou, Y. The main factors controlling spatial variability of soil organic carbon in a small karst watershed, Guizhou Province. China. *Geoderma* **2020**, *357*, 113938. [\[CrossRef\]](#)
74. Pang, D.; Cui, M.; Liu, Y.; Wang, G.; Cao, J.; Wang, X.; Dan, X.; Zhou, J. Responses of soil labile organic carbon fractions and stocks to different vegetation restoration strategies in degraded karst ecosystems of southwest China. *Ecol. Eng.* **2019**, *138*, 391–402. [\[CrossRef\]](#)
75. Han, F.; Hu, W.; Zheng, J.; Du, F.; Zhang, X. Estimating soil organic carbon storage and distribution in a catchment of Loess Plateau, China. *Geoderma* **2010**, *154*, 261–266. [\[CrossRef\]](#)
76. Jia, X.X.; Yang, Y.; Zhang, C.C.; Shao, M.A.; Huang, L.M. A state-space analysis of soil organic carbon in China's Loess Plateau. *L. Degrad. Dev.* **2017**, *28*, 983–993. [\[CrossRef\]](#)
77. Gao, J.; Liang, C.; Shen, G.; Lv, J.; Wu, H. Spectral characteristics of dissolved organic matter in various agri-cultural soils throughout China. *Chemosphere* **2017**, *176*, 108–116. [\[CrossRef\]](#)
78. Huang, X.; Zhang, Z.; Zhou, Y.; Wang, X.; Zhang, J.; Zhou, X. Characteristics of soil organic carbon under different karst landforms. *Carbonates Evaporites* **2021**, *36*, 40. [\[CrossRef\]](#)
79. Wang, J. Study on Nutrient Loss of Fissure Water and Soil in Karst Rocky Desertification Area. Master's Thesis, Guizhou Normal University, Guizhou, China, 2020. (In Chinese).
80. Bunting, B.T.; Lundberg, J. The humus profile-concept, class and reality. *Geoderma* **1987**, *40*, 17–36. [\[CrossRef\]](#)
81. Kleber, M.M. What is recalcitrant soil organic matter? *Environ. Chem.* **2010**, *7*, 320–332. [\[CrossRef\]](#)
82. Sierra, M.M.D.; Giovanela, M.; Parlanti, E.; Esteves, V.I.; Duarte, A.C.; Fransozo, A.; Soriano-Sierra, E.J. Structural description of humic substances from subtropical coastal environments using elemental analysis, FT-IR and ¹³C-solid state NMR data. *J. Coast. Res.* **2005**, *42*, 370–382.
83. Wang, X.W.; Liu, Z.Q.; Xiong, K.L.; He, Q.F.; Li, Y.; Li, K.P. Characteristics and controlling factors of soil dissolved organic matter in the rainy season after vegetation restoration in a karst drainage area, South China. *Catena* **2022**, *217*, 106483. [\[CrossRef\]](#)
84. Chen, X.; Zhang, Z.; Chen, X.; Shi, P. The impact of land use and land cover changes on soil moisture and hydraulic conductivity along the karst hillslopes of southwest China. *Environ. Earth Sci.* **2009**, *59*, 811–820. [\[CrossRef\]](#)
85. Li, Y. The Desertification Hydro-Process and Carbon and Nitrogen Loss in A Typical Catchment of the Karst Plateau-Gorge. Ph.D. Thesis, Guizhou Normal University, Guizhou, China, 2021. (In Chinese).
86. Lan, J. Responses of soil organic carbon components and their sensitivity to karst rocky desertification control measures in Southwest China. *J. Soils Sediments* **2021**, *21*, 978–989. [\[CrossRef\]](#)

87. Song, X.W. Migration and Hydrological Process Differentiation of Carbon and Nitrogen in the Slope of Karst Critical Zone. Master's Thesis, Southwest University, Chongqing, China, 2018. (In Chinese).
88. Yan, L.; Liu, Q.; Liu, C.; Liu, Y.; Zhang, M.; Zhang, Y.; Gu, W. Effect of swine biogas slurry application on soil dissolved organic matter (DOM) content and fluorescence characteristics. *Ecotoxicol. Env. Saf.* **2019**, *184*, 109616. [[CrossRef](#)] [[PubMed](#)]
89. Yan, Y.; Dai, Q.; Hu, G.; Jiao, Q.; Mei, L.; Fu, W. Effects of vegetation type on the microbial characteristics of the fissure soil-plant systems in karst rocky desertification regions of SW China. *Sci. Total Environ.* **2020**, *712*, 136543. [[CrossRef](#)] [[PubMed](#)]
90. Liang, C.; Balser, T.C. Microbial production of recalcitrant organic matter in global soils: Implications for productivity and climate policy. *Nat. Rev. Microbiol.* **2011**, *106*, 303–309. [[CrossRef](#)] [[PubMed](#)]
91. Liang, C.; Schimel, J.P.; Jastrow, J.D. The importance of anabolism in microbial control over soil carbon storage. *Nat. Microbiol.* **2017**, *2*, 17105. [[CrossRef](#)]
92. Weyers, E.; Strawn, D.G.; Peak, D.; Baker, L.L. Inhibition of phosphorus sorption on calcite by dairy manure-sourced DOC. *Chemosphere* **2017**, *184*, 99–105. [[CrossRef](#)]
93. Rhoades, J.D.; Shouse, P.J.; Alves, W.J.; Manteghi, N.A.; Lesch, S.M. Determining soil salinity from soil electrical conductivity using different models and estimates. *Soil Sci. Soc. Am. J.* **1990**, *54*, 46–54. [[CrossRef](#)]
94. Xu, Y.L.; Zhu, W.; Qi, J.M.; Xu, J.Q.; Xi, R.C. Relationship between relative electric conductivity and its nutrient contents in soils at Camellia oleifera forests. *Non-Wood For. Res.* **2016**, *3*, 126–129. (In Chinese)
95. Li, S.; Ren, H.D.; Xue, L.; Chang, J.; Yao, X.H. Influence of bare rocks on surrounding soil moisture in the karst rocky desertification regions under drought conditions. *Catena* **2014**, *116*, 157–162. [[CrossRef](#)]
96. Cory, R.M.; Mcknight, D.M. Fluorescence Spectroscopy Reveals Ubiquitous Presence of Oxidized and Reduced Quinones in Dissolved Organic Matter. *Environ. Sci. Technol.* **2005**, *39*, 8142–8149. [[CrossRef](#)]
97. Ishii, S.K.L.; Boyer, T.H. Behavior of reoccurring parafac components in fluo-rescent dissolved organic matter in natural and engineered systems: A critical review. *Environ. Sci. Technol.* **2012**, *46*, 2006–2017. [[CrossRef](#)] [[PubMed](#)]
98. Kalbitz, K.; Solinger, S.; Park, J.H.; Michalzik, B.; Matzner, E. Controls on the dynamics of dissolved organic matter in soils: A review. *Soil Sci.* **2000**, *165*, 277–304. [[CrossRef](#)]
99. Aiken, G.R.; Hsu-Kim, H.; Ryan, J.N. Influence of dissolved organic matter on the environmental fate of metals, nanoparticles, and colloids. *Environ. Sci. Technol.* **2011**, *45*, 3196–3201. [[CrossRef](#)]
100. Bolan, N.S.; Adriano, D.C.; Kunhikrishnan, A.; James, T.; McDowell, R.; Senesi, N. Chapter one-dissolved organic matter: Biogeochemistry, dynamics, and environmental significance in soils. *Adv. Agron.* **2011**, *110*, 1–75.
101. Deb, S.; Shukla, M.K. An overview of some soil hydrological watershed models. In *Soil Hydro, Land Use. Agric, Measurement. Modelling*; Manoj, K.S., Ed.; MPG Books Group: Bodmin, UK, 2011; Volume 7, pp. 75–116. [[CrossRef](#)]
102. Ren, Z.L.; Tella, M.; Bravin, M.N.; Comans, R.N.; Dai, J.; Garnier, J.M.; Sivry, Y.; Doelsch, E.; Straathof, A.; Benedetti, M.F. Effect of dissolved organic matter composition on metal speciation in soil solutions. *Chem. Geol.* **2015**, *398*, 61–69. [[CrossRef](#)]

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