Frontiers in Environmental Research
Print ISSN: 2960-0251
Online ISSN: 2960-026X
DOI: https://doi.org/10.61784/fer3044

MOLECULAR STRUCTURE OF DISSOLVED ORGANIC MATTER IN MANGROVE SOILS

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Abstract: Mangrove ecosystems act a significant role in climate change adaptation and mitigation strategies. Large quantities of carbon are captured and sequestered in mangrove soils. Dissolved organic matter (DOM) in soils is known as the reactive carbon pool. It is a mixture of heterogeneous organics, involved in biochemical cycles. The molecular composition of DOM encapsulates the key information of carbon transformation and persistence in soils. However, there is still an unknown about the molecular compositions of DOM in mangrove soils. Here, we deciphered molecular constituents of DOM in mangrove soils from China by using the state-of-the-art tool, Fourier-transform ion cyclotron resonance mass spectrometry (FT-ICR-MS). Our study is the first to quantify and qualify soil DOM at molecular levels in mangrove wetlands. We found that DOM molecules in mangrove soils are combined with elements of C, H, O, N, S, and Cl. Soil DOM fates are revealed to be connected to multiple sources coupled with complex reactions in mangrove wetlands. We establish a comprehensive analytical framework of molecular diversity helpful to be extended to apply in other blue carbon ecosystems and provide novel insights into the DOM pool in mangrove wetlands.

Keywords: Dissolved organic carbon; FT-ICR-MS; Molecular composition; Mangrove; Blue carbon

1 INTRODUCTION

Global climate change is reshaping the increasing number of ecosystems in this century [1]. It is likely the greatest challenge of modern civilization[2]. Humans are making efforts towards force mitigation of excessively high greenhouse gases [3]. As a result, nature-based solutions have been progressively received much attention [4], adding more co-benefits to the achievement of the goals of the Paris Agreement. Mangroves are a typical blue carbon ecosystem and are considered efficient carbon sinks [5]. They are recognized to be crucial for climate change mitigation and the limitations of global warming. Large amounts of carbon in mangrove wetlands are stocked in soils over millenary timescales [6], amounting to 41 Tg per year at global scales [7]. The anoxic environment, high productivity, and allochthonous (terrestrial or marine) inputs facilitate long-term carbon storage in mangrove ecosystem [8].

Dissolved organic matter (DOM) is the most active pool in soils and regulates the biogeochemistry processes of soil organics [9]. DOM comprises allochthonous or autochthonous compounds such as polyphenols, aromatics, and aliphatic compounds [10], constituting a complex mixture of organic molecules. DOM is involved in various reactions like biodegradation [11], sorption, and complexation [12]. These transformations leave characteristic imprints in the molecular compositions of DOM [13]. Thus, exploring DOM compositions in soils is key to understanding the fate and preservation mechanisms of carbon in mangrove wetlands. However, DOM in mangrove soils is mostly treated as the black box. There still exists a knowledge gap in DOM compositions in mangrove soils. It is in pressing need to make well understanding of soil DOM from mangrove wetlands at the molecular level.

Fourier-transform ion cyclotron resonance mass spectrometry (FT-ICR-MS) has developed as a state-of-the-art analytical tool for identifying DOM [14]. The method enables analyses of organics at ultrahigh resolution, yielding compositional fingerprints with thousands of molecular formulas [15]. It has been applied in various environments, such as paddy soils [16], riverine sediments [17], and marine sediments [18]. This approach can offer fine information on DOM molecules to open the black box of DOM in mangrove wetlands. Herein, we report the molecular signatures of DOM in mangrove soils by using FT-ICR-MS for the first time.

We collected DOM samples from mangrove wetland soils in China. In this study, the objective is to investigate the molecular compositions of DOM in mangrove soils and interpret the qualitative and quantitative information in detail. It is essential in increasing insight into the carbon dynamics in mangrove wetlands and helping for improving coastal management of blue carbon.

2 MATERIALS AND METHODS

2.1 Sample Locations and Collection

Soil samples were collected at 0-10 cm depth from mangrove wetlands in China (Figure 1). Sampling sites were located in the Fujian, Guangxi, Guangdong, and Hainan provinces. Sampling sites were distributed at Zhangjiang Estuary Mangrove National Nature Reserve in Yunxiao County (YX; n = 7), Beilun River Estuary Mangrove National Nature Reserve (BR; n = 2), Futian National Nature Reserve (FT; n = 1), Zhanjiang Mangrove National Nature Reserve (ZJ; n

= 4), and Dongzhaigang National Nature Reserve (DZ; n = 7). More than 2 replicates were set on each sampling site. The soil was collected in sterile bags, delivered to the laboratory, and placed in the refrigerator at -18 °C. Freeze-dried samples were ground and passed through a 0.149 mm mesh sieve, after removing plants and other residues.

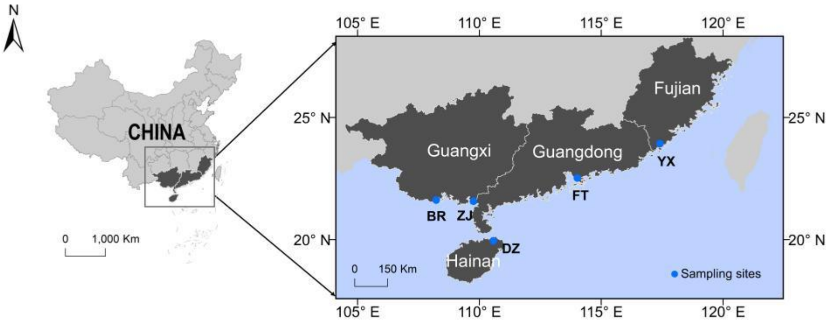

Figure 1 Sampling Sites in Mangrove Soils of China

Sampling areas are colored with dark gray; YX= Yunxiao; BR = Beilun; FT = Futian; ZJ = Zhanjiang; DZ = Dongzhaigang; The sampling map was made using ArcGIS 19.0 software with public map data provided the Ministry of Natural Resources of China (Source: https://cloudcenter.tianditu.gov.cn/administrativeDivision)

2.2 DOM Sample Preparation

DOM samples were extracted from soils mixed with Milli-Q water (w : V = 1 : 40) in centrifuge tubes [19]. Samples were shaken for 24 h (150 rpm, 25 °C), then centrifuged (15 min, 8000 rpm). The supernatant was filtered through a 0.7 GF / F filter, Whatman, England), then a 0.22 μm PES filter (Millipore, USA). Filtered samples were placed in amber glass vials (CNW, Germany), and stored in dark at 4 °C in the refrigerator before analysis. Dissolved organic carbon (DOC) concentration was determined using a TOC analyzer (Vario TOC, Elementar, Germany) after samples were acidified to $pH < 2$. DOC concentration in mangrove soils ranged 0.61 ± 0.01 to 0.97 ± 0.15 g / kg.

For FT-ICR-MS analysis, DOM samples were further isolated with cartridges [16]. Here, FT-ICR-MS samples (n = 5) were respectively from each sampling area. PPL cartridges (Bond Elut PPL, 500 mg, 6 mL, Agilent Technologies) were cleaned by passing through methanol (20 mL; HPLC grade; Merck, Germany) and conditioned with acidified Milli-Q water ($pH < 2$; 20 mL) [20-21]. DOM samples ($pH < 2$) were loaded onto the conditioned PPL cartridges under gravity. They were loaded with a suitable volume to deliver about 100 μg C of each sample [22]. Then, the cartridges were rinsed with acidified Milli-Q water ($pH < 2$; 20 mL) to remove salt and blown by ultrapure N_2 gas to completely dried them [21]. Finally, the cartridges were eluted with methanol (5 mL; HPLC grade) for collecting DOM samples. The elutes were stored in glass vials and stored in dark at -20 °C, before FT-ICR-MS measurement.

2.3 Ultrahigh-Resolution Mass Spectrometry Analysis

Fourier transform ion cyclotron resonance mass spectra (FT-ICR-MS) were analyzed with a 15.0 T Bruker Solarix mass spectrometer (Bruker Daltonics, Germany) and an Apollo II electrospray ionization (ESI) source in negative mode, equipped with a syringe pump at a flow rate of 180 μL / h [16, 22]. Mass range was set at 190 – 750 m / z, with an emitter voltage of 4.8 kV, a flight time of 0.7 ms, and the ions accumulation time of 0.2 s [23-24]. The spectra were acquired with 200 scans per sample with a 4 M transient [24]. As an internal standard, deuterated stearic acid (Sigma-Aldrich) was added for calibration [25]. The peaks found in cartridges extraction blanks and solvent blanks were subtracted from each sample. Molecular formulas of DOM were processed by Data Analysis 4.0 software (Bruker, Germany). Mass peaks were screened out with > 6 of signal-to-noise ratio (S / N) and < 1 ppm of detected errors [26].

The molecular formulas were assigned according to the elements, including $^{12}C_{0-54}$, $^{1}H_{0-100}$, $^{14}N_{0-3}$,$^{16}O_{0-19}$, $^{35.5}Cl_{0-2}$, and $^{32}S_{0-2}$. The formulas were generated and validated by applying sensible chemical constraints. The criteria were set as follows: (1) The number of H must be at least 1 / 3 of C and not more than $2C + N + 2$ [27]; (2) Formulas containing N in odd number and N in even number respectively have even nominal mass and odd nominal mass [28-29]; (3) Double bond equivalents (DBE) ≥ 0 and an integer value [30]; (4) Rules of elemental ratios: $H / C \leq 2.5$, $O / C \leq 1.2$, $N / C \leq 1$, $S / C \leq 0.2$ [25, 27, 31]. Molecular formulas were grouped based on element assignments and chemical structures. DOM compositions can be visualized in Van Krevelen diagrams, based on the unique H / C and O / C values of the formula [32]. Herein, DOM was grouped by elements and comprised of CHN, CHON, CHO, CHOCl, and CHOS formulas.

2.4 Statistical Analysis

One-way analysis of variance (ANOVA) was used to test differences in molecular variables of DOM. Welch's ANOVA with Dunnett's T3 test was applied for datasets with unequal variances. ANOVA with Tukey's post hoc test was used for datasets with equal variances. Data statistical analysis was performed in SPSS 22.0 software.

3 RESULTS

3.1 Molecular Formulas Numbers in DOM

FT-ICR-MS was applied to depict the molecular-level information of DOM from mangrove soils. The negative ion mass spectrum of DOM samples (YX, BR, FT, ZJ, and DZ) are shown in Figure 2. Several thousand peaks of molecular formulas were identified in the mass spectra for each mangrove soil sample. The formula numbers amounted to 7699 in YX, 7507 in BR, 6977 in FT, 3851 in ZJ, and 5152 in DZ, respectively. The molecular formulas contained elements of C, H, N, O, S, and Cl. The average formulas of molecules from YX, BR, FT, ZJ, and DZ were $C_{21.4}H_{27.3}N_{0.3}O_{6.8}S_{0.2}Cl_{0.3}$, $C_{23.2}H_{29.7}N_{0.5}O_{8.5}S_{0.3}Cl_{0.3}$, $C_{20.3}H_{29.4}N_{0.3}O_{6.4}S_{0.3}Cl_{0.3}$, $C_{24.2}H_{38.4}N_{0.6}O_{5.5}S_{0.3}Cl_{0.3}$, $C_{19.8}H_{28.8}N_{0.8}O_{6.2}S_{0.2}Cl_{0.3}$, respectively (Figure 3).

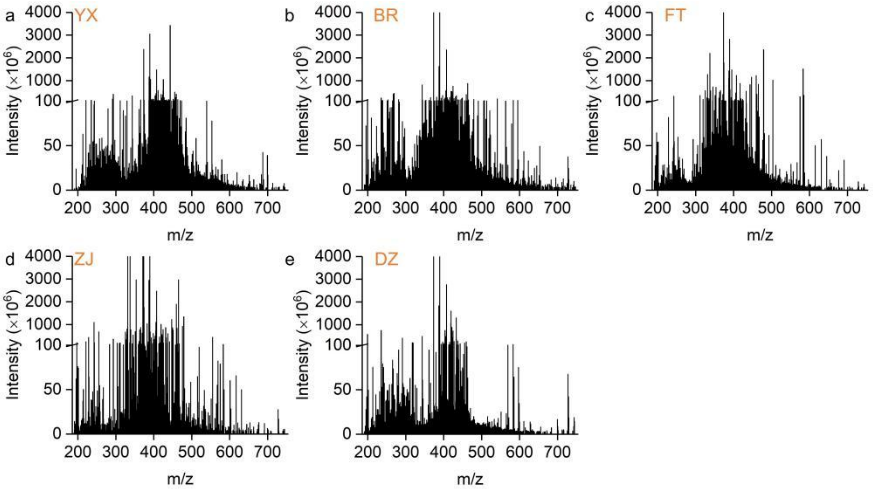

Figure 2 Negative Ion Mass Spectrum (m/z 190–750) of DOM from Mangrove Soils

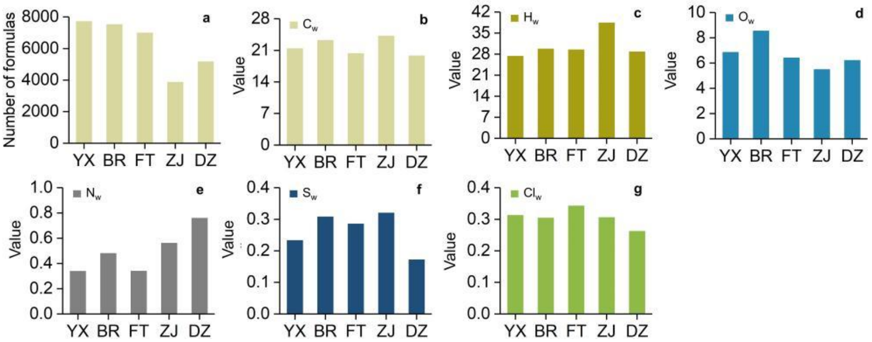

Figure 3 Total Number of Molecular Formulas in Mangrove Soils as Well as the Average Number of Elements (C, H, O, N, S, Cl) for Each Formula

3.2 Molecular Compositions of DOM

Molecular formulas in DOM for mangrove soils were identified into different elemental formula classes, including CHO (containing C, H, O), CHON (containing C, H, O, N), CHOS (containing C, H, O, S), CHOCl (containing C, H, O, Cl), and CHN (containing C, H, N) compounds. DOM molecules represented by colorful points were shown in Van Krevelen diagrams of Figure 4a–e. CHO compounds were presented to be predominant in mangrove soils, with an average abundance of 29.89 ± 1.86 %, ranging from 26.40 to 36.77 % (Figure 4f). The abundance of CHN compounds varied from 0.49 to 0.99 % at the lowest ratio relative to others (Figure 4f). CHON, CHOS, and CHOCl formulas respectively accounted to 22.75 ± 1.04 %, 23.34 ± 3.19 %, 23.21 ± 1.17 % of all formulas on average (Figure 4f).

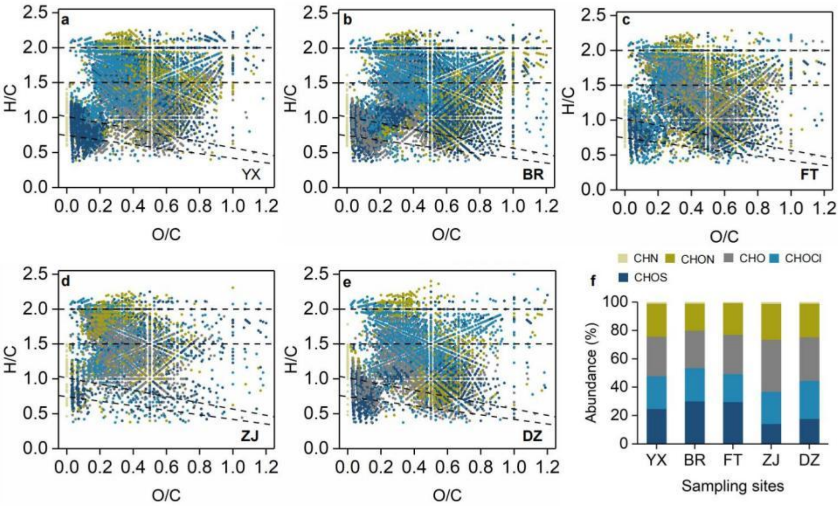

Figure 4 Molecular Compositions of DOM from Mangrove Soils
(a–e) Van Krevelen diagrams; (f) The abundance of compounds. Molecules include CHO, CHON, CHOS, CHOCl, and CHN formulas by elemental classes.

The assigned elemental formulas can be divided into different species classes (O_x, O_xN_y, O_xS_y, O_xCl_y, and N_z), according to the number of heteroatoms (O, N, S, and Cl). The abundance of diverse species for molecular formulas is shown in Figure 4–6. For CHO formulas, the class species of $O_{1–19}$ was identified in mangrove soils (Figure 4a–e). The abundance of O_x class species in samples was all in the skewed normal distribution and $O_{4–9}$ exhibited higher average ratios than other species. In the O_x class species, the abundance of each formula was no more than 5.5 % of all formulas. CHON, CHOS, and CHOCl formulas respectively had species of $O_xN_{1–2}$, $O_xS_{1–2}$, and $O_xCl_{1–2}$ with two classes on each (Figure 5-6). In these species, O_xN_1, O_xS_1, and $OxCl_1$ were the major class with high abundance and a low number of heteroatoms. The abundance of each formula was less than 3.5 %, 2.5 %, and 4.0 % of all formulas respectively for the O_xN_y, O_xS_y, and O_xCl_y class species. The class species of $O_{5–10}N_1$, $O_{6–10}S_1$, and $O_{4–9}Cl_1$ showed relatively prominent proportions higher than 1.5 %. CHN formulas had three class species of N_{1-3}, where the abundance of N_1, N_2, and N_3 averaged 0.37 ± 0.08 %, 0.17 ± 0.03 %, and 0.28 ± 0.05 % (Figure 7).

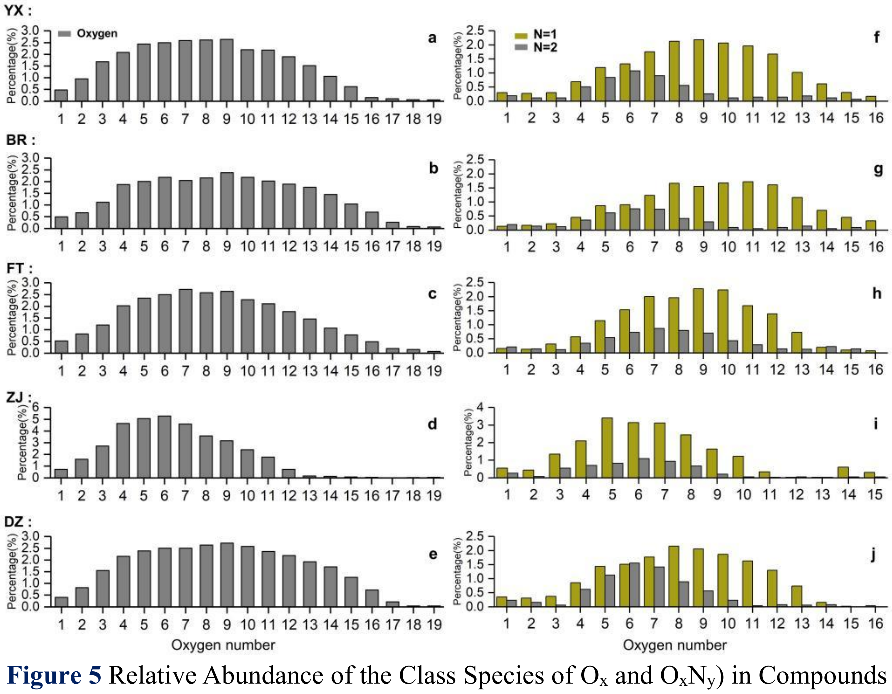

Figure 5 Relative Abundance of the Class Species of O_x and O_xN_y) in Compounds

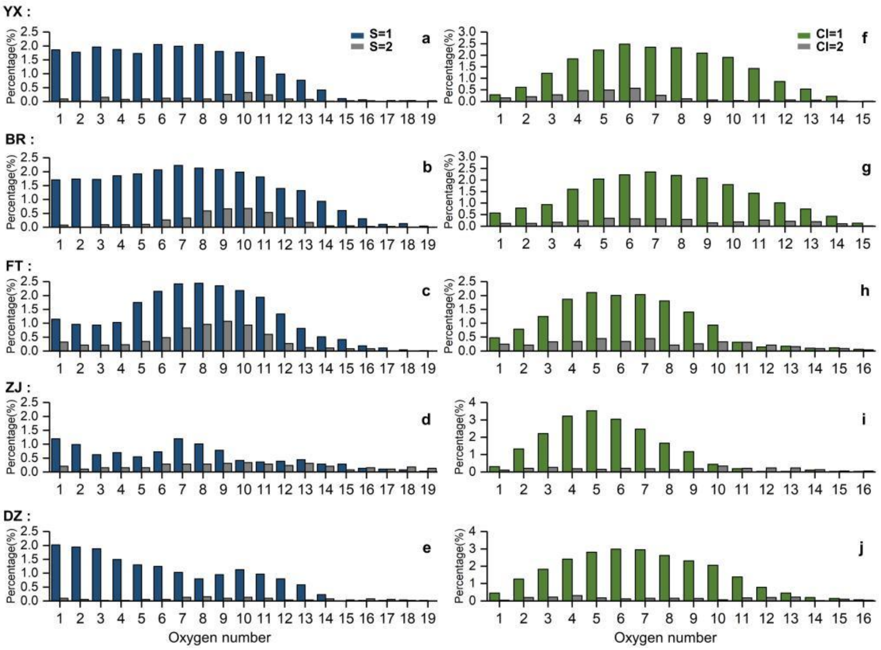

Figure 6 Relative Abundance of the Class Species of O_xS_y and O_xCl_y in Compounds

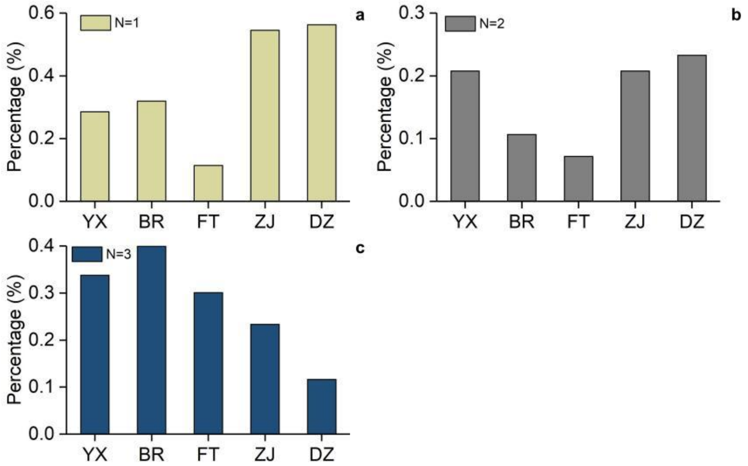

Figure 7 Relative Abundance of the Class Species of Nz in Compounds

4 DISCUSSION

Our study reveals the molecular diversity of DOM in the mangrove soils of China. The heteroatomic (O, N, S, Cl) compounds of DOM demonstrated the differentiation of molecular compositions, increasing the overall diversity in mangrove soils (Figure 3). DOM in mangrove soils is assembled by diverse molecules compositionally, including CHO, CHON, CHOS, CHOCl, and CHN formulas (Figure 3a–e). In molecular formulas, CHO formulas had the highest richness in mangrove soils (29.89 ± 1.86 %; Figure 3f). They are typically considered allochthonous, i.e., derived from degraded plant material [33]. CHO formulas are also found as dominant molecules in aquatic or terrestrial environments [16, 34]. In CHO formulas, chemical groups can be contained like hydroxyl, carboxyl, and carbonyl groups [35]. Molecules with rich carboxyl groups are less biodegradable [36], which contributes to abundant CHO formulas in soil DOM. The abundance of CHO formulas performed Gaussian distribution in mangrove soils (Figure 4a–e), resulting from the relationships of similar origin and precursor structure among CHO molecules [37].

CHON formulas are identified as autochthonous or allochthonous, sourced from N-rich algal dissolution or photo-altered DOM [18, 38]. They had similar abundances with CHO formulas in mangrove soils ($p > 0.05$, Figure 3f), as a consequence of the common source for these formulas [39]. In CHON formulas, O_xN_1 species were in higher proportions than O_xN_2, yet O_xN_3 species were not found (Figure 4f–j). It can be due to the fact that O_xN_3 species are preferentially consumed during anaerobic reduction and $O_xN_{1–2}$ species are accumulated [40]. Compared to O_xN_3 species, $O_xN_{1–2}$ species are less bioavailable or produced in DOM degradation [40].

CHOS formulas in mangrove soils were shown with the non-Gaussian distribution with the $O_xS_{1–2}$ species (Figure 5a–e). The S-containing compounds are produced in anthropogenic perturbations, abiotic pathways, or microbial activities [41-43]. The O_3S and O_5S species are usually rich in human-perturbated environments, as an indicator of anthropogenic input [44]. Herein, O_3S and O_5S class formulas are found in mangrove soils, supporting the contribution of anthropogenic input to DOM. The enrichment of CHOS formulas in soils can be mainly attributed to the production of sulfurization reactions and microbial metabolites under anaerobic conditions in mangrove wetlands. During early diagenesis, sulfur can be incorporated into DOM molecules abiotically in sulfidic sediments, forming organic sulfur compounds [42, 45]. The incorporation of sulfur protects labile organics from alterations from microbes [46]. Reactive DOM species increase, especially when O_2 is absent along with enhanced reductive sulfurization [43]. Microbially derived DOM contains a higher amount of sulfur, thereby microbial activity also influences the richness of CHOS formulas in soils [47-48].

CHOCl formulas are also found in mangrove soils. The series of molecules may result from natural processing, as well as anthropogenic activities including urban wastewater production, fossil fuels, or biomass burning [49]. These halogenated organics are also present in aquatic environments, which are considered natural chlorinated molecules or novel disinfection by-products [50-51]. Mangrove wetlands are flooded by seawater for a long time and capture allochthonous matter delivered with wastewater [52]. The above facts suggest sources of organohalogens for wetlands, which can account for the presence of CHOCl formulas in mangroves. Besides, CHN formulas came from mainly burned biomass materials [53]. The relative single source explains the smallest fractions for CHN formulas of total (less than 1%) in mangrove soils.

5 CONCLUSIONS

Our study resolves molecular compositions of DOM in mangrove soils by ultrahigh-resolution mass spectrometry, to unlock the black box of the DOM pool. Soil DOM in mangroves is confirmed with high chemical diversity. Thousands of molecule formulas or different active compound pools evidence the quantitative diversity of DOM in mangrove wetlands. The molecular fingerprints demonstrate soil DOM fates in mangroves are constrained by allochthonous inputs, autochthonous production, or biotic or abiotic transformations. Taken together, our results highlight the novel mechanism of DOM diversity in mangrove soils. This work provides key information on soil carbon evolutions and persistence in mangroves, as well as opening new avenues for research in blue carbon ecosystems.

COMPETING INTERESTS

The authors have no relevant financial or non-financial interests to disclose.

FUNDING

This work was supported by the Natural Science Foundation of Fujian Province of China (2024J08234), the project of the ecological process research team on microplastic soil pollution (CXTD202406). This work was also supported by Research funding for high-level talents (404080), Fujian Provincial College Student Innovation and Entrepreneurship Training Program (202414683014), and the open subject from the provincial key lab of coastal basin environment in Fujian Polytechnic Normal University. We would like to thank the Shiyanjia lab (www.shiyanjia.com) for the TOC analysis.

AUTHORS' CONTRIBUTIONS

Jiacheng Lin, Yajie Xuan conducted sample collections, investigations, sample tests and data analysis. Shengjie Wu led the writing of the manuscript. All authors contributed critically to the drafts and gave final approval for publication.

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