

Molecular characterization of primary humic-like substances in fine smoke particles by thermochemolysis–gas chromatography–mass spectrometry

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ABSTRACT

In this study, the molecular structures of primary humic-like substances (HULIS) in fine smoke particles emitted from the combustion of biomass materials (including rice straw, corn straw, and pine branches) and coal, and atmospheric HULIS were determined by off-line tetramethylammonium hydroxide thermochemolysis coupled with gas chromatography and mass spectrometry (TMAH-GC/MS). A total of 89 pyrolysates were identified by the thermochemolysis of primary and atmospheric HULIS. The main groups were polysaccharide derivatives, N-containing compounds, lignin derivatives, aromatic acid methyl ester, aliphatic acid methyl ester, and diterpenoid derivatives. Both the type and distribution of pyrolysates among primary HULIS were comparable to those in atmospheric HULIS. This indicates that primary HULIS from combustion processes are important contributors to atmospheric HULIS. Some distinct differences were also observed. The aromatic compounds, including lignin derivatives and aromatic acid methyl ester, were the major pyrolysates (53.0%–84.9%) in all HULIS fractions, suggesting that primary HULIS significantly contributed aromatic structures to atmospheric HULIS. In addition, primary HULIS from biomass burning (BB) contained a relatively high abundance of lignin and polysaccharide derivatives, which is consistent with the large amounts of lignin and cellulose structures contained in biomass materials. Aliphatic acid methyl ester and benzyl methyl ether were prominent pyrolysates in atmospheric HULIS. Moreover, some molecular markers of specific sources were obtained from the thermochemolysis of primary and atmospheric HULIS. For example, polysaccharide derivatives, pyridine and pyrrole derivatives, and lignin derivatives can be used as tracers of fresh HULIS emitted from BB. Diterpenoid derivatives are important markers of HULIS from pine wood combustion sources. Finally, the differences in pyrolysate types and the distributions between primary and atmospheric HULIS suggested that the primary HULIS would undergo many atmospheric processes to reconstruct the macromolecular organic matter in atmospheric aerosols.

1. Introduction

Humic-like substances (HULIS) are unresolved macromolecular water soluble organic compounds (WSOCs), with similar chemical properties to humic substances in natural waters, soils, and sediments (Graber and Rudich, 2006; Zheng et al., 2013). They have been widely reported in atmospheric aerosols in urban, rural, forested, and marine environments (Song et al., 2012; Zheng et al., 2013; Fan et al., 2016a), rain water (Santos et al., 2009, 2010, 2012), cloud water (Kokkola et al., 2006; Kristensen et al., 2014), and fog (Krivacsy et al., 2000; Cappiello et al., 2003; Birdwell and Valsaraj, 2010). As a major component of WSOCs, HULIS is believed to play an important role in atmospheric processes, such as light absorption, light radiation, and cloud droplet formation (Graber and Rudich, 2006; Zheng et al., 2013). Some

studies have demonstrated that HULIS can catalyze the formation of reactive oxygen species, resulting in adverse effects on human health (Lin and Yu, 2011; Velali et al., 2016).

Atmospheric HULIS are generally derived from various sources, including primary emissions and secondary formation via chemical reactions of volatile organic compounds in gaseous and/or aqueous systems (Zheng et al., 2013 and references therein). The combustion of biomass materials, such as tree branches, crop straw, and leaves, has been demonstrated to contribute a significant portion of the atmospheric HULIS (Schmidl et al., 2008a, 2008b; Goncalves et al., 2010; Lin et al., 2010a, 2010b; Fan et al., 2016b; Wang et al., 2017). For example, with regard to carbon content, primary HULIS accounts for 30%–66.1% of WSOC in smoke particles emitted from biomass burning (BB), and their contributions to smoke particles are in the range of 0.6%–21.2%

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(Fan et al., 2016b, and references therein). In addition, the combustion of coal is also an important source of atmospheric HULIS according to our previous study (Fan et al., 2016b).

As an important source of atmospheric HULIS, the primary HULIS from BB and/or coal combustion have been investigated to determine their potential influences on the chemical and optical properties of atmospheric HULIS and their environmental effects (Krivacsy et al., 2008; Baduel et al., 2010; Lin and Yu, 2011; Verma et al., 2012, 2015). For example, the HULIS fractions from BB aerosols have been reported to provide aromatic species to atmospheric HULIS (Krivacsy et al., 2008; Baduel et al., 2010), and also potentially generate reactive oxygen species in the atmospheric environment (Lin and Yu, 2011; Verma et al., 2012, 2015). Recently, the chemical and optical properties of primary HULIS from BB and coal combustion were comprehensively investigated by Fan et al. (2016b) and Park and Yu (2016). These studies showed that the primary HULIS contained more aromatic structures and had a lower content of aliphatic and oxygen-containing groups than atmospheric HULIS. In addition, the chemical properties of primary smoke HULIS were investigated to exhibit some differences according to fuel materials. However, these studies provide general descriptions of the primary HULIS from combustion processes, while structural information at the molecular level is limited.

Off-line tetramethylammonium hydroxide thermochemolysis coupled with gas chromatography and mass spectrometry (TMAH-GC/MS), is an established method for the generation of molecular fingerprints and the qualitative characterization of structurally complex macromolecular compounds (Martin et al., 1995; Li et al., 2006; Iwai et al., 2013). This method has been successfully used to determine the structural features of HULIS and WSOC in atmospheric aerosols (Gelencser et al., 2000; Fan et al., 2013), which then have the potential to reveal the molecular information of HULIS. In the present study, fine particles emitted from the combustion of biomass materials and coal were collected. The primary HULIS fractions in smoke particles were isolated and analyzed with TMAH-GC/MS. In addition, a HULIS sample isolated from ambient aerosol was simultaneously studied and compared with the primary HULIS. The results enable a better understanding of the molecular features of primary HULIS directly emitted from combustion process and their contributions to atmospheric HULIS.

2. Experimental

2.1. Preparation of HULIS fractions

In this study, four types of primary HULIS in fine smoke particles (smoke $PM_{2.5}$) emitted from combustion process were studied. Samples of smoke $PM_{2.5}$ emitted from the combustion of rice straw, corn straw, pine branches, and lignite coal was collected in a laboratory resuspension chamber. As a comparison, ambient $PM_{2.5}$ samples were collected on December 7–10, 2015, in Guangzhou, China. The details of the sampling are provided in our previous study (Fan et al., 2016b).

The HULIS fractions in smoke $PM_{2.5}$ and ambient $PM_{2.5}$ were isolated using a solid phase extraction (SPE) method (Oasis HLB, Waters, Milford, MA, USA). The detailed isolation method was reported in our previous studies (Fan et al., 2012, 2016b; Song et al., 2012). Briefly, each collected smoke $PM_{2.5}$ and ambient $PM_{2.5}$ was firstly extracted with pure water to obtain water extract. Then, the water extract was acidified to pH 2 with HCl and loaded onto a preconditioned HLB cartridge (500 mg, Waters, Milford, MA, USA). The relatively hydrophobic HULIS fraction was retained by the HLB cartridge and then eluted by methanol and dried under a stream of nitrogen followed by freeze dryer. According to our study, the recovery of SRFA (usually seen as surrogate of HULIS) was $91.4 \pm 1.7\%$ based on carbon contents measurement, indicating the HLB protocol is excellent to isolate HULIS fraction. (Fan et al., 2012). In present work, the contributions of HULIS carbon to water soluble organic carbons were observed to be

approximately 66.1%, 59.2%, 56.9%, 45.5% and 60.7% of for rice straw, corn straw, pine branch, coal smoke particles and ambient aerosols, respectively (Fan et al., 2016b).

2.2. TMAH-GC/MS

Details of the TMAH-GC/MS of HULIS are provided in our previous study (Fan et al., 2013). Briefly, a portion of re-dissolved HULIS in methanol was dropped in a glass ampoule with 100 μ L of TMAH (25% in methanol), and dried under a vacuum. The ampoule was sealed under vacuum and heated at 250 °C for 30 min. Then the ampoule was cracked open when it cooled, and washed three times with 1 mL of dichloromethane to extract the pyrolysis products. The extracts were combined and passed through a column filled with anhydrous sodium sulfate. The sample was then concentrated to 100 μ L under a stream of nitrogen gas. Finally, a 2 μ L sample was introduced to a GC/MS system, which consisted of an Agilent 7890 gas chromatograph and 5975 mass spectrometer (Agilent Technologies, Santa Clara, CA, USA). Each sample was run in duplicate.

A HP-5MS capillary column (Agilent Technologies, 30 m length, 0.32 mm ID, 0.25 μ m film thickness) was used to separate the pyrolysis compounds, using helium as the carrier gas. The column temperature was initially kept at 60 °C for 5 min, then increased at 5 °C min^{-1} to 300 °C, and maintained for 5 min. The chromatographically separated products were analyzed by electron impact mass spectrometry (70 eV). The MS detector and transfer line were maintained at a temperature of 250 °C. Mass spectra were scanned from m/z 50 to 500 at a rate of 1.5 scans s^{-1} . GC/MS data was collected and processed with an Agilent Chemstation. The pyrolysis compounds were mainly identified by comparisons of their mass spectra with the National Institute of Standards and Technology 08 (NIST 08) mass spectra library database and data reported in previous studies.

In present work, a mixture of 1,4-benzenedicarboxylic acid, dimethyl ester, cinnamic acid, methyl ester, and hexadecanoic acid, methyl ester were selected as target compounds and tested at the same analytical conditions as for HULIS fractions. The results showed that the recovery of these compounds were in the range of 78%–94%. In addition, one ambient HULIS fraction had been conducted in triplicate to verify the reproducibility of TMAH-GC/MS analysis. It was observed that overall coefficient of variations of the identified pyrolysates were lower than 15%, indicated that this thermochemolysis method had reasonable repeatability. In the current study, the five HULIS fractions were run in duplicate, and the data reported in this paper were average signals obtained from their replicates.

3. Results and discussion

The thermochemograms obtained from the pyrolysis of primary HULIS in smoke $PM_{2.5}$ emitted from the combustion of rice straw (a), corn straw (b), pine branches (c), and coal (d), and atmospheric HULIS in ambient $PM_{2.5}$ (e) are shown in Fig. 1. Numerous peaks were apparent in thermochemograms, and 89 of them were identifiable. The assignments of the major peaks are numbered in Fig. 1, and correspond to the pyrolysis products listed in Table 1.

According to their chemical structures and possible sources, the compounds were classified into seven chemical groups: (A) polysaccharide derivatives, (B) N-containing compounds, (C) lignin derivatives, including methoxy- and hydroxy-benzenes, aromatic ketones and aldehydes, and methoxy-aromatic acid methyl ester, (D) aromatic acid methyl ester, (E) aliphatic acid methyl ester, (F) diterpenoid derivatives, and (G) others. The molecular structures of some representative pyrolysis products are shown in Table 2. To quantitatively compare the structural characteristics of different HULIS samples, the relative abundance of pyrolysis products for each HULIS fraction was calculated by normalizing each individual peak area to the total peak area of identifiable compounds. The relative abundances of the major

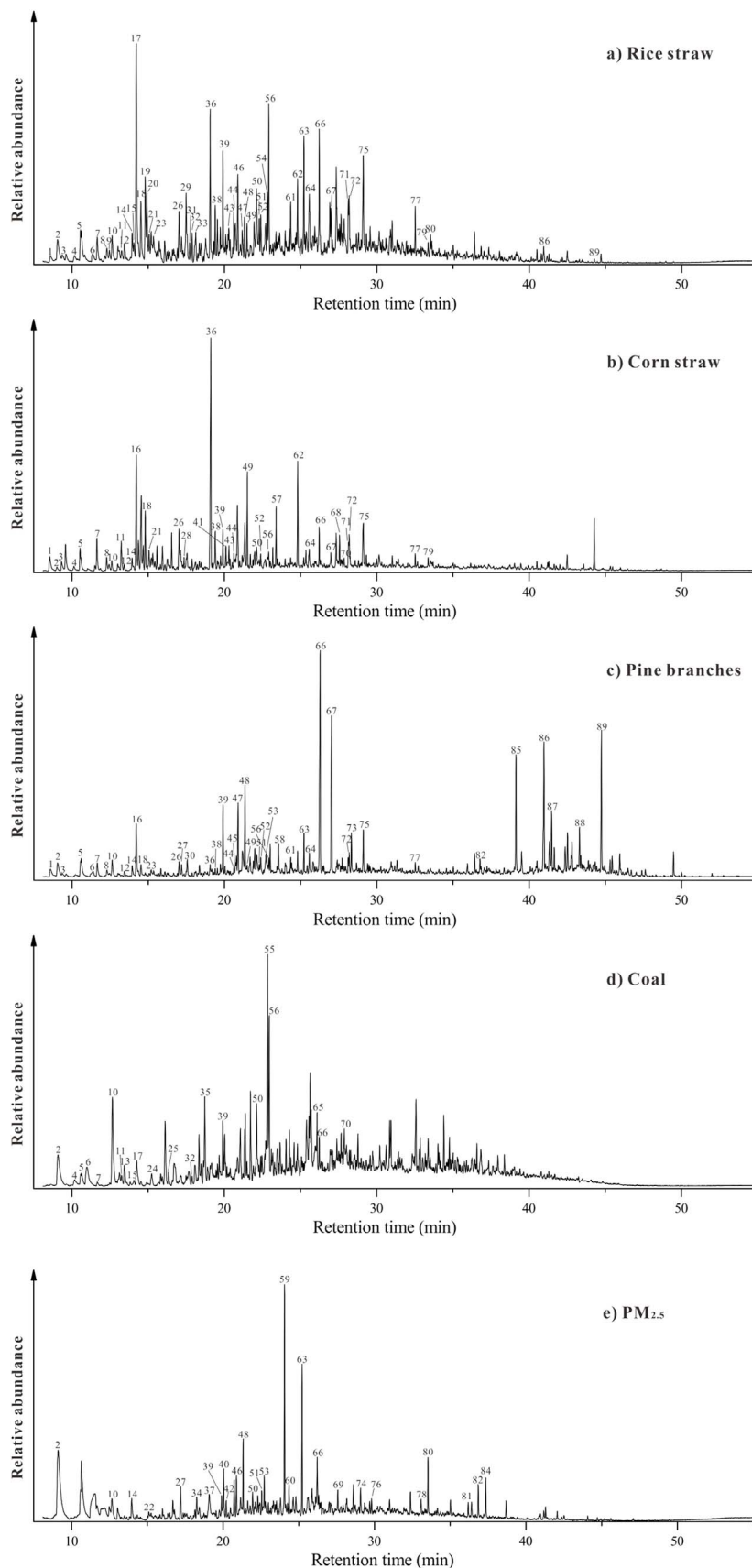


Fig. 1. Total ion chromatogram of the tetramethylammonium hydroxide (TMAH) thermochemolysis products of primary humic-like substances (HULIS) in smoke PM_{2.5} emitted from the combustion of rice straw (a), corn straw (b), pine branches (c) coal (d), and atmospheric HULIS in ambient PM_{2.5} (e). For peak identifications refer to Table 1.

Table 1

List of pyrolysates identified from the tetramethylammonium hydroxide (TMAH) thermolysis of primary humic-like substances (HULIS) emitted from the combustion of rice straw, corn straw, pine branches, and coal, and atmospheric HULIS. Peak numbers correspond to the chromatographic signals in Fig. 1.

No.	Compounds	Groups
1	2-Furancarboxylic acid, methyl ester	A
2	Benzyl methyl ether	G
3	3-Methoxypyridine	B
4	3-Methoxytoluene	C
5	Succinic acid, dimethyl ester	E
6	Benzyl dimethylamine	B
7	Succinic acid, methyl-, dimethyl ester	E
8	2-Methoxyphenol	C
9	1-Methyl-2,5-pyrrolidinedione	B
10	Benzoic acid, methyl ester	D
11	1-Ethyl-4-methoxybenzene	C
12	Methyl 1-methylpyrrole-2-carboxylate	B
13	2,5-Dimethylanisole	C
14	Glutaric acid, dimethyl ester	E
15	1-ethenyl-3-methoxybenzene,	C
16	1,2-Dimethoxybenzene	C
17	3,4-Dimethylanisole	C
18	1-ethenyl-4-methoxybenzene	C
19	1,4-Dimethoxybenzene	C
20	1,3-Dimethoxybenzene	C
21	2,3-Dimethoxytoluene	C
22	Glutaric acid, 2-methyl-, dimethyl ester	E
23	Benzeneacetic acid, methyl ester	D
24	2-Methylbenzoic acid, methyl ester	D
25	4-Methylbenzoic acid, methyl ester	D
26	3,4-Dimethoxytoluene	C
27	Hexanedioic acid, dimethyl ester	E
28	2,5-Dimethoxytoluene	C
29	5-Methoxybenzofuran	A
30	4-Methoxybenzaldehyde	C
31	7-Methoxybenzofuran	A
32	3,5-Dimethoxytoluene	C
33	Benzenepropanoic acid, methyl ester	D
34	2-Hexenedioic acid, dimethyl ester	E
35	5-Methoxyindane	C
36	1,2,3-Trimethoxybenzene	C
37	Phthalic anhydride	G
38	4-Ethyl-1,2-dimethoxybenzene	C
39	3-Methoxybenzoic acid methyl ester	C
40	Phthalide	G
41	1,3-Dimethoxy-2-hydroxybenzene	C
42	8-Methoxyoctanoic acid, methyl ester	E
43	3-Methoxyacetophenone	C
44	4-ethenyl-1,2-dimethoxybenzene	C
45	1,2,4-Trimethoxybenzene	C
46	4-Methoxybenzoic acid methyl ester	C
47	Cinnamic acid, methyl ester	D
48	1,6-Anhydro- π D-glucose, trimethyl ether	A
49	3,4,5-Trimethoxytoluene	C
50	N-Methylphthalimide	B
51	Methyl 3-methoxy-4-methylbenzoate	C
52	Benzeneacetic acid, 3-methoxy-, methyl ester	E
53	Octanedioic acid, dimethyl ester	C
54	1-Methoxynaphthalene	G
55	1,2-Benzenedicarboxylic acid, dimethyl ester	D
56	2-Methoxynaphthalene	G
57	3,5-Dimethoxy-4-hydroxyacetophenone	C
58	3,4-Dimethoxybenzaldehyde	C
59	1,4-Benzenedicarboxylic acid, dimethyl ester	D
60	1,3-Benzenedicarboxylic acid, dimethyl ester	D
61	5-Amino-2-methoxyphenol, N,N-methyl-, methyl ether	B
62	Benzenepropanoic acid, 4-methoxy-, methyl ester	C
63	Nonanedioic acid, dimethyl ester	E
64	3,4-Dimethoxyacetophenone	C
65	4-Ethyl-3-methylcinnoline	B
66	Benzoic acid, 3,4-dimethoxy-, methyl ester	C
67	Benzeneacetic acid, 3,4-dimethoxy-, methyl ester	C
68	1,2,3-Trimethoxy-5-[(1E)-1-propenyl]benzene	C
69	Decanedioic acid, dimethyl ester	E
70	4-Methoxy-biphenyl	C
71	3,4,5-Trimethoxyacetophenone	C

Table 1 (continued)

No.	Compounds	Groups
72	Cinnamic acid, <i>p</i> -methoxy-, methyl ester	C
73	3,4-dimethoxy-benzenepropanol	C
74	3,4,5-Trimethoxybenzoic acid, methyl ester	C
75	Benzenepropanoic acid, 3,4-dimethoxy-, methyl ester	C
76	Undecanedioic acid, dimethyl ester	E
77	Cinnamic acid, 3,4-dimethoxy-, methyl ester	C
78	Dimethyl [1,1'-biphenyl]-2,3'-dicarboxylate	D
79	4,4'-Dimethoxy-1,1'-biphenyl	C
80	Hexadecanoic acid, methyl ester	E
81	2,2-Bis(4'-methoxyphenyl) propane	C
82	Methyl deisopropyldehydroabietate	F
83	11-Octadecenoic acid, methyl ester	E
84	Octadecanoic acid, methyl ester	E
85	Methyl 3,4a,7,10a-tetramethyl-3-vinyldodecahydro-1H-benzo[f]chromene-7-carboxylate	F
86	Dehydroabietic acid methyl ester	F
87	Methyl 13-methoxypodocarpa-8(14),9(11),12-trien-15-oate	F
88	Methyl 12-methoxyabieta-8,11,13-trien-20-oate	F
89	7-Oxodehydroabietic acid, methyl ester	F

(A) Polysaccharide derivatives, (B) N-containing compounds, (C) Lignin derivatives, (D) Aromatic acid methyl ester, (E) Aliphatic acid methyl ester, (F) Diterpenoid derivatives and (G) Others.

groups of pyrolysis products of HULIS fractions were summarized and the results are given in Table 3.

3.1. Polysaccharide derivatives

The polysaccharide derivatives identified in the study mainly consisted of furans, such as 2-furancarboxylic acid methyl ester (No. 1), 5-methoxybenzofuran (No. 29), and 7-methoxybenzofuran (No. 31), and pyran compounds such as 1,6-anhydro- π D-glucose, trimethyl ether (No. 48). They were identified in the thermochemolysis products of primary HULIS emitted from BB, which accounted for 2.6%–6.5% of total pyrolysates. However, none of them were identified in the pyrolysis products of coal HULIS, indicating that polysaccharide derivatives may be tracers of HULIS from BB. The 1,6-anhydro- π D-glucose, trimethyl ether was also identified in the pyrolysis products of atmospheric HULIS in both this study and our previous work (Fan et al., 2013), suggesting that BB is a significant primary source of atmospheric HULIS.

Some differences were found among the HULIS emitted from the combustion of three types of biomass. It was found that 2-furancarboxylic acid methyl ester (No. 1) was present in the pyrolysates of all primary HULIS from BB, but 5-methoxybenzofuran (No. 29) and 7-methoxybenzofuran (No. 31) were only detected in the pyrolysates of rice straw HULIS. These furan type pyrolysates were absent in the atmospheric HULIS in this study and our previous study (Fan et al., 2013), but they were present in the pyrolysates of humic acid-like substances in dustfalls (Zhao et al., 2012). None of the furan compounds were identified in atmospheric PM_{2.5}, and it was therefore speculated that they may have been incorporated into water insoluble macromolecules in atmospheric particles. The pyran derivative, 1,6-anhydro- π D-glucose, trimethyl ether (No. 50), was identified in the primary HULIS from the combustion of rice straw and pine branches and in atmospheric HULIS. Because levoglucosan would be excluded from HULIS fractions when using HLB protocol for isolation (Fan et al., 2012), the occurrence of 1,6-anhydro- π D-glucose, trimethyl ether (No.48) in HULIS indicated that it may have been derived from the derivatives of 1,6-anhydro- π D-glucose in HULIS macromolecules. These results implied that polysaccharide derivatives such as 1,6-anhydro- π D-glucose can be used as a tracer of HULIS derived from BB sources.

3.2. N-Containing compounds

Seven N-containing compounds (Nos. 3, 6, 9, 12, 50, 61, and 65) were identified in the HULIS samples. These compounds were pyridine,

Table 2
The structures of the representative thermochemolysis products in primary and atmospheric humic-like substances (HULIS).












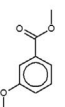
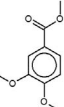
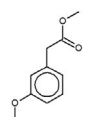
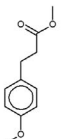
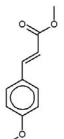



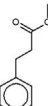
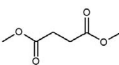
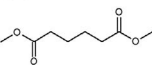
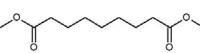
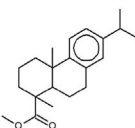
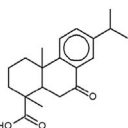


Groups	The structures of representative pyrolysis products		
Polysaccharide derivatives			
N-containing compounds	5-methoxybenzofuran	1,6-anhydro-D-glucose, trimethyl ether	
Lignin derivatives			
	3-methoxypyridine	N-methylphthalimide	
			
	1,2-dimethoxybenzene	3,4-dimethylanisole	3,4-dimethoxytoluene
			
	1,2,3-Trimethoxybenzene	4-ethenyl-1,2-dimethoxybenzene	3,4,5-Trimethoxytoluene
			
	3,4-dimethoxyacetophenone	3-Methoxybenzoic acid methyl ester	Benzoic acid, 3,4-dimethoxy-, methyl ester
			
	Benzenoacetic acid, 3-methoxy-, methyl ester	Benzenepropanoic acid, 4-methoxy-, methyl ester	Cinnamic acid, 4-methoxy-, methyl ester
Aromatic acid methyl ester			
	Benzoic acid, methyl ester	1,4-Benzenedicarboxylic acid, dimethyl ester	
			
	Benzenoacetic acid, methyl ester	Benzenepropanoic acid, methyl ester	
Aliphatic acid methyl ester			
	Succinic acid, dimethyl ester	Hexanedioic acid, dimethyl ester	
			
	Nonanedioic acid, dimethyl ester		
Diterpenoid derivatives			
	Dehydroabiatic acid methyl ester	7-Oxodehydroabiatic acid, methyl ester	
Others			
	Benzyl methyl ether	2-Methoxynaphthalene	

Table 3
Relative abundances (%) of the main families of thermochemolysis products in primary and atmospheric humic-like substances (HULIS).

	HULIS fractions				
	Rice straw	Corn straw	Pine branch	Coal	PM _{2.5}
HULIS/PM(%) ^a	23.4	11.2	11.4	5.3	10.7
Relative abundances of pyrolysate groups (%)					
Polysaccharide derivatives	6.5	2.6	6.3	n.d. ^b	4.5
N-containing compounds	6.8	3.5	2.8	16.8	1.0
Lignin derivatives	62.8	84.0	50.9	27.9	12.2
Aromatic acid methyl ester	5.6	0.9	2.1	33.2	20.1
Aliphatic acid methyl ester	8.5	7.5	7.8	1.6	29.8
Diterpenoid derivatives	1.0	n.d.	26.9	n.d.	n.d.
Others	8.9	1.6	3.2	20.4	32.4

^a Refer to the average contributions of the mass of HULIS to smoke particles and ambient PM_{2.5} reported in our previous study (Fan et al., 2016b).

^b Not detected.

pyrrole, and amine/amide derived compounds. These N-containing compounds have been shown to be abundant in HULIS fractions in BB aerosols and ambient aerosols influenced by BB (Laskin et al., 2009; Wang et al., 2017). They are reported to be released from the pyrolysis of N structures, such as proteins/amino acids in organic matter (Becker et al., 1998; Hendricker and Voorhees, 1998; Zhao et al., 2009), and can probably be produced by the reaction of TMAH with organic compounds or with itself (Romero, 2006).

In this study, N-containing compounds accounted for 2.8%–6.8% of the pyrolysis products among BB smoke HULIS and 16.8% among coal smoke HULIS (Table 3). In contrast, they only accounted for 1.0% of the pyrolysis products in atmospheric HULIS in the present work. The higher distribution of N-containing pyrolysates in BB smoke HULIS indicates these fractions contain more protein/amino derived structures (Nos. 3 and 12), which is in agreement with the observations of significant protein-like bands in the three-dimensional excitation-emission matrix (3-DEEM) spectra of primary HULIS reported in our previous study (Fan et al., 2016b). Coal smoke HULIS contained the highest contents of N-containing compounds (16.8%). Most of them are amines and amides linked to a benzene ring (Nos. 6, 50, and 65), which may be originate from the pyrolysis of N-containing structures in coal or the reactions of aromatic structures with TMAH. These differences in N-containing groups suggest that the fresh primary HULIS in smoke particles contained more easily decomposed N structures, and also suggests that BB and coal combustion may be potential sources of N structures in atmospheric HULIS.

Among the individual pyrolysis products, benzyldimethylamine (No. 6) and N-methylphthalimide (No. 50) were simultaneously identified in the pyrolysates in primary HULIS from BB and coal combustion, and atmospheric HULIS. These compounds may have various sources, including the pyrolysis of N-containing structures in organic matter or the reactions of aromatic structures with TMAH. Pyridine and pyrrole compounds such as 3-methoxypyridine (No. 3) and methyl 1-methylpyrrole-2-carboxylate (No. 12), were identified in the pyrolysis products of BB HULIS, but were absent in the pyrolysis products of coal smoke HULIS. In contrast, 4-ethyl-3-methylcinnoline (No. 67) was only identified in the pyrolysates of coal smoke HULIS. This indicated that pyridine and pyrrole derivatives might be important markers of BB (Zhao et al., 2009; 2012), and N-containing heterocyclic compounds such as cinnoline might be derived from N-containing aromatic structures in organic matter. Aromatic amine/amide pyrolysates should be carefully considered for an explanation of their sources.

3.3. Lignin derivatives

The lignin derived compounds are the predominant pyrolysates for

the HULIS fractions emitted from the combustion of rice straw, corn straw, and pine branches, which accounted for 62.8%, 84.0%, and 50.9% of the total identifiable pyrolysates, respectively (Table 3). They were also important compounds released by the pyrolysis of HULIS in coal combustion smoke particles and ambient aerosol, in which they accounted for 27.9% and 12.2% of the total identifiable pyrolysates, respectively. These lignin derivatives can be classified into three groups based on their molecular structure: methoxy-/hydroxy-benzenes; methoxy-aromatic ketones and aldehydes; and methoxy-aromatic acid methyl esters. The distribution of these species is discussed in detail below.

3.3.1. Methoxy-/hydroxy-benzenes

As shown in Tables 1 and 3, a lot of methoxy- and hydroxy-benzene compounds were identified by the pyrolysis of HULIS fractions. The molecular structures of these representative pyrolysate compounds are partly shown in Table 2. They mainly include monomethoxybenzenes (Nos. 4, 11, 13, 17, 18, 35, 70, 73, 79, and 81), dimethoxybenzenes (Nos. 16, 19, 20, 21, 26, 28, 32, 38, and 44), and trimethoxybenzenes (Nos. 36, 49, and 68). These types of methoxy-benzenes are commonly found in the pyrolysis products of natural humic and fulvic acids (del Rio et al., 1998; Iwai et al., 2013). Noteworthy, it is difficult to distinguish methoxyl benzenes whether formed in the thermochemolysis or were the originally occurring methylated structures emitted from biomass burning. This might be attributed to the limitation of TMAH-GC/MS (Martin et al., 1994, 1995; Peuravuori et al., 2002). Regardless, the methoxy- and hydroxy-benzenes (including methoxyphenols) were generally ascribed to the pyrolysis of lignin-derived structures in natural organic matter reported in many previous studies (Martin et al., 2001; Iwai et al., 2013; Benlboukht et al., 2016). Therefore, in this study, these methoxy- and hydroxy-benzene pyrolysates of primary HULIS and ambient HULIS could be attributed to lignin-derived phenol structures.

The relative abundance of these pyrolysates in the four primary HULIS fractions were different, and ranged from 10.4% for pine smoke HULIS to 60.0% for corn smoke HULIS (Fig. 2). This was much higher than their relative abundance (0.9%) in atmospheric HULIS. This indicates that methoxy- and hydroxy-benzenes are the predominant substructures of HULIS from BB and coal combustion. It concurs with the results of our investigation of more apparent phenol-like fluorescence bands in 3-DEEM spectra for primary HULIS in our previous study (Fan et al., 2016b).

For the four primary HULIS, the dominant individual methoxy-/hydroxyl-benzenes in the pyrolysates were also different. There were 12 methoxy-/hydroxyl-benzenes pyrolysates (Nos. 4, 8, 11, 16, 19, 21, 26, 36, 38, 44, 49, and 79) that were simultaneously identifiable in the smoke HULIS from the combustion of rice and corn straws, and they were present at higher levels than in the other two types of primary HULIS from the combustion of pine branches and coal. Among these compounds, 2-methoxyphenol (No. 8), 1,2-dimethoxybenzene (No. 16), 3,4-dimethoxytoluene (No. 26), 1,2,3-trimethoxybenzene (No.36), 4-ethyl-1,2-dimethoxybenzene (No. 38), 4-ethenyl-1,2-dimethoxybenzene (No. 44), and 3,4,5-trimethoxytoluene (No. 49) were also identified in the pyrolysates of pine smoke HULIS, but with relatively lower abundances. For coal smoke HULIS, the higher abundance methoxy-/hydroxy-benzenes pyrolysates were 2,5-dimethylanisole (No. 13), 3,4-dimethylanisole (No. 17), 1,2,3-trimethoxybenzene (No. 35), and 4-methoxy-biphenyl (No. 70). They were absent or present in very low concentrations in the pyrolysates of BB smoke HULIS. These different compositional features could be ascribed to the differences in fuel materials and combustion processes. As a comparison, 2,2-bis(4'-methoxyphenyl) propane (No. 81) was the only methoxy-/hydroxy-benzenes pyrolysate observed in the pyrolysis products of atmospheric HULIS, and was also found among the pyrolysates in ambient HULIS in our previous study (Fan et al., 2013). The apparent differences in the pyrolysates and their distributions between primary and atmospheric

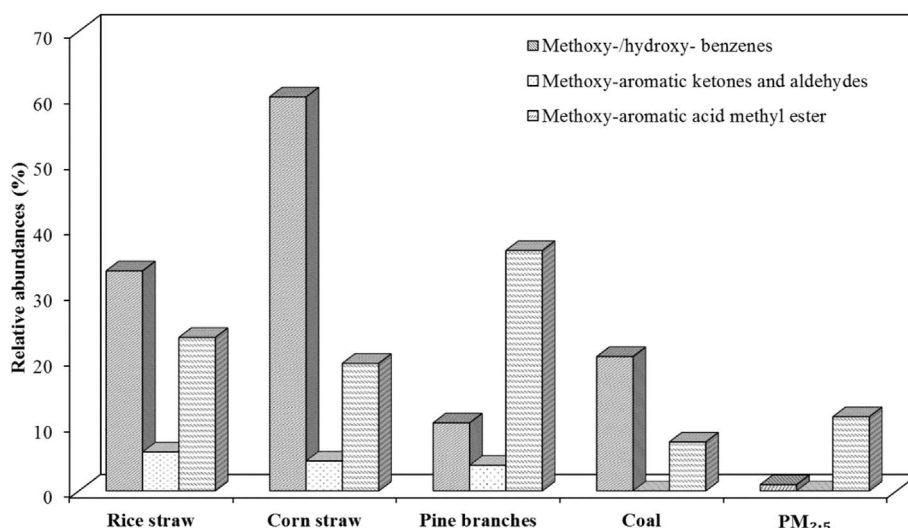


Fig. 2. The relative abundances of three types of lignin derived pyrolysates in the primary humic-like substances (HULIS) emitted from the combustion of rice straw, corn straw, pine branches, and coal, and atmospheric HULIS.

HULIS implied that these low molecular weight aromatic compounds went through various photooxidation reactions (i.e., Fenton-like reactions) to form highly polyconjugated aromatic building blocks (Santos and Duarte, 2015; Santos et al., 2016a; b).

3.3.2. Methoxy-aromatic ketones and aldehydes

Methoxy-aromatic ketones and aldehydes (Nos. 30, 43, 58, 64, and 71) were identified in the three types of BB smoke HULIS, but they were absent in coal smoke and atmospheric HULIS. These types of compounds have been reported to be emitted from the pyrolysis of natural humic substances and can be formed from lignin derived structures in organic macromolecules (del Rio et al., 1998; Iwai et al., 2013; Benboukht et al., 2016). However, these types of pyrolysates were absent in the atmospheric HULIS analyzed in our previous study (Fan et al., 2013), and are also not present in the organic matter in atmospheric fine particles (Gelencser et al., 2000) and humic acid like substances in dustfalls and fine particles (Subbalakshmi et al., 2000; Zhao et al., 2012). This can be attributed to the further oxidation of aromatic ketones and aldehydes in primary HULIS in the atmospheric environment. For example, it has been reported that aromatic ketones and aldehydes can easily undergo oxidation reactions, such as the Cannizzaro reaction with benzaldehyde derivatives (Tanczos et al., 1997, 1999). These results suggest that atmospheric HULIS have strong oxidative properties.

3.3.3. Methoxy-aromatic acid methyl ester

A number of methoxy-aromatic acid methyl ester compounds were identified following the pyrolysis of HULIS samples. The distribution of these methoxy-aromatic acid methyl ester compounds for five types of HULIS had distinct features (Fig. 2). The relative abundance of total methoxy aromatic acid derivatives for the four primary HULIS followed the order of pine branch (36.6%) > rice straw (23.4%) > corn straw (19.4%) > coal (7.4%). The proportional contribution of these compounds in atmospheric HULIS was 11.3%, which was lower than BB HULIS, but higher than coal combustion HULIS. These compounds are commonly reported from the pyrolysis of lignin, and have also been found in atmospheric HULIS and organic aerosols (Gelencser et al., 2000; Subbalakshmi et al., 2000; Fan et al., 2013).

These compounds can be classified into two groups: 1) the carboxylic acid functional group attached to a benzene ring with a methoxy group (MA1) (Nos. 39, 46, 51, 66, and 74), and 2) the carboxylic acid functional group attached to alkyl side-chains of a benzene ring with a methoxy group (MA2) (Nos. 52, 62, 67, 72, 75, and 77). The

differences among these HULIS fractions were further investigated in terms of the abundance of these two types of methoxy-aromatic acid derivatives. The relative abundance of MA1 components for the three types of BB smoke HULIS was initial 4.6%–21.7%, which compared with the values of 7.4% and 11.3% for coal smoke and atmospheric HULIS, respectively. Among the MA1 components, 3-methoxybenzoic acid methyl ester (No. 39), 4-methoxybenzoic acid methyl ester (No. 46), and benzoic acid, 3,4-dimethoxy-, methyl ester (No. 66) were identified in almost all the primary and atmospheric HULIS, whereas 3,4,5-trimethoxybenzoic acid, methyl ester (No. 74) was only detected in atmospheric HULIS. These results indicated that combustion processes may be important sources for methoxybenzoic acid derivatives in atmospheric HULIS. Trimethoxybenzoic acid compounds in atmospheric HULIS may be due to the aging of methoxybenzoic acids or benzoic acids in the atmospheric samples. The MA2 groups mainly include methoxy-benzeneacetic acid methyl ester (Nos. 52 and 67), methoxy-benzenepropanoic acid methyl ester (Nos. 62 and 75), and methoxy-cinnamic acid methyl ester (Nos. 72 and 77). These compounds were only identified in the pyrolysates of BB smoke HULIS, which accounted for 11.8%–14.9% of the total pyrolysates identified in BB smoke HULIS. They were absent in the pyrolysates from coal smoke and atmospheric HULIS. These results clearly indicate that these types of aromatic acid derivatives are markers of fresh HULIS emitted from BB. They were absent in the atmospheric HULIS possibly because of the degradation and transformation of these organic compounds in atmospheric processes.

3.4. Aromatic acid methyl ester

Aromatic acid derivatives (Nos. 10, 23, 24, 25, 33, 47, 55, 59, 60, and 78) were identified in the study. These aromatic compounds have been identified in the pyrolysis of atmospheric HULIS fractions (Fan et al., 2013), humic acid like substances in dustfalls, and atmospheric fine particles (Subbalakshmi et al., 2000; Zhao et al., 2012). In the atmospheric environment these compounds mainly originate from direct automobile exhaust (Simoneit, 1984), the photooxidation of polycyclic aromatic hydrocarbons (Kawamura and Ikushima, 1993), and the hydrolysis of commonly used plasticizers (Rogge et al., 1993; Okamoto et al., 2011; Zeng et al., 2017). Their relative abundances in HULIS samples are very different (Table 3). The three types of BB smoke HULIS had a relatively low content (0.9%–5.6%) of aromatic acid methyl esters, which was much lower than the 33.2% content in coal smoke HULIS. These differences may be due to the relatively higher

aromaticity of coal materials. In addition, the atmospheric HULIS also contained a relatively higher content (20.1%) of aromatic acid derivatives than the BB smoke HULIS.

For further analysis, these compounds were classified into two groups: 1) benzoic acid derivatives (BA 1), including monocarboxylic acids (Nos. 10, 24, 25, and 78), dicarboxylic acids (Nos. 55, 59, and 60), and 2) the carboxylic acid functional group attached to alkyl side-chains of benzene ring (BA2), including benzenoacetic acids (No. 23), benzenepropanoic acid (No. 33), and cinnamic acid (No. 47). There were differences between the relative abundances of these two aromatic acid groups in different HULIS fractions. The three types of BB smoke HULIS had the lowest content (0.9%–1.6%) of BA1 derivatives, which was significantly lower than the 33.2% for coal smoke HULIS and 18.9% for atmospheric HULIS. In addition, monocarboxylic acid (benzoic acid) derivatives were identified in all primary and atmospheric HULIS samples. However, benzenedicarboxylic acid derivatives (Nos. 55, 59, and 60) were only detectable in the pyrolysates from coal smoke and atmospheric HULIS, and were absent in the pyrolysates from BB smoke HULIS. These benzenedicarboxylic acid derivatives contained 1,2-benzenedicarboxylic acid, dimethyl ester (No. 55), 1,4-benzenedicarboxylic acid, dimethyl ester (No. 59), and 1,3-benzenedicarboxylic acid, dimethyl ester (No. 60), which are often found among the substructure of atmospheric HULIS (Gelencser et al., 2000; Fan et al., 2013). The benzenedicarboxylic acid, especial for phthalic acid, are commonly recognized to be originated from plastic-waste burnings (Kumar et al., 2015 and references therein). However the existence of their derivatives in pyrolysates of coal smoke HULIS may indicated that coal combustion is also an important contributor to this type of compounds. These findings suggested that the complex sources of benzenedicarboxylic molecular structures in ambient HULIS. The ratio of dicarboxylic acids/monocarboxylic acids in pyrolysates of atmospheric HULIS was 4.7, which was significantly higher than the 0.9 for coal smoke HULIS. Compared with the four primary types of HULIS, a much higher content of dicarboxylic acid was observed in atmospheric HULIS, which could be attributed to the primary HULIS being oxidized after being emitted into the atmospheric environment. Other sources such as secondary formation from individual aromatic organic compounds may also contribute to there being more dicarboxylic acid in atmospheric HULIS. The BA2 compounds (Nos. 23, 33, and 47) were only identified in pyrolysates of BB smoke HULIS. They were absent in the atmospheric HULIS, which may be the result of the degradation and transformation of these organic compounds. These differences imply that BA2 compounds such as benzenoacetic acid methyl ester (No. 23), benzenepropanoic acid methyl ester (No. 33), and cinnamic acid methyl ester (No. 47) could serve as markers of fresh HULIS emitted directly from BB.

3.5. Aliphatic acid methyl ester

Fourteen aliphatic acid methyl ester compounds were identifiable in the samples (Table 1). These pyrolysates were also detected previously in pyrolysis products from atmospheric HULIS (Fan et al., 2013) and natural humic substances (Martin et al., 1994, 1995). They are mainly derived from the decomposition of fatty acids/lipids in vegetation, oxidation of fatty acids emitted from plants, and oxidative degradation of aromatic compounds (Martin et al., 1994, 1995; del Rio et al., 1998; Iwai et al., 2013). The relative abundances of aliphatic acid pyrolysates for the three types of BB smoke HULIS were 7.5%–8.5% (Table 2). These values were much higher than the 1.6% identified for coal smoke HULIS. These differences could be ascribed to the BB smoke HULIS containing a relatively large amount of aliphatic structures. As a comparison, the relative abundance of aliphatic acid methyl ester compounds in the pyrolysates of atmospheric HULIS was 29.8%, which was much higher than their abundance in the primary HULIS from combustion processes.

The aliphatic acid methyl ester compounds mainly included two groups based on the number of carboxylic groups: monocarboxylic

acids (Nos. 80, 83, and 84) and dicarboxylic acids (Nos. 5, 7, 14, 22, 27, 34, 53, 63, 69, and 76). The monocarboxylic acids included hexadecanoic acid, methyl ester (No. 80), 11-octadecenoic acid, methyl ester (No. 83), and octadecanoic acid, methyl ester (No. 84). They were only identified in rice smoke HULIS and with a very low content (0.9%) in the four primary HULIS, whereas they accounted for a relatively high contribution (8.1%) of the atmospheric HULIS. These differences could be due to other sources making a significant contribution to the aliphatic structures in atmospheric HULIS.

The dicarboxylic acids (Nos. 5, 7, 14, 22, 27, 34, 53, 63, 69, and 76) are the major components of aliphatic acids, with a carbon number ranging from 4 to 11. These pyrolysates was observed in all the primary and atmospheric HULIS. The dicarboxylic acids are often found in atmospheric HULIS, and other organic materials in atmospheric aerosols (Gelencser et al., 2000; Subbalakshmi et al., 2000; Zhao et al., 2012; Fan et al., 2013). Their relative abundances in the three BB smoke HULIS were 7.5%–7.8%, i.e., higher than the 1.6% abundance in the coal smoke HULIS. The relatively high dicarboxylic acid content in BB smoke HULIS could be due to the relatively high levels of aliphatic structures in the biomass residues. These results indicated that combustion processes, especial for BB, are important sources of aliphatic structures in atmospheric HULIS. In addition, a much higher content of dicarboxylic acid was identified in atmospheric HULIS, which accounted for 21.7% of the total pyrolysates. It is particularly noteworthy that most dicarboxylic acids present in the pyrolysates of primary HULIS were short chain acids, with the aliphatic chain of the dicarboxylic acids in atmospheric HULIS distributed over a relatively large range (C5–11). Succinic acid, dimethyl ester (No. 5, C4) and succinic acid, methyl-, dimethyl ester (No. 7, C4) were identified in the four primary HULIS fractions, and were believed to originate from the oxidation of unsaturated fatty acids (Kawamura and Ikushima, 1993; Kourtchev et al., 2008). Among these aliphatic acid derivatives, nonanedioic acid, dimethyl ester (No. 63, C9) and hexadecanoic acid, methyl ester (No. 80, C16) were abundant in the aliphatic acid pyrolysates from atmospheric HULIS. It has been suggested that they are derived from secondary formation due to atmospheric chemical reactions. For example, nonanedioic acid and hexadecanoic acid may be formed from the oxidation of *cis*-9-octadecenoic (oleic) acid and cyclic hexane, respectively (Kawamura and Sakaguchi, 1999; Ziemann, 2002).

3.6. Diterpenoid derivatives

Diterpenoid derivatives were detectable in the pyrolysates from the pine branch and rice straw combustion HULIS fractions (Tables 1 and 2). These compounds were enriched by up to 26.9%, in pyrolysates from pine branch smoke HULIS, but they only accounted for 1.0% in the pyrolysates of rice straw smoke HULIS. These compounds commonly originated from the pyrolysis of conifer resins, such as pine trees, (Simoneit and Mazurek, 1982; Simoneit, 2002; Schmidl et al., 2008b), and therefore can be regarded as molecular markers for pine wood combustion. Among these diterpenoid compounds, dehydroabietic acid (No. 86) and its oxidized analogue 7-oxodehydroabietic acid (No. 89) had relatively high abundances. These compounds have also been identified in the pyrolysis products from atmospheric HULIS and among the humic acids in dustfalls in previous studies (Zhao et al., 2012; Fan et al., 2013). The absence of these compounds in the atmospheric HULIS in the current study was likely due to the insignificant contribution of the combustion of pine trees to the atmospheric HULIS.

3.7. Others

In addition to the pyrolysates discussed previously, benzyl methyl ether (No. 2), phthalic anhydride (No. 37), phthalide (No. 40), 1-methoxynaphthalene (No. 54), and 2-methoxynaphthalene (No. 56) were also detectable. Benzyl methyl ether (No. 2) was identified in all four types of primary HULIS and atmospheric HULIS. It accounted for

0.5%–9.1% of the total pyrolysates in the primary HULIS from combustion processes and 24.1% of the pyrolysates in atmospheric HULIS. It was also found in the pyrolysates of atmospheric HULIS in our previous study (Fan et al., 2013). The relatively high content of benzyl methyl ether in atmospheric HULIS suggests that this substructure is an important constituent of atmospheric HULIS.

4. Environmental implications and conclusions

BB and fossil fuel combustion are believed to be the major source of atmospheric HULIS. In our previous study, we found many similarities and differences in the chemical properties of primary and atmospheric HULIS (Fan et al., 2016b). In the present study, the molecular structures of primary and atmospheric HULIS were investigated, and the results have provided a better understanding of the contributions of BB and coal combustion to atmospheric HULIS in terms of their molecular structures.

In this study, polysaccharide derivatives, N-containing compounds, lignin derivatives, aromatic acid methyl ester, aliphatic acid methyl ester, and diterpenoid derivatives were all identified following the thermochemolysis of primary and atmospheric HULIS. The types of pyrolysates and their distributions in primary HULIS were comparable to that of atmospheric HULIS in this and our previous study (Fan et al., 2013), and in other organic materials in atmospheric aerosols (Gelencser et al., 2000; Subbalakshmi et al., 2000; Zhao et al., 2009, 2012). This indicates that combustion processes including BB and coal combustion are significant sources of atmospheric HULIS.

However, there were many distinct differences among these HULIS fractions. As discussed previously, pyrolysates from primary HULIS emitted from BB and coal combustion were enriched with lignin derivatives, with distributions of 27.9%–84.0%, which was much higher than the 12.2% found in atmospheric HULIS. In contrast, aliphatic acid methyl esters only contributed 1.6%–8.5% to the total pyrolysates from the four types of primary HULIS, which was significantly lower than the 29.8% contribution among atmospheric HULIS. The relatively high content of aliphatic species in atmospheric HULIS suggested that other sources, such as secondary formation by the photochemical reactions of biomass volatile organic compounds, makes a significant contribution to atmospheric HULIS. Moreover, aromatic pyrolysates, including lignin derivatives and aromatic acid methyl ester, were the most important pyrolysates in all HULIS fractions, with total distributions ranging from 53.0% to 84.9% in the primary HULIS emitted from BB and coal combustion. This was much higher than the 32.3% content in atmospheric HULIS. The results suggest that primary HULIS significantly contributed to the aromatic structures in atmospheric HULIS. This was supported by the fact that a higher aromaticity has been reported in atmospheric HULIS in BB aerosols (Lin et al., 2010a; Fan et al., 2016b; Park and Yu, 2016) and ambient aerosols influenced by BB (Baduel et al., 2010; Song et al., 2012; Fan et al., 2016a).

Some molecular markers for specific sources were obtained from the thermochemolysis of primary and atmospheric HULIS. For example, polysaccharide derivatives, pyridine and pyrrole derivatives, and lignin derivatives can be used as tracers of fresh HULIS emitted from BB. Diterpenoid derivatives, which typically originate from the pyrolysis of conifer resin, are also important markers of HULIS from pine wood combustion sources. In terms of ambient HULIS studies in present work, some source apportionment information could be obtained based on these molecular markers. 1,6-anhydro- α -D-glucose, trimethyl ether was identified for ambient HULIS, indicating the apparent contributor from BB. A high distribution of methoxybenzoic acid, methyl ester was observed in the ambient HULIS, suggesting the significant BB contribution from pyrolysis of lignin-derived products. It is obvious that ambient HULIS also contain higher contents of dicarboxylic acids, dimethyl ester than primary HULIS fractions, suggesting the apparent characteristics of secondary oxidation. In addition, benzenedicarboxylic acid, dimethyl ester was abundant pyrolysates of ambient HULIS, indicating the

contribution of plastic-waste burnings and/or coal combustion. Overall, the present ambient HULIS has complex sources with significant sources of BB and secondary formation.

Some compounds identified among the pyrolysates from primary HULIS were absent in the pyrolysates from atmospheric HULIS. In contrast, some of the dominant pyrolysates in atmospheric HULIS were also absent in primary HULIS. These results suggest that the primary HULIS may undergo and/or take part in atmospheric processes to reconstruct the atmospheric macromolecular organic compounds, such as the HULIS fractions. For example, the lignin derived substructures in primary HULIS may be further decomposed and polymerized into macromolecular HULIS under a complex series of reactions in the atmospheric environment. In future studies, the oxidation or aging of primary WSOs in the atmospheric environment will be investigated, to better understand the chemical composition and the environmental effects of atmospheric HULIS.

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