

Molecular Fingerprints of Soil Organic Matter in a Typical Freshwater Wetland in Northeast China

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Abstract: Natural wetlands are known to store huge amounts of organic carbon in their soils. Despite the importance of this storage, uncertainties remain about the molecular characteristics of soil organic matter (SOM), a key factor governing the stability of soil organic carbon (SOC). In this study, the molecular fingerprints of SOM in a typical freshwater wetland in Northeast China were investigated using pyrolysis gas-chromatography/mass-spectrometry technology (Py-GC/MS). Results indicated that the SOC, total nitrogen (TN), and total sulfur contents of the cores varied between 16.88% and 45.83%, 0.93% and 2.82%, and 1.09% and 3.79%, respectively. The bulk $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ varied over a range of 9.85‰, between -26.85‰ and -17.00‰ , and between -0.126‰ and 1.002‰ , respectively. A total of 134 different pyrolytic products were identified, and they were grouped into alkyl (including *n*-alkanes (C : 0) and *n*-alkenes (C : 1), aliphatics (Al), aromatics (Ar), lignin (Lg), nitrogen-containing compounds (Nc), polycyclic aromatic hydrocarbons (PAHs), phenols (Phs), polysaccharides (Ps), and sulfur-containing compounds (Sc). On average, Phs moieties accounted for roughly 24.11% peak areas of the total pyrolysis products, followed by Lg (19.27%), alkyl (18.96%), other aliphatics (12.39%), Nc compounds (8.08%), Ps (6.49%), aromatics (6.32%), Sc (3.26%), and PAHs (1.12%). Soil organic matter from wetlands had more Phs and Lg and less Nc moieties in pyrolytic products than soil organic matters from forests, lake sediments, pastures, and farmland. $\delta^{13}\text{C}$ distribution patterns implied more C3 plant-derived soil organic matter, but the vegetation was in succession to C4 plant from C3 plant. Significant negative correlations between Lg or Ps proportions and C3 plant proportions were observed. Multiple linear analyses implied that the Ar and Al components had negative effects on SOC. Alkyl and Ar could facilitate ratios between SOC and total nitrogen (C/N), while Al plays the opposite role. Al was positively related to the ratio of dissolved organic carbon (DOC) to SOC. In summary, SOM of wetlands might characterize by more Phs and lignin and less Nc moieties in pyrolytic products. The use of Pyrolysis gas-chromatography/mass-spectrometry (Py-GC/MS) technology provided detailed information on the molecular characteristics of SOM from a typical freshwater wetland.

Keywords: molecular fingerprint; soil organic matter; pyrolysis gas-chromatography/mass-spectrometry; freshwater marsh; Northeast China

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1 Introduction

Wetlands are typical ecozones characterized by unique

ecological environment features different from those of typical terrestrial and aquatic ecosystems (Brinson and Malvárez, 2002; Reddy and DeLaune, 2008; Mao et al.,

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2018). Wetlands are usually defined by the hydrological processes, soil conditions, and plant communities adapted to the wet environment (Zhang et al., 2016). They accumulate large amounts of organic matter in the soils due to their high productivity and water-logged soil conditions (Bernal and Mitsch, 2012; Adame et al., 2015). Soil organic carbon (SOC) content can exceed 70% in typical peatlands (Bao et al., 2010; Page et al., 2011). Despite occupying only 6%–8% of the global freshwater surface area, wetlands are estimated to account for about one-third of the world's organic soil carbon pool (Wan et al., 2018). Global tidal and saline wetlands store at least 44.6 Tg C every year and probably more (Chmura et al., 2003). High soil organic matter is recognized as one of the main characteristics of a wetland.

Soil organic matter and its persistence are regarded as an ecosystem property (Schmidt et al., 2011). Many studies have focused on estimation of the soil carbon pool (Pant et al., 2003), and the potential effects of greenhouse gas emissions on wetlands (Badiou et al., 2011). However, few studies have explored the features of organic matter in wetland soils on the molecular level (Dodla et al., 2012). Soil organic matter is a mixture of diverse organic components forming dynamic associations stabilized by hydrophobic interactions and hydrogen bonds (Sutton and Sposito, 2005). The chemical features of soil organic matter depend on its components and are primarily governed by functional group species and mutual proportions (Nebbioso and Piccolo, 2013). The intrinsic properties of function groups dominate the persistence and stability of soil organic matter (Feng and Simpson, 2011). Therefore, deciphering the molecular fingerprints of wetland soils will allow us to better explore and define the uniqueness of wetlands, and may reveal key molecular-level mechanisms of carbon circulation in wetlands.

Pyrolysis gas-chromatography/mass-spectrometry (Py-GC/MS) is widely used to research the chemical composition of soil organic matter because it provides detailed information at the molecular level (Belgacem, 2000; Nebbioso and Piccolo, 2013). It is a powerful tool for exploring unknown complex mixtures of materials (González-Pérez et al., 2012; Schellekens et al., 2017). Pyrolysis of soil organic matter generates a wide range of products with diverse chemical properties that can be related to their biochemical origin. Therefore, pyrolysis

moieties could be used for biomarkers to mirror properties of soil organic matter. In wetlands, soil organic matter originates from various sources and is composed by numerous chemical compounds, and it is necessary to explore unique chemical composition characteristics of soil organic matter from wetlands for source apportionment or quality assessment of soil carbon pool. The goals of the present study are to 1) decipher the molecular fingerprints of soil organic matter in a typical freshwater wetland in Northeast China using Py-GC/MS technology; 2) to interpret relationships between SOC, DOC, isotopic features ($\delta^{13}\text{C}$ and $\delta^{15}\text{N}$), and pyrolytic products; and 3) to characterize wetlands from the perspective of the molecular components of soil organic matter.

2 Materials and Methods

2.1 Sample collection and preparation

Xingkai Lake is the largest freshwater lake in Northeast China. Wetlands are representative and predominant ecosystems here and are rarely affected by human activities in the national reserve. Soil accretion rates are steady and undisturbed, and they conserve intact biomarkers to mirror wetland unique properties different from other ecosystems.

Cores were collected from a freshwater marsh near to Xingkai Lake (45°22'52"N, 132°19'37"E) in August 2017. The water table was within 20 cm of the surface, and the predominant vegetation is *Typha* mixed with *Carex* and *Glyceria spiculosa*. Soil cores with three replicates were collected to a depth of 2 m and sliced in the field into 5 cm intervals from the surface to 20 cm, and 10 cm intervals from 20 cm to 200 cm. In total, 22 soil samples were obtained from each core, sealed in polyethylene bags, and brought back to the laboratory. Each sample was divided into two subsamples. One subsample was freeze-dried, ground to pass a 2 mm nylon mesh, and preserved at -20°C before analysis. The other was used for bulk density determination, which was calculated from the dry weight per unit volume for each depth increment after validation for the moisture content of that subsample that was air-dried at 105°C .

2.2 Chemical analysis

Soil organic carbon (SOC), total nitrogen (TN), total hydrogen, and total sulphur were determined by dry

combustion at 900°C using an Elemental Analyzer (Vario EL III, Germany). All of the samples were analyzed in parallel to assure accuracy and precision. The differences between replicates were within 0.5%, 0.1%, and 0.5% for SOC, TN, and total sulphur, respectively. Analysis of Chinese standard soil reference (No. GBW07401) yielded recovery rates of 100% (w/w) for carbon (C) and 96% (w/w) for nitrogen (N). All glass bottles used were soaked in a 3 mol/L HNO₃ solution, rinsed with deionized water, and then oven-dried at 105°C before use.

Dissolved organic carbon (DOC) was extracted according to Dodla et al. (2012). Specially, 5.00 g soil were mixed with 30 mL deionized water in Erlenmeyer flasks and shaken for 30 min. After shaking, the mixtures were centrifuged and filtered through a 0.45 µm filter.

δ¹³C and δ¹⁵N were measured using stable isotope analysis (NA 1500 NCS Elemental Analyser-Finnigan Delta plus IRMS, analytical precision < 0.1‰). Detailed procedures for isotope analysis were same as Choi et al. (2001).

The pyrolyzer was a Frontier Lab EGA 3030s model coupled with a gas chromatography and mass spectrometry unit (GC/MS, LTD-5975T, Agilent, CA, USA). The temperature of the injector and transfer line were kept at 320°C, while the column temperature was increased from 50°C to 300°C at a rate of 20°C/min and held at 300°C for 40 min. Mass spectra were recorded in electron impact mode (70 eV) at one scan s⁻¹ in the 45–600 mass-to-charge ratios (*m/z*) range (Pascaudet et al., 2017). The identification of pyrolysis products was based on a comparison of their mass spectra with those of standard compounds using the NIST 2011 mass spectral library, literature data, and *m/z* characteristics. The AMDIS analysis software was used to assist with compound identification. Relative distributions (*RF*, %) of products were estimated using the peak areas of total ion current (TIC) pyrograms. Pyrolytic compounds were grouped according to the method of González-Pérez et al. (2012), which was based on probable origin and chemical similarity, into alkyl (including *n*-alkanes (C : 0) and *n*-alkenes (C : 1) and other alkyls), aliphatics (Al), aromatics (Ar), lignin (Lg), nitrogen containing compounds (Nc), polycyclic aromatic hydrocarbons (PAHs), phenols (Phs), polysaccharides (Ps), and sulfur containing compounds (Sc).

2.3 Statistical analysis

All statistical analyses were performed by Statistica (Version 6.0); *P* < 0.05 was considered as the threshold value for significance. Multiple regression analysis allows for the recognition of correlations between variables and the detection of structures in the data set. It is a primary method for reducing the number of variables (González-Pérez et al., 2012). Prior to statistical analysis, tests for normality of the raw were performed.

3 Results

3.1 Bulk sample SOC, TN, Sulfur, δ¹³C, and δ¹⁵N

The SOC, TN, and total sulfur contents of soil cores varied between 16.88% and 45.83%, 0.93% and 2.82%, and 1.09% and 3.79%, respectively. SOC, TN, and total sulfur were high in the upper 110 cm of the core with little variation; the lowest SOC and TN were measured at 200 cm and lowest total sulfur contents were measured at 130 cm. DOC contents varied from 1952 mg/kg to 6047 mg/kg. The C/N ratios varied between 14.08 and 22.10, and increased with depth. The upper 110 cm had fairly constant C/N ratios in the range 14.08–16.84; C/N increased to 22.10 at 170 cm depth. The bulk δ¹³C varied over a range of 9.85‰ between –26.85‰ and –17.00‰. δ¹³C varied greatly in the upper 80 cm but subsequently remained consistent to the bottom. The bulk δ¹⁵N varied between –0.126‰ to 1.002‰ throughout the core, with a mean value of 0.484‰. In the upper 100 cm (with exception of the surface 15 cm), δ¹⁵N remained relatively consistent, exhibiting a brief drop to –0.126‰ at the 110 cm level and subsequent increase to 1.002‰ at the 140 cm depth (Fig. 1).

3.2 Pyrolytic products of wetland soils

Initially, more than 400 different pyrolytic products were recognized in all samples obtained from soils (Fig. 2). This number was reduced to 134 by eliminating products that could not be identified and those that were not common. The remaining 134 products (Supplement Table, A1) were quantified by measuring the surface of the two or three main fragment ions of each compound by *m/z* values, and they accounted for more than 70% of TIC on average. For each sample, TIC of all measured compounds was set at 100% (total ion current), and relative abundances were recalculated.

On average, Phs compounds were dominant, being

responsible for roughly 24.11% of the total pyrolysis products for the whole core, followed by lignin (19.27%), Alkyl (18.96%), other aliphatics (12.39%),

nitrogen containing compounds (8.08%), Ps (6.49%), aromatics (6.32%), Sc (3.26%), and PAHs (1.12%) (Fig. 3).

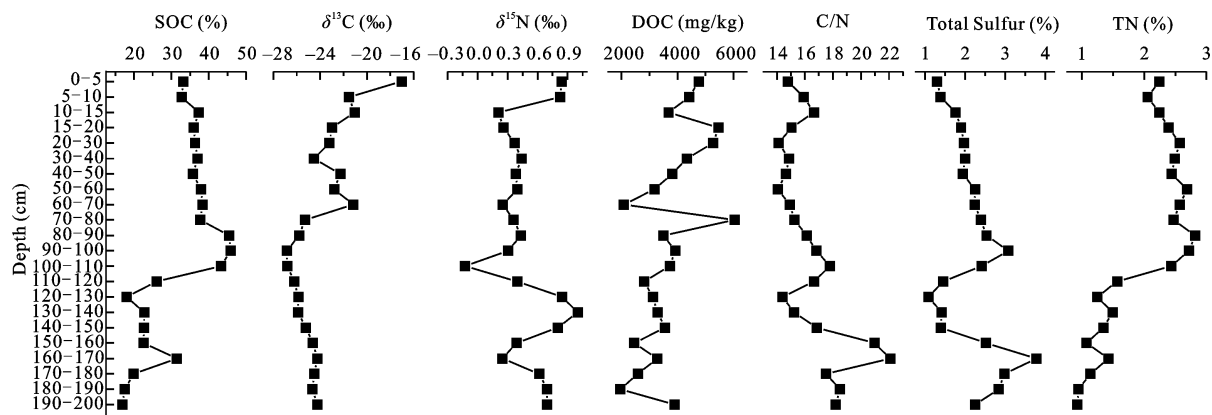


Fig. 1 Vertical distribution pattern of soil organic carbon (SOC), $\delta^{13}\text{C}$, $\delta^{15}\text{N}$, dissolved organic carbon (DOC), C/N, total sulfur and total nitrogen (TN)

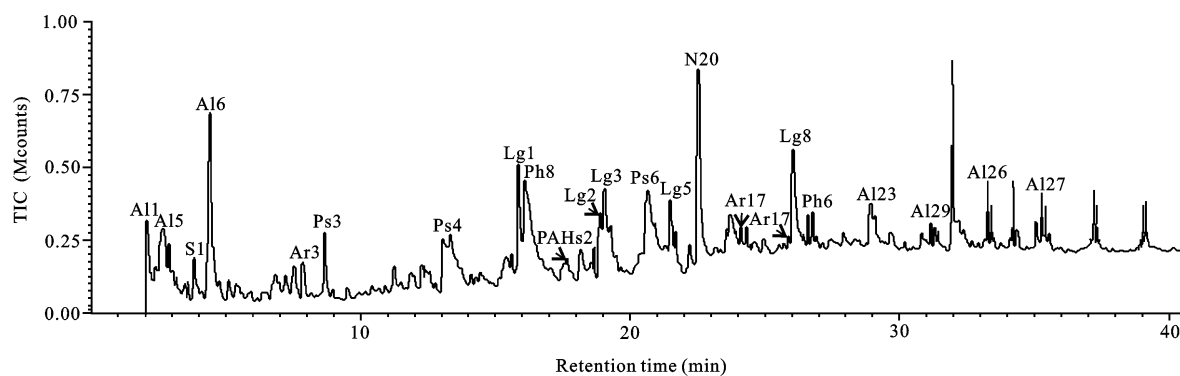


Fig. 2 A typical total ion current (TIC) pyrograms of wetland soil samples in 20–30 cm depth. Major peak names were labelled as shown in Supplement Table

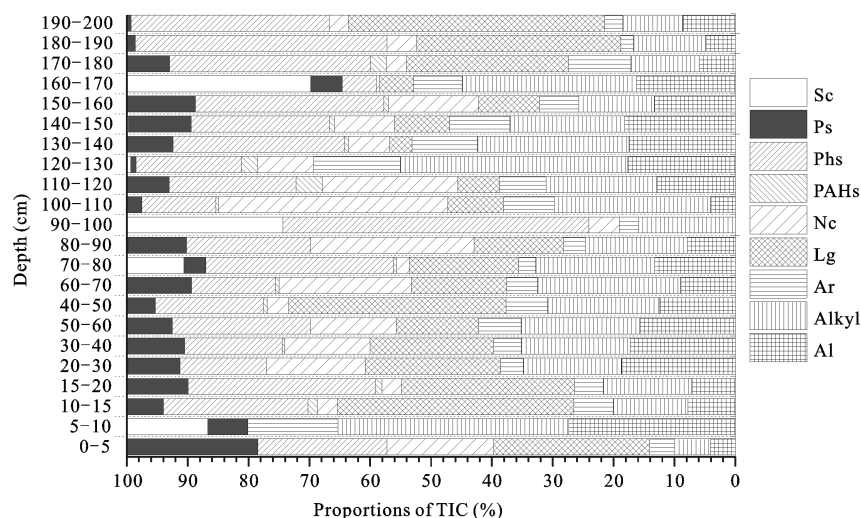


Fig. 3 Proportions of different pyrolytic compounds in soil horizons. TIC, total ion current; Al, aliphatics; Ar, aromatics; Lg, lignin; Nc, nitrogen-containing compounds; PAHs, polycyclic aromatic hydrocarbons; Phs, phenols; Ps, polysaccharides; Sc, sulfur-containing compounds

Most alkyl moieties were heterocyclic, with an abundance of 61.38%. The most three common heterocyclic hydrocarbon moieties were Spiro [2.4] hepta-4-6-diene, 1-3-5-Cycloheptatriene, and Bi-2-cyclohexen-1-yl, which made up about 32.55%, 8.54%, and 3.82% of total alkyl TIC counts, respectively. The series of *n*-alkanes and *n*-alkenes were identified in all horizons, and they represent about 38.62% of total alkyl TIC counts. The three most common moieties were 1-Hexacosene, 7-Tetradecene, and 10-Heneicosene, which were about 10.32%, 5.86%, and 2.41% of total alkyl TIC counts, respectively. Odd-numbered chain lengths were dominant. Mid-chain (C16–C26) alkanes (21.55%) and alkenes were more abundant than short-chain (16.42%) and long-chain ones (1.45%).

Aliphatics of pyrolytic products included alcohols, ketones, carboxylic acids, and esters, which represented 56%, 10 %, 13%, and 21% of total aliphatic TIC counts, respectively. 2-Hexyl-1-octanol, 1-Dodecanol, and 1-Eicosanol were the most common alcohols. The predominant ester compound was 4-Penten-1-yl acetate. There was much more cyclohexanone than there was of the other ketons, and erucic acid was the main moiety of the carboxylic acid compounds.

The most abundant aromatic compounds were O-xylene, ethylbenzene, and P-xylene, which were identified in all soil horizons. O-xylene relative abundance was 22.40%. P-xylene is isomerized of O-xylene with around 7.00%, on average, in all horizons. The second abundant aromatic compound was ethylbenzene, making up about 20% of the total aromatic TIC counts.

The dominant lignin moiety was guaiacol, with an

abundance of 79.54% of total lignin compounds. The four most common guaiacol species with abundances over 10% were 2-methoxy-4-vinylphenol (19.00%), phenol-4-ethyl-2-methoxy (17.66%), phenol-2-methoxy-4-methyl (11.41%), and phenol-3-methoxy-2-methyl (10.02%). Syringol represented about 20.46% of total lignin moiety, and the most common syringol species was phenol-2-6-dimethoxy, with an abundance of 15.58%.

The most abundant phenolic compounds were phenol, phenol-3/4-methyl, and phenol-3-ethyl. These three moieties represented about 77.60% of total phenol compounds, and they were identified in all soil horizons.

Furan, cyclopentene, and their derivatives were main polysaccharide products. The most common products were benzofuran-2-3-dihydro, furan-2-methyl, and furan-2-5-dimethyl, which accounted for 59.33%, 14.04%, and 8.03% of total Ps moieties, respectively.

Only three Sc compounds were identified-methanethiol, thiophene-2-3-dimethyl, and 3-4-dimethylthiophene. Methanethiol was overwhelming and accounted for 98.00% of total Sc compounds. Most PAHs were indene, naphthalene, and their derivatives. There was more naphthalene (and its derivatives, 60.20%) than indene (39.80%).

3.3 Correlations among pyrolytic products

Results of correlation analysis showed no significant positive relations among pyrolytic compounds. However, significantly negative correlations were observed for Lg vs. Al, Lg vs. alkyl, Phs vs. alkyl, Phs vs. Nc, Ps vs. alkyl, Sc vs. Lg and Nc; correlation coefficients ranged from −0.676 to −0.451 (Table 1).

Table 1 Correlation analysis among pyrolytic compounds

| Taxa | Al | Alkyl | Ar | Lg | Nc | Phs | Ps | PAHs | Sc |
|-------|---------|----------|--------|---------|---------|--------|--------|-------|----|
| Al | 1 | | | | | | | | |
| Alkyl | 0.361 | 1 | | | | | | | |
| Ar | 0.193 | 0.155 | 1 | | | | | | |
| Lg | −0.536* | −0.582** | −0.381 | 1 | | | | | |
| Nc | 0.154 | −0.111 | 0.027 | −0.317 | 1 | | | | |
| Phs | −0.162 | −0.541* | −0.211 | 0.448 | −0.470* | 1 | | | |
| Ps | −0.260 | −0.451* | 0.211 | −0.145 | 0.079 | −0.143 | 1 | | |
| PAHs | 0.034 | −0.078 | 0.036 | 0.117 | 0.213 | 0.064 | −0.074 | 1 | |
| Sc | 0.199 | 0.402 | −0.237 | −0.676* | −0.557* | 0.317 | −0.229 | 0.013 | 1 |

Notes: * $P < 0.05$; ** $P < 0.01$; Al, aliphatics; Ar, aromatics; Lg, lignin; Nc, nitrogen-containing compounds; PAHs, polycyclic aromatic hydrocarbons; Phs, phenols; Ps, polysaccharides; Sc, sulfur-containing compounds

4 Discussion

Soil matter originates from litter input and microbial products; litter decomposition usually contributes to soil organic matter in soils. In wetlands, soil organic matter is also derived from algae (Mitsch et al., 2010). Differences in soil organic matter sources shape variations in the molecular characteristics of soil organic matter (Quideau et al., 2001). Compared with soils from forests, lakes, pastures, and farmland, soil organic matter from wetlands had more Phs and lignin and less Nc moieties in pyrolytic products than those from the forest, lake sediments, pastures, and farmland. Other compounds exhibited no obvious differences (Table 2). More Phs and Lg proportions in soil organic matter pyrolytic products from wetlands were attributed to water-logged or saturated soil conditions. Phs moieties are probably tannins and lignin pyrolysis products (Nierop and Verstraten, 2006). Lignin mainly comes from living terrestrial biomass and is the most abundant aromatic compound on Earth (Baraibaret al., 2011). Due to its aromatic structures, as well as rigidity and the heterogeneity of its intramolecular bonds, lignin has long been suspected to contribute substantially to the stable carbon pool in soil (Feng and Simpson, 2011). Though more biomass is returned to soil carbon pools in forests yearly than to those in wetlands, more lignin moieties were found in soil organic matter from the wetlands. This implies that lignin in wetlands could be selectively preserved due to acidic and water-saturated soil conditions. In addition, fungus is the main decomposer of lignin (Hammel, 1997; Bahri et al., 2006), and the low pH

values of wetland soils could inhibit fungus activities and consequently prevent lignin decomposition (Schellekens et al., 2015; Thevenot et al., 2010).

Nc proportions ranged from 5.07% to 8.08% in wetland soils (Table 2); this ratio was much lower than the ratios measured in soils/sediments from lakes, forests, and pastures. The most abundant Nc compounds in wetland soils were pyridine, indole, pyrrole, and their derivatives, which are mostly pyrolytic products of proteins from microbial activities. Lower Nc proportions in the soil organic matter of wetland soils were in good agreement with nitrogen limitations prevalent in wetlands, which have been confirmed experimentally and theoretically.

However, comparison of molecular characteristics of soil organic matter between wetland and other ecosystems are circumscribed, non-directive, and prospective because a globally integrated database of soil organic matter pyrolytic products of different ecosystems is not available at present. Comparison of the present work is based on limited data from the literature, and comparison results should be amended when more data are introduced to the dataset.

Vegetation is the factor controlling soil organic matter composition. In California, there was more carbonyl C under oak, more O-alkyl C under manzanita, and more alkyl C under coniferous vegetation (Quideau et al., 2001). Globally, plants with different photosynthetic pathways, termed C3 and C4 plants, have distinct $\delta^{13}\text{C}$ ranging from -23‰ to -34‰ and -9‰ to -17‰ , respectively (Chmura and Aharon, 1995). Distinguished by $\delta^{13}\text{C}$, contributions of C3 and C4 plants to soil organic

Table 2 Comparison of molecular features of soil organic matter for different ecosystems

| Taxa | Al | Alkyl | Ar | Lg | Nc | Phs | Ps | PAHs | Sc | Reference |
|------------------------------|-------------------|-------|-------|-------|-------|-------|-------|------|-------|--------------------------------|
| Lake sediments | 1.20 ^a | 29.60 | 4.50 | 4.10 | 10.00 | 8.00 | 30.00 | 1.40 | – | Tolu et al., 2017 |
| Forest soil ^b | 3.20 | 13.00 | 14.10 | 7.20 | 24.20 | 11.60 | 24.30 | 2.80 | – | da Silva Oliveira et al., 2016 |
| Pasture soil ^c | 4.60 | 12.90 | 12.60 | 11.90 | 21.90 | 12.50 | 20.80 | 2.70 | – | da Silva Oliveira et al., 2016 |
| Pasture soil | 11.38 | 11.38 | 9.56 | 29.00 | 39.97 | 15.56 | 2.97 | | 11.16 | Zhang et al., 2018 |
| Sugarcane soil | 15.63 | 44.93 | 13.20 | 2.47 | 5.07 | 16.13 | 1.30 | 1.63 | – | Zhang et al., 2019 |
| Sugarcane soil | 2.80 | 9.20 | 13.60 | 15.50 | 21.80 | 15.60 | 18.60 | 3.10 | – | da Silva Oliveira et al., 2016 |
| Marsh soil | 9.27 | 34.00 | 11.37 | 12.87 | 5.07 | 23.33 | 4.07 | 0.01 | – | Zhang et al., 2019 |
| Coastal Wetland ^d | 3.20 | 12.20 | 22.70 | 13.40 | 6.00 | 29.60 | 9.60 | – | 0.50 | González-Pérez et al., 2012 |
| Freshwater marsh soil | 12.39 | 18.96 | 6.32 | 19.27 | 8.08 | 24.10 | 6.49 | 1.12 | 3.26 | The present work |

Notes: ^a represented by steroids; ^b forest was characterized by sclerophyllous and xeromorphic species; ^c pasture was covered by *Brachiaria* and *Cynodon* spp.; ^d soil depth within 130 cm; –, no data; Al, aliphatics; Ar, aromatics; Lg, lignin; Nc, nitrogen-containing compounds; PAHs, polycyclic aromatic hydrocarbons; Phs, phenols; Ps, polysaccharides; Sc, sulfur-containing compounds

matter were roughly estimated based on the assumption that soil organic matter from microbial activities could be ignored because it was dominated by soil organic matter from litter input (Fig. 4a). This indicates that more soil organic matter in the present work originated from C3 plants. However, contributions from C4 plants were concentrated in the top 70 cm, accounting for no more than 20% of total SOC from 70 cm to 200 cm depth. These $\delta^{13}\text{C}$ distribution patterns also indicate that plant vegetation was in succession to C4 plants from C3 plants. Significant negative correlations were observed between Lg or Ps proportions and C3 plant proportions (Fig. 4b). This means that more C3 plants would introduce fewer biomass materials characterized by Lg and Ps. Most Ps moieties were pyrolytic products of carbohydrate and the lignin that makes up plant cell walls (Saizjimenez and Deleeuw, 1986). Vascular bundle sheath cells usually are small and have no chlorophyll in the C3 plant leaf. No carbohydrates and less lignin are present in sheath cells of C3 plants than those of C4 plants (Nobel, 1991). This might be exhibited by a negative relation between Ps and Lg and C3 plant proportions (Fig. 4b). Lignin is generally considered to be recalcitrant; it degrades at a lower rate than other major components of plant litters (Kiem and Kögel-Knabner, 2003). Vegetation succession from C3 to C4 plants might increase soil carbon pool storage and stability.

Soil carbon pool storage and stability in wetlands are affected by many factors, including net primary productivity (Zhang et al., 2016), climate (Zhang et al., 2017), fauna (Fox et al., 2006), and microbial activities

(Kögel-Knabner, 2002). The molecular characteristics of soil organic matter are also considered to be some of the main drivers governing soil carbon pool contents and stability. In the present work, multiple linear analysis was employed to reveal which component had vital impacts on SOC, DOC, C/N, and DOC/SOC. Results showed that Ar and Al components had negative effects on SOC. Alkyl and Ar could facilitate C/N, while Al played the opposite role. Al had positive effects on the ratio of DOC to SOC, which could mirror soil carbon stability. No components had significant effects on DOC (Table 3). Generally, Al moieties of soil organic matter pyrolytic products mirrored decomposition intensions by microbial activities (Grandy et al., 2009). Alkyl mainly comes from litter input. It is apparent that more alkyl and less Al increase SOC and C/N. Usually, aliphatic moieties accumulate when decomposition proceeds (Nierop, 1998); this is reflected in the negative relations between SOC, C/N, and Al, and positive relations between DOC/SOC and Al. Most alkyl compounds come from plant leaf. In the present, the long chain alkanes ($> \text{C}_{26}$) were probably decay products of protective waxes of leaves (Fontaine et al., 2007); their presence indicates fresh organic matter inputs or materials that are anaerobically preserved (Grandy and Neff, 2008). It is perplexing that Ar has negative effects on SOC because Ar usually proxies the existence of cellulose, which could be selectively preserved. Despite predictions, the contents of aromatic compounds were reported to increase, decrease, or remain unchanged with decomposition (Nierop, 1998).

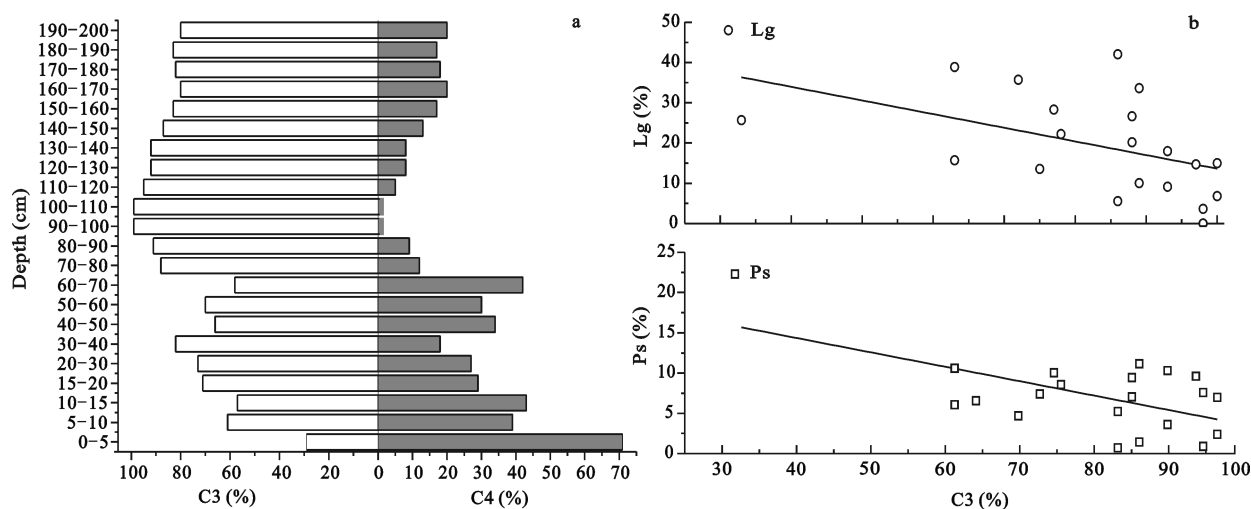


Fig. 4 Contributions of C3 and C4 plants on soil organic matter (a) and their relations with Ps and Lg compounds (b)

Table 3 Summary of multiple linear regression models between SOC, C/N, DOC/SOC, DOC, and pyrolytic products

| Taxa | Model | R ² |
|---------|--|----------------|
| SOC | SOC = 63.143–1.237Ar–1.094Al | 0.707 |
| C/N | C/N = 11.877+0.733Ar+0.289Alkyl–0.299Al | 0.890 |
| DOC/SOC | DOC/SOC=26.161+5.156Al | 0.372 |
| DOC | No variable was introduced at $P < 0.05$ level | – |

Note: SOC, soil organic carbon; DOC, dissolved organic carbon

5 Conclusions

In summary, Py-GC/MS provided us detailed information on molecular fingerprints of soil organic matter from a typical freshwater wetland, which was characterized by more Phs and lignin and less Nc moieties in pyrolytic products than is found in soil organic matter from forests, lake sediments, pastures, and farmland. Phs and lignin compounds are resistant to degradation and could be preserved in soil carbon pools for decades or even to centuries, and high lignin and Phs moieties in soil organic matter from wetlands might mirror why wetlands could function as the most important carbon sink in Earth. However, more work should be conducted to establish and integrate the dataset of soil organic matter pyrolytic products so as to summarize molecular features of soil organic matter and predominant vegetation from different ecosystems. Vegetation shifts also have important impacts on the molecular features of soil organic matter. Aromatics, aliphatics, and alkyls were the most important three moieties related closely to SOC, DOC, and soil stability. They also, at least partly, indicated important impacts of soil organic matter sources on soil organic carbon persistence.

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Supplement Table

Identified pyrolysis products from the analyzed soil samples

| Groups | Retention time (min) | Peak Name | m/z^a | Codes |
|---|----------------------|--|--------------|-------|
| Aklyl (including <i>n</i> -alkanes, <i>n</i> -alkenes and heterocyclic hydrocarbons) | 3.593–37.766 | C6 : 0–C19 : 0 | – | 1–26 |
| | | C6 : 1–C26 : 1 | | |
| Aliphatics | 2.027 | 2-Chloroethanol | 31, 43 | Al1 |
| | 2.035 | Propanoic acid, 2-methyl-, 2-ethyl-1-pro | 43, 71 | Al2 |
| | 2.035 | 2,5-Dimethyl-4-hydroxy-3-hexanone | 43 | Al3 |
| | 2.482 | Z,Z-2,5-Pentadecadien-1-ol | 57, 82 | Al4 |
| | 2.702 | Oxirane | 43 | Al5 |
| | 4.441 | 4-Penten-1-yl acetate | 43, 68 | Al6 |
| | 3.023 | Pentane, 1-butoxy- | 43, 57 | Al7 |
| | 3.377 | 1-Hexanol | 43, 56 | Al8 |
| | 4.746 | 1,2-Ethandiol, 1,2-di-1-cyclopenten-1-y | 97 | Al9 |
| | 5.54 | 2-Propanone | 43 | Al10 |
| | 5.492 | Borneol | 95 | Al11 |
| | 18.65 | Oxacyclotetradecan-2-one, 13-methyl- | 41, 83 | Al12 |
| | 9.29 | 4-Chloro-3-n-hexyltetrahydropyran | 56, 69 | Al13 |
| | 31.168 | Hexadecenoic acid, Z-11- | 41, 97, 111 | Al14 |
| | 14.458 | cis-p-Mentha-2,8-dien-1-ol | 91, 134 | Al15 |
| | 36.622 | 1-Eicosanol | 57, 97, 111 | Al16 |
| | 26.631 | 1-Heptadecanol | 56, 97, 111 | Al17 |
| | 27.868 | Erucic acid | 55, 69 | Al18 |
| | 32.011 | 2-Hexyl-1-octanol | 57, 85 | Al19 |
| | 25.899 | 2-Methyl-Z,Z-3,13-octadecadienol | 55, 81 | Al20 |
| | 33.399 | 1-Docosanol | 56, 83 | Al21 |
| | 27.14 | 6-(3-Isopropenylcycloprop-1-enyl)-6-meth | 161 | Al22 |
| | 28.936 | 3-Ethyl-4-hydroxybicyclo[3.3.1]non-3-en- | 41, 165, 180 | Al23 |
| | 38.64 | 1-Decanol, 2-hexyl- | 57, 85 | Al24 |
| | 37.651 | 3,7,11,15-Tetramethyl-2-hexadecen-1-ol | 67, 81, 123 | Al25 |
| | 33.15 | Z,E-3,13-Octadecadien-1-ol | 68 | Al26 |
| | 35.033 | 1-Dodecanol, 3,7,11-trimethyl- | 55, 71, 97 | Al27 |
| | 34.713 | Z,Z-3,15-Octadecadien-1-ol acetate | 43, 96 | Al28 |
| | 31.158 | Oleic Acid | 41, 83, 111 | Al29 |
| Aromatics | 4.39 | Benzene | 78, 77 | Ar1 |
| | 10.461 | Ethylbenzene | 91, 106 | Ar2 |
| | 7.924 | o-Xylene | 91, 106 | Ar3 |
| | 10.933 | Benzene, propyl- | 91, 120 | Ar4 |
| | 11.345 | Benzene, 1-ethyl-3-methyl- | 105, 120 | Ar5 |
| | 11.246 | Benzene, 1,2,4-trimethyl- | 105, 120 | Ar6 |
| | 11.949 | Benzene, 1-ethyl-2-methyl- | 105, 120 | Ar7 |
| | 12.351 | Benzene, 1,2,3-trimethyl- | 105, 120 | Ar8 |
| | 14.267 | Benzene, 1-ethyl-4-methyl- | 105 | Ar9 |
| | 12.361 | Benzene, 1,3,5-trimethyl- | 105, 120 | Ar10 |

Continuing Table

| Groups | Retention time (min) | Peak Name | m/z^a | Codes |
|-------------------------------|----------------------|--|----------------|-------|
| Aromatics | 12.514 | Benzene, 2-propenyl- | 117 | Ar11 |
| | 17.368 | Benzene, ethoxy- | 66, 94, 122 | Ar12 |
| | 14.256 | Benzene, 1-propynyl- | 115 | Ar13 |
| | 14.212 | Benzene, 1-ethynyl-4-methyl- | 115 | Ar14 |
| | 14.854 | Benzene, 1-methyl-2-propyl- | 105 | Ar15 |
| | 15.115 | 1,2-Ethanediol, 1,2-diphenyl- | 77, 107 | Ar16 |
| | 23.912 | Benzaldehyde, 3-methyl- | 65, 91 | Ar17 |
| Lignin | 15.967 | Phenol, 2-methoxy- | 81, 109 | Lg1 |
| | 18.95 | Mequinol | 53, 109 | Lg2 |
| | 19.175 | Phenol, 3-methoxy-2-methyl- | 123, 138 | Lg3 |
| | 22.038 | Phenol, 2-methoxy-4-methyl- | 123 | Lg4 |
| | 21.592 | Phenol, 4-ethyl-2-methoxy- | 137, 152 | Lg5 |
| | 22.905 | 2-Methoxy-4-vinylphenol | 107, 135 | Lg6 |
| | 23.588 | Phenol, 2-methoxy-4-(2-propenyl)-, aceta | 149, 164 | Lg7 |
| | 26.338 | Eugenol | 149, 164 | Lg8 |
| | 23.623 | Phenol, 2,6-dimethoxy- | 65, 11, 154 | Lg9 |
| | 23.706 | Phenol, 2-methoxy-6-(1-propenyl)- | 149, 164 | Lg10 |
| | 23.707 | Phenol, 3,4-dimethoxy- | 139, 154 | Lg11 |
| | 26.224 | Phenol, 2-methoxy-4-(1-propenyl)- | 164 | Lg12 |
| | 27.216 | 2,4-Dimethoxyphenol | 1139, 154, 111 | Lg13 |
| | 27.91 | Trimethoxyamphetamine, 2,3,5- | 167 | Lg14 |
| | 29.295 | Ethanone, 1-(3,4-dimethoxyphenyl)- | 165, 180 | Lg15 |
| | 35.819 | Phenol, 2,6-dimethoxy-4-(2-propenyl)- | 91, 194 | Lg16 |
| Nitrogen containing compounds | 2.362 | Dimethylamine | 44 | N1 |
| | 2.488 | (-)-cis-Myrtanlyamine | 81 | N2 |
| | 6.903 | 1-Nonanamine | 30, 55 | N3 |
| | 7.136 | sec-Butyl nitrite | 43, 57 | N4 |
| | 3.593 | Piperidine, 2-pentyl- | 94 | N5 |
| | 3.862 | 1H-Pyrrole, 1-methyl- | 81 | N6 |
| | 6.339 | Pyridine, 3-methyl- | 66, 93 | N7 |
| | 6.776 | 1H-pyrrole, 2,5-dimethyl- | 95 | N8 |
| | 8.969 | Hydroxylamine, O-decyl- | 41, 43, 71 | N9 |
| | 7.176 | 1H-Pyrrole, 2-methyl- | 80 | N10 |
| | 7.208 | 1H-Pyrrole, 3-methyl- | 80 | N11 |
| | 7.458 | 2(1H)-Pyridinone, 5-methyl- | 81, 109 | N12 |
| | 10.422 | 1H-Pyrrole, 2,3-dimethyl- | 94 | N13 |
| | 12.935 | Allophanic acid, phenyl ester | 94 | N14 |
| | 13.124 | Carbamic acid, butylmethyl-, phenyl este | 65, 94 | N15 |
| | 17.567 | Benzene, 1-isocyano-4-methyl- | 90, 117 | N16 |
| | 19.082 | dl-Leucine | 57, 108 | N17 |
| | 22.191 | m-Aminophenylacetylene | 117 | N18 |
| | 22.318 | Indole | 90, 117 | N19 |
| | 22.641 | 4-Amino-3,5-diethylpyridine | 150 | N20 |
| | 22.518 | Phenyl-1,2-diamine, N,4,5-trimethyl- | 150 | N21 |

Continuing Table

| Groups | Retention time (min) | Peak Name | m/z^a | Codes |
|---------------------------------|----------------------|--|--------------|-------|
| Polycyclic aromatic hydrocarbon | 17.443 | 2-Methylindene | 130 | PAH1 |
| | 17.52 | 1,4-Dihydronaphthalene | 130 | PAH2 |
| | 20.815 | Naphthalene, 1,4-dimethyl- | 130 | PAH3 |
| | 20.367 | 1H-Indene, 3-methyl- | 51, 128 | PAH4 |
| Phenols | 13.239 | Phenol | 94 | Ph1 |
| | 15.527 | Phenol, 2-methyl- | 79, 108 | Ph2 |
| | 18.324 | Phenol, 3,4-dimethyl- | 121 | Ph3 |
| | 18.129 | Phenol, 3,5-dimethyl- | 122 | Ph4 |
| | 21.201 | Phenol, 2,4-dimethyl- | 77, 107, 121 | Ph5 |
| | 27.173 | Phenol, 2,5-dimethyl- | 139, 154 | Ph6 |
| | 19.416 | Phenol, 3-methyl- | 79, 108 | Ph7 |
| | 16.265 | Phenol, 4-methyl- | 77, 107 | Ph8 |
| | 22.951 | Ethanone, 1-(2-hydroxy-5-methylphenyl)- | 150 | Ph9 |
| | 25.546 | 4-Hydroxy-3-methylacetophenone | 150 | Ph10 |
| polysaccharide | 2.087 | Furan, 2-methyl- | 53, 43, 82 | Ps1 |
| | 3.176 | Furan, 2,5-dimethyl- | 43, 96 | Ps2 |
| | 8.738 | 3(2H)-Furanone, dihydro-2,2-dimethyl-5-p | 104 | Ps3 |
| | 12.956 | 2-Cyclopenten-1-one, 2-methyl- | 53, 67, 96 | Ps4 |
| | 16.121 | 2-Cyclopenten-1-one | 81, 109 | Ps5 |
| | 20.773 | Benzofuran, 2,3-dihydro- | 119, 120 | Ps6 |
| | 22.648 | Naphtho[2,3-b]furan-2-one | 135, 150 | Ps7 |
| | 27.466 | 4H-1-Benzopyran, 4,4,5,8-tetramethyl- | 173 | Ps8 |
| Sulfur containing compounds | 4.087 | Methanethiol | 45, 47 | S1 |
| | 8.147 | 3,4-Dimethylthiophene | 97, 111 | S2 |
| | 8.543 | Thiophene, 2,4-dimethyl- | 97 | S3 |

Note: ^amass-to-charge ratio, this value was used to identify chemical compounds represented by peaks in mass spectrums