Atmospheric
Chemistry
and Physics
Discussions

Comprehensive characterization of humic-like substances in smoke PM$_{2.5}$ emitted from the combustion of biomass materials and fossil fuels

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Abstract. Humic-like substances (HULIS) in smoke PM$_{2.5}$ emitted from the combustion of biomass materials (rice straw, corn straw, and pine branch) and fossil fuels (lignite coal and diesel fuel) were comprehensively studied in this work. The HULIS fractions were first isolated with a one-step solid phase extraction method and were then investigated with a series of analytical techniques: elemental analysis, total organic carbon analysis, UV-vis spectroscopy, excitation–emission matrix (EEM) fluorescence spectroscopy, Fourier transform infrared spectroscopy, and ^{1}H-nuclear magnetic resonance spectroscopy. The results indicated that HULIS accounted for a significant proportion of the particle matter, total carbon (TC), and water soluble organic carbon in smoke PM$_{2.5}$ emitted from the combustion of biomass materials and coal. This suggests that biomass burning and coal combustion are both important sources of HULIS in atmospheric aerosols. However, HULIS in diesel soot only accounted for ~0.8% of the soot particles, suggesting that vehicular exhaust may not be a significant primary source of HULIS. Primary HULIS and atmospheric HULIS display many similar chemical characteristics, as indicated by the instrumental analytical characterization, while some distinct features

Atmospheric
Chemistry
and Physics
Discussions

were also apparent. A high spectral absorbance in the UV-vis spectra, a distinct band at λex/λem ≈ 280/350 nm in EEM spectra, lower H/C and O/C molar ratios, and a high content of [Ar–H] were observed for primary HULIS. These results suggest that primary HULIS contains more aromatic structures, and a lower content of aliphatic and oxygen-containing groups than atmospheric HULIS. Among the four primary sources of HULIS, HULIS from BB had the highest O/C molar ratios (0.43–0.54) and [H–C–O] content (10%–50%), indicating that HULIS from this source mainly consisted of carbohydrate and phenolic like structures. HULIS from coal combustion had a lower O/C molar ratio (0.27), and a higher content of [H–C–C=] (40%) and [Ar–H] (31%), suggesting that aromatic compounds were extremely abundant in HULIS from this source.

1 Introduction

In recent decades, many studies have investigated the water soluble unresolved polyacidic compounds in atmospheric aerosols, rainwater, and fog/cloud samples (Zheng et al., 2013 and references therein). Due to their similarities to naturally occurring humic substances in terrestrial and aqueous environments, with regard to their complex physical and chemical properties, as revealed by techniques such as UV-vis spectroscopy, fluorescence spectroscopy, Fourier transform infrared (FTIR) spectroscopy, and nuclear magnetic resonance (NMR) spectroscopy, they are operationally defined as humic-like substances (HULIS) (Graber and Rudich, 2006;Zheng et al., 2013). HULIS are present ubiquitously in fine particles from urban, rural, marine, and biomass burning (BB) sources (Decesari et al., 2007;Salma et al., 2007;Lin et al., 2010b;Fan et al., 2012;Song et al., 2012;Zheng et al., 2013). They are believed to play important roles in several atmospheric processes, including light absorption, radiative forcing (Hoffer et al., 2006;Dinar et al., 2008), hygroscopicity, and cloud droplet formation (Dinar et al., 2007;Salma et al., 2008). Moreover, they are also reported to be harmful to human health (Lin and Yu, 2011).

Many field studies have suggested that HULIS are abundant in organic aerosols. They constitute a

Atmospheric
Chemistry
and Physics
Discussions

significant portion of the organic matter (OM) in atmospheric aerosols (up to about 30%) collected in urban and rural environments, and in aerosols produced by BB (Mayol-Bracero et al. 2002; Krivacsy et al. 2008; Lin et al. 2009, 2010). Their carbon (C) mass accounts for 9%−72% of the C content of water soluble organic carbon (WSOC) in atmospheric aerosols (Fan et al., 2012;Lin et al., 2010b;Krivacsy et al., 2008;Song et al., 2012;Feczko et al., 2007). These atmospheric HULIS materials are found ubiquitously in various environments, and are derived from various sources. Their possible sources include: biomass burning (BB) (Baduel et al., 2010;Lin et al., 2010a;Feczko et al., 2007), vehicular emissions (El Haddad et al., 2009), marine emissions (Krivacsy et al., 2008), the oxidation of soot (Decesari et al., 2002;Li et al., 2015;Li et al., 2013), and secondary processes via the transformation of gas and condensed-phase species by chemical reactions (Baduel et al., 2010;Salma et al., 2007;Salma et al., 2013).

Among the various sources listed above, BB is generally considered to be a significant source of atmospheric HULIS (Schmidl et al., 2008a;Schmidl et al., 2008b;Goncalves et al., 2010;Lin et al., 2010a;Lin et al., 2010b). HULIS fractions have been found in smoke particles emitted from wood and the combustion of leaves, which accounts for 0.57%−21.2% of the total mass of particles (Schmidl et al., 2008a;Schmidl et al., 2008b;Goncalves et al., 2010). Moreover, HULIS has also found to be abundant in fresh burning emissions from rice straw and sugar cane leaves, accounting for 7.6%−12.6% of the particle mass, 28%−34% of the organic C and about 30% of the WSOC (Lin et al., 2010a;Lin et al., 2010b). Unfortunately, these studies have only focused on the amount of HULIS emitted from BB, with their chemical properties and structures remaining unresolved.

In this study, smoke $PM_{2.5}$ emitted from the combustion of biomass materials (including rice straw, corn straw, and pine branch) and fossil fuels (including lignite coal and diesel fuel) were collected in a laboratory chamber. The HULIS fractions were isolated from these emitted particles by a solid phase extraction (SPE) method, and the chemical properties and structures were comprehensively investigated using total organic carbon (TOC) analysis, elemental analysis, UV-vis spectroscopy, excitation-emission

matrix (EEM) fluorescence spectroscopy, FTIR spectroscopy, and ^{1}H-NMR spectroscopy. To further understand the contributions of primary HULIS to atmospheric HULIS, the HULIS fractions isolated from ambient $PM_{2.5}$ collected in Guangzhou, China, were simultaneously studied and compared with the above primary HULIS. Moreover, the results obtained were also compared with those reported in

5 the literature for HULIS in various atmospheric environments. The information obtained will enable a better understanding of the chemical nature, as well as the environmental, health, and climate effects of primary HULIS from direct combustion emissions, and their contribution to atmospheric HULIS.

2 Experimental

10 ### 2.1 Sampling

In this study, five types of smoke $PM_{2.5}$ samples were collected to investigate the primary HULIS emitted from the combustion of biomass materials and fossil fuels. These were biomass smoke $PM_{2.5}$ samples emitted from the combustion of rice straw, corn straw and pine branch, and coal smoke $PM_{2.5}$ and diesel soot. Rice straw and corn straw were chosen primarily because rice and corn are the

15 dominant crops in China. The combustion of these crop straws is reported to have an important influence on the atmospheric aerosol in China (Streets et al., 2003;Zheng et al., 2006). These crop residues are usually burned in open locations by farmers during and after the harvest season, and are also used as cooking fuels in rural areas throughout the year. In addition, pine branch are also important biomass cooking fuel in rural areas of China and therefore may make a significant contribution to the

20 atmospheric aerosol in some regions. Therefore, samples of the smoke emitted from the combustion of these three biomass materials were used to study the BB derived HULIS. Samples of the smoke emitted from the combustion of coal and diesel fuel were also studied in this work. Coal was chosen because it has been reported that more than 68% of black carbon (BC) emissions in China are related to the use of coal (Cao et al., 2006). The combustion of coal is an important source of atmospheric aerosols in China.

25 In addition, the soot particles derived from the combustion of diesel fuel was also studied because

Atmospheric
Chemistry
and Physics
Discussions

vehicular emissions have been suggested to be a possible source of atmospheric HULIS (El Haddad et al., 2009).

In this study, samples of the smoke $PM_{2.5}$ emitted from the combustion of rice straw, corn straw, pine branch, and lignite coal were collected in a laboratory resuspension chamber. This sampling system included a combustion stove and two $PM_{2.5}$ samplers (Tianhong Intelligent Instrument Plant, Wuhan, China). The instrument is described in detail in Duan et al. (2012). Whatman quartz filters (Ø 90 mm) were used to collect $PM_{2.5}$ with the sampler at a flow rate of 100 L/min. For soot, a reference sample (SRM 2975) from the combustion of diesel fuel was purchased from the U.S. National Institute of Standards and Technology (Gaithersburg, MD, USA). It was emitted from a heavy-duty diesel engine and represents diesel fuel combustion from a vehicular exhaust.

In addition to the smoke $PM_{2.5}$ samples emitted directly from the combustion process, ambient $PM_{2.5}$ samples were also collected during December, 2015 in Wushan, Guangzhou, China. Detailed information regarding the sampling sites was provided in our previous studies (Fan et al., 2012;Song and Peng, 2009). These $PM_{2.5}$ samples were collected on Whatman quartz fiber filters (20.3 $\times$ 25.4 cm) using a high-volume air sampler at flow rates of 1.05 m^3/min (Tianhong Intelligent Instrument Plant, WuHan, China). All filters had been pre-baked at 450^oC for 4 h to remove all organic contaminants.

2.2 Isolation of HULIS

In this study, to obtain accurate results for TC, HULIS, WSOC, and other parameters, five filters for each type of sample were selected for analysis. The isolation of HULIS was performed by a one-step SPE procedure, which was applied in our previous study (Fan et al., 2012). Briefly, the filter samples were ultrasonically extracted with 40 mL of 18.2 MΩ Milli-Q water, and then the extract solutions were filtered with polytetrafluoroethylene (PTFE) membranes (pore size: 0.22 μm) to remove solid impurities and filter debris. The pH value of the filtrate was adjusted to 2 with HCl, and then 20 mL was introduced into a pre-conditioned SPE cartridge (Oasis HLB, 500mg, Waters, Milford, MA, USA). The

Atmospheric
Chemistry
and Physics
Discussions

exposed column was rinsed with water to remove inorganics and dried in a freeze-drier. Finally, the retained organics were eluted with methanol and the eluate was evaporated to dryness under a gentle nitrogen stream. Later, according to the requirements of TOC, UV-vis spectroscopy, and EEM fluorescence spectroscopy analysis, the resulting HULIS samples were re-dissolved in 20 mL of Milli-Q water. Moreover, more filters were used to obtain enough HULIS for the analysis of the elemental composition, as well as FTIR and ^{1}H NMR spectrometry.

2.3 Analysis

2.3.1 Total carbon (TC) and TOC analysis

The TC content of smoke $PM_{2.5}$ was measured directly on 2 cm^2 punches of the particle filters using an elemental analyzer (Elementar Vario EL CUBE, Hanau, Germany), following a standard high-temperature combustion procedure. A replicate analysis was also conducted for accuracy. The TOC in HULIS and WSOC were measured using a high-temperature catalytic oxidation instrument (Shimadzu – TOC –VCPH analyzer, Shimadzu, Kyoto, Japan) following the non-purgeable organic carbon protocol. The concentrations of all chemically measured species were corrected for their respective blank concentration.

2.3.2 Elemental composition

Elemental composition (C, H, N) of the isolated HULIS was measured with an elemental analyzer following a standard high temperature combustion procedure. A portion of the HULIS (re-dissolved in methanol) was transferred into a pre-cleaned tin capsule of known weight. Then, the sample was dried under vacuum. The mass of the dried organic matter (OM) in the tin capsule was determined using a micro balance, with a resolution of 0.01 μg (Sartorius, Göttingen, Germany), and then the tin capsule was placed into the elemental analyzer. In the instrument, the C, H, and N content of the OM were determined by catalytic burning in oxygen at 1020°C, followed by chromatographic separation of the

Atmospheric
Chemistry
and Physics
Discussions

oxidation products and thermoconductivity detection. The elemental analyzer was calibrated with an acetanilide standard. Based on the analyses of triplicates for each sample, the calculated relative standard deviation was less than 3%. The O content was calculated as the rest of the mass, by assuming that the concentrations of other possible elements (e.g., sulfur, phosphorus) were negligible: O% = 100

5 − (C+H+N)%.

2.3.3 UV–visible spectroscopy

About 3 mL of HULIS and WSOC solution were placed in a 1 cm quartz cuvette and scanned from 200 to 700 nm using a UV-vis spectrophotometer (Lambda 850, Perkin Elmer, Waltham, MA, USA).

10 Milli-Q water was used as a blank reference and to obtain the baseline. The absorption index, specific absorbance at 254 nm (SUVA254) and absorptivity ratios between 250 and 365 nm (E_{250}/E_{365}) were used to characterize the optical properties of HULIS and WSOC, with the details reported in our previous studies (Fan et al., 2012;Fan et al., 2016).

2.3.4 EEM fluorescence spectroscopy

15 The fluorescence spectra of each HULIS sample were recorded on a spectrophotometer (F-2700, Hitachi, Tokyo, Japan), using a 1 cm path-length quartz cuvette. Excitation and emission wavelength ranges were set from 210 to 400 nm and 230 to 510 nm, respectively, and their scanning intervals were all set at 5 nm. The excitation and emission slit widths were fixed at 5 nm and the scan speed was set at

20 1500 nm/min. The peaks due to water Raman scatter were eliminated from all sample EEMs by subtracting the Milli-Q water blank EEMs.

2.3.5 FT-IR Spectrometry

The FTIR spectra (4000–400 cm^{-1}) of HULIS were recorded at room temperature using an FTIR

25 spectrometer (Vertex-70, Bruker, Mannheim, Germany). About 1 mg of HULIS (re-dissolved in

Atmospheric
Chemistry
and Physics
Discussions

methanol) was first mixed with 60 mg of KBr, and then dried in a freeze dryer. Finally, the above

mixture was grated and pressed into pellets for analysis. For each measurement, 64 scans were collected

at a resolution of 2 cm^{-1}.

5   ## 2.3.6 ^{1}H-NMR spectroscopy

About 10 mg of dried HULIS were re-dissolved in 1 mL of MeOD. The ^{1}H NMR spectra were

recorded on a 400 MHz NMR spectrometer (Avance III, Bruker). For each sample, 128 scans were

collected, resulting in an analysis time of approximately 1 h. The identification of functional groups in

the NMR spectra was based on their chemical shift (δH) relative to that of sodium

10   3-trimethylsilyl-2,2,3,3-d_4-propanoate (δH= 0 ppm), which was used as an internal standard.

3 Results and discussion

3.1 The abundance of HULIS in smoke PM$_{2.5}$ and ambient PM$_{2.5}$

The average abundance of the HULIS fractions and their contributions to particle matter (PM), TC,

15   and WSOC in smoke PM$_{2.5}$ emitted from the combustion of biomass materials, fossil fuels, and in

ambient PM$_{2.5}$ are shown in Table 1. It can be seen that the mass of the HULIS fractions accounted for

11.2–23.4% of the PM in smoke PM$_{2.5}$ emitted from BB, which is comparable to the results for BB

reported by Lin et al. (2010). It is worth noting that the highest HULIS abundance (23.4 $\pm$ 5.5%) was

detected in rice straw smoke PM$_{2.5}$, which is about double the 12.4% reported for similar samples by

20   Lin et al. (2010). These differences may be ascribed to their different combustion conditions and

sampling methods. The abundance of HULIS in rice straw smoke PM$_{2.5}$ (10.7 $\pm$ 0.8%) was also

significantly higher than in ambient PM$_{2.5}$ in this study, and in some previous studies (as listed in Table

1). The abundance of HULIS in smoke PM$_{2.5}$ emitted from the combustion of corn straw and pine

branch (11.2 $\pm$ 7.5% and 11.4 $\pm$ 3.8%, respectively) was significantly lower than in smoke PM$_{2.5}$ from

25   rice straw. This was similar to the results for ambient PM$_{2.5}$ in this study and values reported by Lin et al

Atmospheric
Chemistry
and Physics
Discussions

(2010), although they were higher than the 6.7% reported by Salma et al. (2007) and an annual observation (5.4%) in the same location, reported in our previous study (Fan et al., 2016).

In comparison with the three BB smoke $PM_{2.5}$ samples, the relative contribution of HULIS in coal smoke $PM_{2.5}$ was relatively low ($5.3 \pm 0.4\%$). This was significantly lower than the level in $PM_{2.5}$ in this study and that reported by Lin et al (2010), but was similar to the annual average result (5.4%) for ambient $PM_{2.5}$ in our previous study (Fan et al., 2016). According to data reported by Cao et al. (2006), more than 68% of BC emissions in China are related to the use of coal. Therefore, it is expected that coal combustion is an important primary source of atmospheric HULIS. It is noteworthy that HULIS only accounts for ~0.8% of diesel soot, suggesting that the primary source of atmospheric HULIS from vehicle exhaust may be negligible. Because the abundance of HULIS in diesel soot were so low, it was difficult to characterize this HULIS fraction.

As an important carbonaceous component, the C content of HULIS (HULIS-C) in smoke $PM_{2.5}$ particles emitted from the combustion of rice straw, corn straw, and pine branch accounted for 21.7 ± 4.0, 14.7 ± 6.9, and $8.0 \pm 2.9\%$ of the TC, respectively. These results are very consistent with the results reported for BB in previous studies (Goncalves et al., 2010;Schmidl et al., 2008a;Schmidl et al., 2008b;Lin et al., 2010b). The HULIS-C in coal smoke $PM_{2.5}$ was $5.2 \pm 0.3\%$, which was significantly lower than that ($22.6 \pm 3.7\%$) in ambient $PM_{2.5}$. The contribution of HULIS-C to the TC of diesel soot was about 0.7%, which was similar to the 1.0%−1.3% reported for vehicular exhaust in El Haddad et al. (2009). These very low HULIS-C/TC ratios also suggest that the primary vehicular exhaust source for atmospheric HULIS may be negligible.

It is well known that HULIS is an important component in WSOC. In this study, the contribution of HULIS to WSOC was investigated by the determination of TOC and UV-vis absorbance at 250 nm (UV250), respectively. As indicated in Table 1, the HULIS-C/WSOC ratios in the five types of smoke $PM_{2.5}$ were 45.5%−66.1% (TOC, %) and 58.3%−79.5% (UV250, %), indicating that HULIS was the major component in WSOC for the samples studied here. These percentages lie within the range of

Atmospheric
Chemistry
and Physics
Discussions

19%−72% that has been reported for fine aerosols in many earlier studies (as listed in Table 1). Although relatively high HULIS-C/WSOC ratios were observed for all of the different smoke $PM_{2.5}$ particles, some differences were apparent. The HULIS-C/WSOC for the three types of biomass smoke $PM_{2.5}$ was 56.9%−66.1 and 68.1%−79.5%, as determined by TOC and UV250, respectively. They are similar to the values obtained for atmospheric HULIS in this study, at 60.7 and 70.7%, respectively. These results are also comparable with those reported for ambient aerosols (Zheng et al., 2013 and references therein). The HULIS-C/WSOC was relatively low for coal smoke $PM_{2.5}$, at 45.5 and 64.4%, as determined by TOC and UV250, respectively. For the diesel soot, despite the very low HULIS-C/TC, the HULIS/WSOC for diesel soot was relatively high, at 62.3 and 58.3% as determined by TOC and UV250, respectively. It should be noted that the values of HULIS-C/WSOC determined by UV250 were mostly higher than those obtained by TOC. These differences have been derived from similar measurement methods and have been reported in many previous studies (Fan et al., 2012;Baduel et al., 2009), mainly as the result of the enrichment of highly conjugated π bond compounds in HULIS fractions. A more detailed explanation is given in section 3.3.

3.2 Elemental composition

The elemental compositions (C, H, N, and O) of HULIS in smoke $PM_{2.5}$ from the combustion of rice straw, corn straw, pine branch, and coal, and in ambient $PM_{2.5}$ are shown in Table 2. The mean C, H, N, and O contents for the primary HULIS samples were 52.9%−66.1, 5.5%−7.1, 2.0%−4.1, and 23.6%−38.3%, respectively, by mass. This indicates the dominance of C and O, which together contributed 89.7%−91.4% of the total mass. These results are comparable with those for atmospheric HULIS in this and other previous studies (Krivacsy et al., 2001;Kiss et al., 2002;Duarte et al., 2007;Salma et al., 2007;Song et al., 2012;Fan et al., 2013).

Only a limited amount of information regarding the different HULIS could be obtained from the elemental composition data, but more qualitative information was obtained by an examination of the

Atmospheric
Chemistry
and Physics
Discussions

O/C, H/C, and N/C molar ratios. These atomic ratios are often used to describe characteristic and structural changes of organic macromolecules (Duarte et al., 2007;Salma et al., 2007;Fan et al., 2013). The O/C molar ratios for the primary HULIS ranged from 0.27 to 0.54, indicating the existence of O containing functional groups. However, these ratios were significantly lower than 0.61–0.68 for the

5   standard fulvic acids of the International Humic Substances Society (Duarte et al., 2007), indicating that primary HULIS was less oxidized when compared to the fulvic acids. Among the four types of primary HULIS, the O/C ratios of the three types from BB were in the range of 0.43–0.54, which were comparable with data (0.41–0.76) for atmospheric HULIS reported here and in previous studies (Kiss et al., 2002;Krivacsy et al., 2001;Song et al., 2012;Salma et al., 2007;Duarte et al., 2007;Fan et al., 2013).

10   The O/C ratio of HULIS in coal smoke $PM_{2.5}$ was 0.27, which was significantly lower than for atmospheric HULIS samples. These results suggest that HULIS in the fresh coal smoke $PM_{2.5}$ could be regarded as less oxidized than HULIS in ambient aerosols. The H/C and N/C molar ratios of the four primary types of HULIS were in the ranges of 1.15 to 1.43 and 0.03 to 0.06, respectively, with both being similar to the results for atmospheric HULIS (Table 2).

15   As shown in Table 2, the ratio of OM to organic C (OM/OC) mass ratios of the four types of primary HULIS ranged from 1.51 to 1.89, which were generally similar to the data (1.71–2.28) reported for atmospheric HULIS in here and previous studies (Kiss et al., 2002;Krivacsy et al., 2001;Song et al., 2012;Salma et al., 2007;Duarte et al., 2007;Fan et al., 2013). The OM/OC ratio of HULIS in coal smoke $PM_{2.5}$ particles was 1.51, which was slightly lower than in HULIS in the BB smoke $PM_{2.5}$ particles,

20   indicating that the primary HULIS in coal smoke $PM_{2.5}$ particles contained more organic C and unsaturated components.

In summary, the four types of primary HULIS among the smoke $PM_{2.5}$ samples had many similarities, in terms of its elemental composition, to atmospheric HULIS samples. However, there were also some distinct differences. The HULIS samples in the three types of biomass smoke $PM_{2.5}$ had a

25   relatively lower C content, higher O content, higher O/C molar ratio, and higher OM/OC ratio than in

Atmospheric
Chemistry
and Physics
Discussions

coal smoke $PM_{2.5}$. These results indicated that the HULIS in BB smoke contained a relatively higher content of O-containing components and a relatively lower content of unsaturated structures. In contrast, the HULIS in coal smoke had a relatively lower content of O-containing components and a higher content of unsaturated structures. On the other hand, no significant differences were observed among

5   the three types of primary HULIS in the smoke $PM_{2.5}$ from BB.

3.3 UV-vis properties

UV-vis absorbance has been widely used to characterize the properties of organic matter in soils, waters, and atmospheric systems. Figure 1 shows the UV-vis spectra of the four primary types of

10   HULIS in smoke $PM_{2.5}$ emitted from BB and coal combustion, and one atmospheric HULIS sample from ambient $PM_{2.5}$. The spectra were all normalized by the C content of HULIS to avoid the effects of different concentrations and were easily compared with each other. As shown in Figure 1, the UV-vis spectra of all HULIS fractions were featureless, while they displayed a generally decreasing absorbance as the wavelength increased. Such spectra are similar to the typical UV-vis spectra of

15   atmospheric HULIS in previous studies (Fan et al., 2012;Baduel et al., 2009, 2010;Krivacsy et al., 2008;Duarte and Duarte, 2005;Havers et al., 1998;Kiss et al., 2002;Duarte et al., 2005;Varga et al., 2001) and in naturally occurring humic substances (Peuravuori and Pihlaja, 1997;Domeizel et al., 2004;Traina et al., 1990;Chen et al., 2002). These results suggest that the primary HULIS in smoke $PM_{2.5}$ has a similar chemical structure to HULIS in atmospheric aerosols.

20   Although the spectra appeared to be broad and featureless, some differences in the absorption intensity were apparent. The spectra obtained for the four types of primary HULIS in smoke $PM_{2.5}$ exhibited a higher normalized absorbance in shorter wavelength regions, and less absorbance in the longer wavelength regions than atmospheric HULIS. A clear shoulder in the region 250 to 300 nm was observed in the spectra of primary HULIS fractions in smoke $PM_{2.5}$ emitted from BB and coal

25   combustion. This is generally attributed to π-π^* electron transitions in moieties containing C=C and

Atmospheric
Chemistry
and Physics
Discussions

C=O double bonds, and is also a characteristic of fulvic acids (Peuravuori and Pihlaja, 1997;Domeizel et al., 2004). These results suggest that the primary HULIS in smoke $PM_{2.5}$ may contain a higher concentration of polycyclic aromatic and conjugated compounds than ambient HULIS.

Among of the four types of primary HULIS, HULIS in smoke $PM_{2.5}$ emitted from corn straw burning had a higher normalized UV-vis absorbance in the overall spectra than the other primary HULIS fractions. HULIS in coal smoke had a lower normalized absorbance than the other types of primary HULIS, and was even much lower than that for atmospheric HULIS in the region of 350 to 535 nm, with its absorbance mainly focused in region of 235 nm to 385 nm. This may suggest that polycyclic aromatic and/or conjugated compounds are the most important components in this type of HULIS, and was in strong agreement with the results obtained from the ^{1}H NMR analysis.

The ($SUVA_{254}$) and (E_{250}/E_{365}) have been found to be correlated with molecular weight and aromaticity in natural occurring humic acids (Peuravuori et al., 2001;Fuentes et al., 2006;Chen et al., 2002). They have also been successfully used to characterize HULIS in atmospheric aerosols (Duarte and Duarte, 2005;Fan et al., 2012;Baduel et al., 2009, 2010;Krivacsy et al., 2008;Duarte et al., 2005). In this study, these parameters were used to perform comparisons between HULIS in smoke $PM_{2.5}$ and in ambient $PM_{2.5}$, with the results shown in Table 3. The $SUVA_{254}$ values of primary smoke HULIS samples ranged from 3.7 to 3.9 L (m mgC)$^{-1}$, which was higher than the value of the atmospheric HULIS fractions obtained in this study and our previous studies (Fan et al., 2016;Fan et al., 2012). These results indicate that the primary HULIS contained higher aromatic degree and/or higher molecular weight conjugated compounds. In this study, the E_{250}/E_{365} ratios were 5.8 $\pm$ 0.5, 4.5 $\pm$ 0.2, 4.4 $\pm$ 0.3, and 14.7 $\pm$ 0.7 for primary HULIS emitted from the combustion of rice straw, corn straw, pine branch, and coal, respectively. The E_{250}/E_{365} ratio generally exhibits a negatively relationship with the aromaticity or molecular weight of humic-like substances (Fan et al., 2012). The E_{250}/E_{365} ratios of primary HULIS in smoke $PM_{2.5}$ from BB were in the range of 2.9–8.9, which corresponded to that of atmospheric HULIS in this study and previous studies.

There were also some distinct features among the different types of primary HULIS in terms of their UV-vis properties. No significant differences in $SUVA_{254}$ were identified among the primary HULIS from the combustion of rice straw, corn straw, pine branch, and coal. However, the E_{250}/E_{365} ratios of the four types of primary HULIS ranged from 4.4 to 14.7, with the highest values for the

5 HULIS from coal combustion. It was noteworthy that the E_{250}/E_{365} ratio of HULIS in coal soot was 14.7, which was much higher than for the HULIS in biomass smoke $PM_{2.5}$ and in atmospheric $PM_{2.5}$, but the $SUVA_{254}$ value was in a similar range for all of these types of HULIS. Therefore, caution should be expressed when using just the spectra parameter of E_{250}/E_{365} for the characterization of HULIS.

10 **3.4 Fluorescence properties**

Fluorescence spectroscopy has been used as a technique for classifying and distinguishing between humic substances of various origins and natures. It has been widely applied to characterize HULIS in atmospheric aerosols (Santos et al., 2009;Santos et al., 2012;Duarte et al., 2004). Figure 2 shows the EEM fluorescence spectra of HULIS in smoke $PM_{2.5}$ from BB and coal combustion, and in ambient

15 $PM_{2.5}$. To avoid concentration effects, the fluorescence spectra were normalized by the WSOC content of HULIS, and are shown here as specific fluorescence intensities (a.u.L/(gC)).

As shown in Figure 2, the four types of primary HULIS in smoke $PM_{2.5}$ have similar fluorescence features, with two main types of fluorophores at $\lambda_{ex}/\lambda_{em} \approx$ (245–255)/(420–435) nm (peak A) and $\lambda_{ex}/\lambda_{em} \approx$ (265–290)/(335–370) (peak B). Bands in the same range as peaks A and B have been already

20 identified in the EEM fluorescence spectra of water-soluble organic matter from rainwater (Santos et al., 2009;Santos et al., 2012;Kieber et al., 2006), fogwater (Birdwell and Valsaraj, 2010), and atmospheric aerosols (Duarte et al., 2004), and have been assigned to fulvic-like and protein-like fluorophores (Kieber et al., 2006), respectively. Our results indicate that the primary HULIS fractions had similar fulvic-like and protein-like organic fractions to atmospheric HULIS (Duarte et al., 2004;Santos et al.,

25 2009;Santos et al., 2012). However some differences in peak A and B were identified between the four

Atmospheric
Chemistry
and Physics
Discussions

types of primary HULIS and the atmospheric HULIS. For peak A, the Ex/Em wavelengths in the EEM fluorescence spectra of primary HULIS had peaks at longer excitation and emission wavelengths ($\lambda_{ex}/\lambda_{em} \approx$ (245–255)/(420–435) nm) than those ($\lambda_{ex}/\lambda_{em} \approx$ 245/405 nm) of atmospheric HULIS. This suggests that primary HULIS fractions contain more aromatic structures and condensed unsaturated bond systems, but fewer aliphatic structures (Krivacsy et al., 2008;Duarte et al., 2004;Graber and Rudich, 2006;Santos et al., 2009;Peuravuori et al., 2002). For peak B, the four types of primary HULIS all had a protein-like fluorescence band at a similar λex/λem in the EEM fluorescence spectra. In all four types of primary HULIS the band was clearly stronger than the band in ambient HULIS described in this and previous studies (Santos et al., 2009;Santos et al., 2012;Duarte et al., 2004). Our results indicate that these four types of primary HULIS contain mostly low molecular weight compounds, such as protein-like, phenol-like, and aromatic amino acids (Peuravuori et al., 2002;Coble, 1996;Kieber et al., 2006;Duarte et al., 2004).

Compared to the ambient HULIS in this and previous studies (Santos et al., 2009;Santos et al., 2012;Duarte et al., 2004), a distinct band at $\lambda_{ex}/\lambda_{em} \approx$ 295/405 nm (peak C), which is generally attributed to humic-like compounds (Coble and Green, 1990;Coble, 1996) was not present in the EEM fluorescence spectra of primary smoke HULIS. This peak C is normally identified in naturally occurring humic acids and atmospheric HULIS, and has been assigned to marine humic-like compounds (Santos et al., 2009;Santos et al., 2012;Duarte et al., 2004;Kieber et al., 2006;McKnight et al., 2001). Peak C only occurred in EEMs of atmospheric HULIS, which suggests marine sources were also an important contributor to HULIS in atmospheric aerosols in the Pearl River Delta (PRD) region (Fan et al., 2016;Lin et al., 2010a).

3.5 FTIR spectroscopy

The FTIR spectra of the HULIS in smoke $PM_{2.5}$ emitted from the combustion of rice straw, corn straw, pine branch, and coal, and in ambient $PM_{2.5}$ were within the region of 4000–1000 cm^{-1}, as shown

Atmospheric
Chemistry
and Physics
Discussions

in Figure 3. All spectra were characterized by a number of absorption bands, exhibiting variable relative intensities, which is typical of humic(-like) materials (Duarte et al., 2007;Senesi et al., 1989;Havers et al., 1998). As shown in Figure 3, the spectra of primary HULIS were similar to those of the atmospheric HULIS and WSOC in this and previous studies (Fan et al., 2013;Krivacsy et al., 2001;Duarte et al.,

5   2005;Kiss et al., 2002;Havers et al., 1998;Polidori et al., 2008;Santos et al., 2009). The interpretation of these spectra was based on the assignments given in the literature referred to above for humic(-like) substances, resulting in the major characteristic bands that are marked in Figure 3, with the corresponding assignments listed in Table 4.

      As shown in Figure 3, the FTIR spectra of the four types of primary HULIS fractions

10   predominantly exhibit the presence of O-containing functional groups, aliphatic C-H groups, and aromatic ring groups, with the majority of the valence vibrations also being characteristics. The broad and strong band centered at around 3420 cm^{-1} is generally attributed to the OH stretching of phenol, hydroxyl, and carboxyl groups. The strong band near 1720 cm^{-1} is usually assigned to C=O stretching, mainly of carboxyl groups. However, to a lesser extent, ketonic and/or aldehydic C=O groups can also

15   give rise to absorption near this wavenumber, and their contribution should not be neglected. Some bands were also displayed near 1610 and 1637 cm^{-1}, indicating the presence of aromatic groups. These results suggest that primary smoke HULIS are complex compounds, mainly containing aliphatic chains, carboxylic groups, and aromatic groups. These FTIR spectra features are similar to those of the atmospheric HULIS described in this and other studies (Fan et al., 2013;Krivacsy et al., 2001;Duarte et

20   al., 2005;Song et al., 2012).

      There were many discriminatory characteristics between primary HULIS and atmospheric HULIS. The weak band at 1610 cm^{-1} is generally attributed to the C–C stretching of aromatic rings (Watanabe and Kuwatsuka, 1992), and was observed in spectra of primary HULIS from direct combustion emissions. However, it was absent in the FTIR spectra of atmospheric HULIS fractions in this and some

25   previous studies (Fan et al., 2013;Duarte et al., 2005;Krivacsy et al., 2001). This indicates that more

Atmospheric
Chemistry
and Physics

Open Access

EGU

Discussions

aromatic rings are present in the primary HULIS from BB and coal combustion than in atmospheric HULIS. In addition, the bands near 1516 and 1115 cm^{-1}, which are ascribed to the stretching vibrations of aromatic C=C and C–O bonds, were apparent in spectra of primary HULIS from BB, but absent from the atmospheric HULIS in this and some other studies (Fan et al., 2013;Santos et al., 2009;Santos et al.,

5   2012). Because these wavenumber regions are often typically displayed in the spectra of lignin, they can be used as a marker to reflect BB contributions to atmospheric HULIS. For example, this band has been observed in the FTIR spectra of atmospheric HULIS in the autumn and winter seasons, when HULIS is likely to be significantly influenced by BB (Duarte et al., 2005;Duarte et al., 2007). Simultaneously, a relatively strong band at 1045 cm^{-1} was found in the spectra of primary HULIS from BB, which is often

10   attributed to the C–O bond stretching of polysaccharides (Havers et al., 1998), and is also a characteristic of BB sources.

There were also some discriminatory differences between the primary HULIS fractions in the minor bands, and in the shape and intensity of the major bands in the 2000–1000 cm^{-1} region of FTIR spectra. As shown in Figure 3, relatively sharper and stronger peaks at 1637, 1610, 1458, and 1385 cm^{-1}

15   were displayed in the spectra of HULIS fractions in smoke PM$_{2.5}$ from coal combustion than those from BB. These results indicated that coal smoke HULIS consisted of more aromatic structures. It was noteworthy that additional peaks at 3160 and 1400 cm^{-1} were observed in the spectra of HULIS from the burning of corn straw. They are related to the stretching of C–O and O–H bonds (Chen et al., 2002;Watanabe and Kuwatsuka, 1992), indicating that there were more oxygenated phenolic structures

20   in the HULIS from corn straw burning. This is consistent with the results derived from the elemental analysis, in which a higher O/C molar ratio was obtained for HULIS from corn straw burning. One distinct feature of the primary HULIS from BB was the occurrence of one sharper and stronger peak at 1516 cm^{-1} on the FTIR spectra. This band is generally assigned to stretching vibrations of aromatic C=C bonds and C–O bonds, and is often observed in the spectra of compounds derived from lignin

25   (Watanabe and Kuwatsuka, 1992;Duarte et al., 2003;Santos et al., 2000). Consequently, primary HULIS

from BB displayed the characteristic of containing a lignin-like structure in its molecules, which can be seen as an important indicator of a BB source.

3.6 ^{1}H-NMR spectroscopy

^{1}H NMR spectroscopy can provide useful information regarding the major organic functional groups of natural organic matter, and has been successfully used to measure the water soluble HULIS fraction in aerosol, fog, cloud, and rain water (Fan et al., 2013;Ziemba et al., 2011;Song et al., 2012;Decesari et al., 2000;Graham et al., 2002;Decesari et al., 2005;Decesari et al., 2007). Figure 4 shows the ^{1}H NMR spectra of the four types of primary HULIS in smoke $PM_{2.5}$ emitted from the combustion of rice straw (a), corn straw (b), pine branch (c), and lignite coal (d), and atmospheric HULIS in ambient $PM_{2.5}$ (e). The four types of primary HULIS displayed similar spectra to the atmospheric HULIS spectra in this and other studies (Fan et al., 2013;Ziemba et al., 2011;Song et al., 2012;Decesari et al., 2000;Graham et al., 2002;Decesari et al., 2005;Decesari et al., 2007).

As shown in Figure 4, compared with the atmospheric HULIS, more distinct sharp signals of organic species could be seen in the ^{1}H NMR spectra of primary HULIS. According to the results of Fan et al. (2012), some low molecular weight organic compounds (e.g., suberic, 3,5-dihydroxybenzoic, and phthalic acids) are generally present in isolated HULIS fractions. Thus, these sharp peaks in the ^{1}H NMR spectra of primary HULIS can be ascribed to low molecular weight organic species in the smoke $PM_{2.5}$. The relatively few and/or weak sharp peaks in the ^{1}H NMR spectra of atmospheric HULIS may be the result of low molecular weight organic compounds that have been removed by oxidation or transformed to HULIS. Among these sharp signals, a limited number of resonances could be attributed to specific organic species by comparison with previous studies (Cavalli et al., 2006;Chalbot et al., 2014;Decesari et al., 2000;Decesari et al., 2001;Matta et al., 2003;Suzuki et al., 2001). For example, some sharp resonances occurred between 3.5–3.8 ppm in the spectra of HULIS in the smoke $PM_{2.5}$ from BB, and could attributed to the occurrence of levoglucosan (Chalbot et al., 2014;Matta et al., 2003). The

Atmospheric
Chemistry
and Physics
Discussions

relatively high abundance of signals between 6.5–8.5 ppm could ascribed to aromatic structures, such as substituted phenols and alkylbenzenes (around 6.6–7.0 ppm), benzoic acids, esters, and nitroaromatics (Suzuki et al., 2001;Chalbot et al., 2014). The sharp resonances around 7.6 and 8.0 ppm displayed in the spectra of HULIS emitted from coal combustion could be assigned to phthalic and terephthalic acids, respectively (Suzuki et al., 2001;Chalbot et al., 2014).

Although some sharp peaks were identified above, most of the signals in the spectra of all HULIS fractions appeared as a continuous unresolved distribution. This suggests that HULIS consists of a complex mixture of organic substances (Fan et al., 2013;Song et al., 2012;Samburova et al., 2007;Decesari et al., 2005;Decesari et al., 2007;Cavalli et al., 2006). The integrated ^{1}H NMR signal over specific ranges of chemical shift has been used previously to quantify the contribution of organic functional groups in HULIS from atmospheric aerosols, fog, and rain samples (Fan et al., 2013;Song et al., 2012;Santos et al., 2012;Decesari et al., 2005;Miller et al., 2009). Accordingly, four main regions of chemical shifts were assigned and integrated in the spectra: $\delta H = 0.6$–2.0 ppm (aliphatic protons in alkyl chains, [H–C]); $\delta H = 2.0$–3.2 ppm (aliphatic protons attached to C atoms adjacent to a carbonyl or aromatic group [H–C–C=]); $\delta H = 3.4$–4.4 ppm (protons on C atoms singly bound to O or other heteroatoms, indicative of protons associated with carbohydrates, ethers, or esters, [H–C–O]); and $\delta H = 6.5$–8.5 ppm (aromatic protons, [Ar–H]). It is worth noting that a few distinct weak peaks between 9 and 10 ppm were observed in the primary HULIS in fresh soot particles, and can be attributed to aldehydic protons, H–C=O (Ziemba et al., 2011). However, they were absent in the atmospheric HULIS in this and other studies (Fan et al., 2013;Song et al., 2012;Samburova et al., 2007;Decesari et al., 2005;Decesari et al., 2007;Cavalli et al., 2006). This region only accounts for a minor fraction (<2%), and therefore was not considered further.

Table 5 shows the distribution of the four types of protons described above, estimated from the area of the observed ^{1}H NMR regions for different HULIS samples. The four types of primary HULIS in fresh smoke particles contained a relatively high content of R-H (27%–45%), H–C–C= (22%–40%),

and Ar–H (19%–31%) groups, and a relatively low content of the H–C–O group (2-19%). These four

functional groups have also been observed in the ^{1}H NMR spectra of atmospheric HULIS in this and

other studies. They usually contain a relatively high signal for two bonds, aliphatic protons and aliphatic

protons linked to C atoms adjacent to C=C or C=O, and a relatively low signal for the two bonds of [H–

5   C–O] and [Ar–H] (Fan et al., 2013;Song et al., 2012;Decesari et al., 2007). It was clear that the relative

content of Ar–H groups in primary HULIS was significantly higher than that in atmospheric HULIS.

This suggests that primary HULIS contained more aromatic structures, which is consistent with the

elemental composition, UV-vis spectra, EEM fluorescence spectra, and FTIR spectra results.

Although similarities existed, some differences were also observed between the primary HULIS

10   from coal combustion and BB. As shown in Table 5, there was a relatively higher content of [H–C–C=]

(40%) and [Ar–H] (31%) in HULIS from coal combustion than from BB, indicating that the primary

HULIS in coal smoke contained more aromatic structural groups. In addition, the content of [H–C–O]

in HULIS from coal combustion was only 2%, which was significantly lower than in HULIS from BB.

As described above, the [H–C–O] group was assigned to protons associated with carbohydrates and

15   ethers. Therefore, these differences could be ascribed to the fact that the HULIS from BB contained a

relatively high content of carbohydrate derived compounds. The lower molar O/C and mass OM/OC

ratios, and lower intensity of peaks at 1516 and 1045 cm^{-1} and higher intensity of peaks at 1637, 1610,

1458, and 1385 cm^{-1} in the FTIR spectra of HULIS from coal burning all support this finding. For the

HULIS from BB, a relatively high content of [C–H] and low content of [H–C–C=] and [Ar–H] were

20   observed for HULIS from pine branch combustion when compared to the HULIS from rice straw and

corn straw combustion. These results suggest that the primary HULIS from crop straw combustion

contained more aromatic protons and fewer aliphatic protons than the HULIS from pine branch

combustion.

25   **3.7 Comparison of primary HULIS in smoke PM$_{2.5}$ with atmospheric HULIS in ambient PM$_{2.5}$**

aerosols

As reported in many previous studies (Baduel et al., 2010;Lin et al., 2010a;Feczko et al., 2007;El Haddad et al., 2009), combustion processes such as BB and vehicle engines are generally accepted as significant sources of atmospheric HULIS. In the study, the abundance, chemical composition, and structure of HULIS in smoke $PM_{2.5}$ from the combustion of rice straw, corn straw, pine branch, coal, and diesel fuel were systematically investigated and compared with those in atmospheric aerosols. Some similarities and differences between primary HULIS and atmospheric HULIS were identified. These results may be useful to better understanding the contributions of primary HULIS fractions to the bulk HULIS in atmospheric aerosols.

3.7.1 Similarities between primary and atmospheric HULIS

Many similarities were observed between primary and atmospheric HULIS. The results of an elemental analysis showed that C and O were the dominant elements among the four types of primary HULIS, and the results were comparable with those for atmospheric HULIS. In addition, the O/C, H/C, and N/C molar ratios for the primary HULIS were similar to the data for atmospheric HULIS. These findings indicate that the primary HULIS had a similar chemical composition to atmospheric HULIS.

Many similarities in chemical properties and structures were detected by UV-vis, EEM fluorescence, FTIR, and ^{1}H NMR spectroscopy. For example, the UV-vis spectra of the four types of primary HULIS and atmospheric HULIS were all characterized by features that indicated the absorbance decreased as the wavelength increased. For the EEM fluorescence spectra, two main peaks assigned to fulvic-like (peak A) and protein-like (peak B) fluorophores were not only observed in the EEM spectra of primary HULIS in smoke $PM_{2.5}$, but were also found in the EEM spectra of atmospheric HULIS. These data suggest that primary HULIS fractions may contribute significant fulvic-like and protein-like organic fractions to atmospheric HULIS. The FTIR spectra of the four primary HULIS in smoke $PM_{2.5}$ were similar to those of atmospheric HULIS. They were exhibited

Atmospheric
Chemistry
and Physics
Discussions

predominantly the presence of O-containing functional groups, aliphatic C–H groups and aromatic ring groups. In the case of the ^{1}H NMR analysis, the spectra of the four types of primary HULIS in smoke PM$_{2.5}$ also displayed similar spectra to atmospheric HULIS. Four main regions of chemical shifts, assigned to [H–C], [H–C–C=], [H–C–O] and [Ar–H] in the primary HULIS, were found in the ^{1}H NMR

5   spectra of both primary and atmospheric HULIS. The similarities between primary and atmospheric HULIS suggest they have similar chemical compositions and properties. The direct combustion of biomass and fossil fuels are therefore important potential sources of atmospheric HULIS.

3.7.2 Differences between primary and atmospheric HULIS

10   Although the primary and atmospheric HULIS were very similar, there were some differences between them. For example, the O/C atomic ratios of HULIS in smoke PM$_{2.5}$ from BB were similar to those in ambient aerosols, while the O/C ratio of HULIS in coal soot particles was significantly lower than the ratio for atmospheric HULIS samples. The UV-vis spectra of the four types of primary HULIS indicated a higher absorbance in shorter wavelength regions than the spectra of atmospheric HULIS,

15   and the SUVA$_{254}$ values of primary HULIS were also higher than those of atmospheric HULIS, indicating that the primary HULIS fractions contained a higher content of polycyclic aromatic and conjugated compounds than atmospheric HULIS. These findings were also supported by the EEM fluorescence, FTIR, and ^{1}H NMR spectroscopy results. For example, the Ex/Em wavelengths of peak A in the EEM fluorescence spectra of primary HULIS had peaks at longer excitation and emission

20   wavelengths than the spectra of atmospheric HULIS, suggesting that primary HULIS fractions had a higher content of aromatic structures and condensed unsaturated bond systems, and a lower content of aliphatic structures. In FTIR spectroscopy, a weak band at 1610 cm^{-1} is generally attributed to the C–C stretching of aromatic rings, and this was observed in the spectra of the four types of primary HULIS, but was absent in the FTIR spectra of atmospheric HULIS fractions. Finally, the relative content of the

25   [Ar–H] group in primary HULIS was significantly higher than in atmospheric HULIS, as shown by the

^{1}H NMR analysis.

Many sharp signals of organic species were observed in the ^{1}H NMR spectra of primary HULIS, but they were not as abundant in the ^{1}H NMR spectra of atmospheric HULIS. These sharp peaks may be ascribed to low molecular weight aromatic organic compounds in the isolated HULIS fractions. The

5 relatively few and/or weak sharp peaks in the ^{1}H NMR spectra of atmospheric HULIS may be the result of low molecular weight organic compounds being removed by oxidation or transformed to HULIS. In addition, atmospheric HULIS also had some special characteristics. For example, a distinct band at $\lambda_{ex}/\lambda_{em} \approx 295/405$ nm in the EEM spectra was only present in atmospheric HULIS, mainly suggesting that a marine source was important for atmospheric HULIS in the study region.

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3.7.3 Differences among the four types of primary HULIS

Although the four types of primary HULIS had many similarities, some distinct differences were also apparent. For example, the BB HULIS had a relatively lower C content, higher O content, and higher O/C molar ratio than HULIS from coal combustion, indicating that the BB HULIS contained a

15 relatively higher content of O-containing components and a relatively lower content of unsaturated structures. Some differences were also detected following the FTIR and ^{1}H NMR analysis. Stronger peaks at 1637, 1610, 1458, and 1385 cm^{-1} were displayed in the FTIR spectra of HULIS from coal combustion than the spectra from BB, indicating that coal smoke HULIS contained more aromatic structures. These results are consistent with the ^{1}H NMR spectroscopy results, where a higher content of

20 [H–C–C=] and [Ar–H] was present in the HULIS from coal combustion. The FTIR and ^{1}H NMR analysis identified the presence of lignin-like and carbohydrate derived structures in the molecules of primary HULIS from BB. For example, the content of [H–C–O] in HULIS from BB was significantly higher than in the HULIS from coal combustion.

For the three types of biomass HULISs, a relatively high content of [C–H] and low content of [H–

25 C–C=] and [Ar–H] were observed for pine branch smoke HULIS than the rice straw and corn straw

Atmospheric
Chemistry
and Physics
Discussions

Open Access

smoke HULIS fractions. These results may suggest that the primary HULIS from straw burning contained more aromatic protons and fewer aliphatic protons than those from wood combustion.

4   Conclusions

In this work, the primary HULIS fractions in smoke $PM_{2.5}$ emitted from the combustion of biomass materials and fossil fuels were isolated and comprehensively characterized by various analytical methods, including TOC analysis, elemental analysis, UV-vis, EEM fluorescence, FTIR, and ^{1}H NMR spectroscopy. The main conclusions were:

(1) The HULIS fractions were important components of smoke $PM_{2.5}$ obtained from the combustion of biomass materials and coal, and accounted for 5.3%− 23.4% of PM, 5.2%− 21.7% of TC, and 45.5%−66.1% of WSOC, respectively. These results indicate that BB and coal combustion are all important sources of HULIS in atmospheric aerosols. However, the HULIS fractions in diesel soot only accounted for 0.8% of soot particles, suggesting that vehicular exhaust may not be a significant primary source of HULIS.

(2) The primary and atmospheric HULIS were very similar in many aspects. For example, they had a similar elemental composition, in which C and O were the dominant elements. The two main peaks assigned to fulvic-like and protein-like fluorophores were both observed in the EEM spectra of primary and atmospheric HULIS. The ^{1}H NMR features indicated that the chemical shifts assigned to [H–C], [H–C–C=], [H–C–O], and [Ar–H] were both found in the ^{1}H NMR spectra of primary and atmospheric HULIS.

(3) There were also some differences identified between primary and atmospheric HULIS. For example, the primary HULIS fractions contained more polycyclic aromatic and conjugated compounds than atmospheric HULIS, as revealed by the UV-vis, EEM fluorescence, FTIR, and ^{1}H NMR spectroscopy analysis. In addition, many sharp signals of organic species were only observed in the ^{1}H NMR spectra of primary HULIS, indicating that there were some low molecular weight organic

compounds in the primary HULIS.

(4) Some distinct features were also identified among the four types of primary HULIS. For example, a lower C content, higher O content, and higher O/C molar ratio were observed in HULIS from BB than in HULIS from coal combustion, suggesting that biomass smoke HULIS contained a higher content of O-containing components and a lower content of unsaturated structures. The results from the FTIR and ^{1}H NMR spectroscopy indicated that the primary HULIS from BB contained lignin-like and carbohydrate derived structures, while the primary HULIS from coal combustion contained relatively high levels of aromatic structures.

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Chemistry
and Physics
Discussions

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and Physics
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Atmospheric
Chemistry
and Physics
Discussions

Open Access

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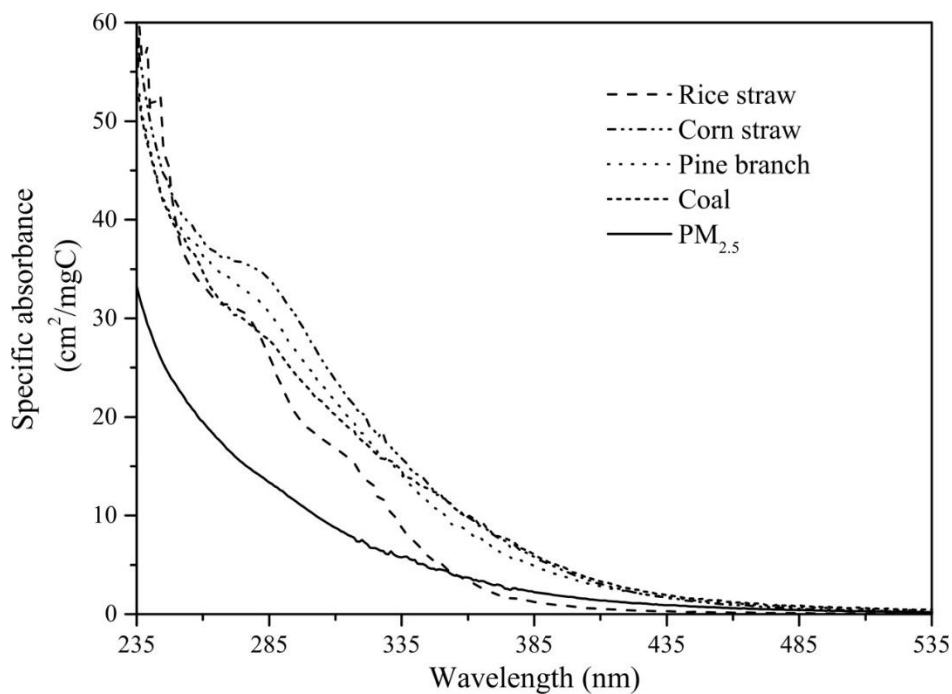
Figure 1. The normalized UV-vis spectra with TOC (units: cm^2/mgC) of HULIS in smoke $PM_{2.5}$ from combustion of rice straw, corn straw, pine branch and coal, and in ambient $PM_{2.5}$.

Atmospheric
Chemistry
and Physics
Discussions

Open Access

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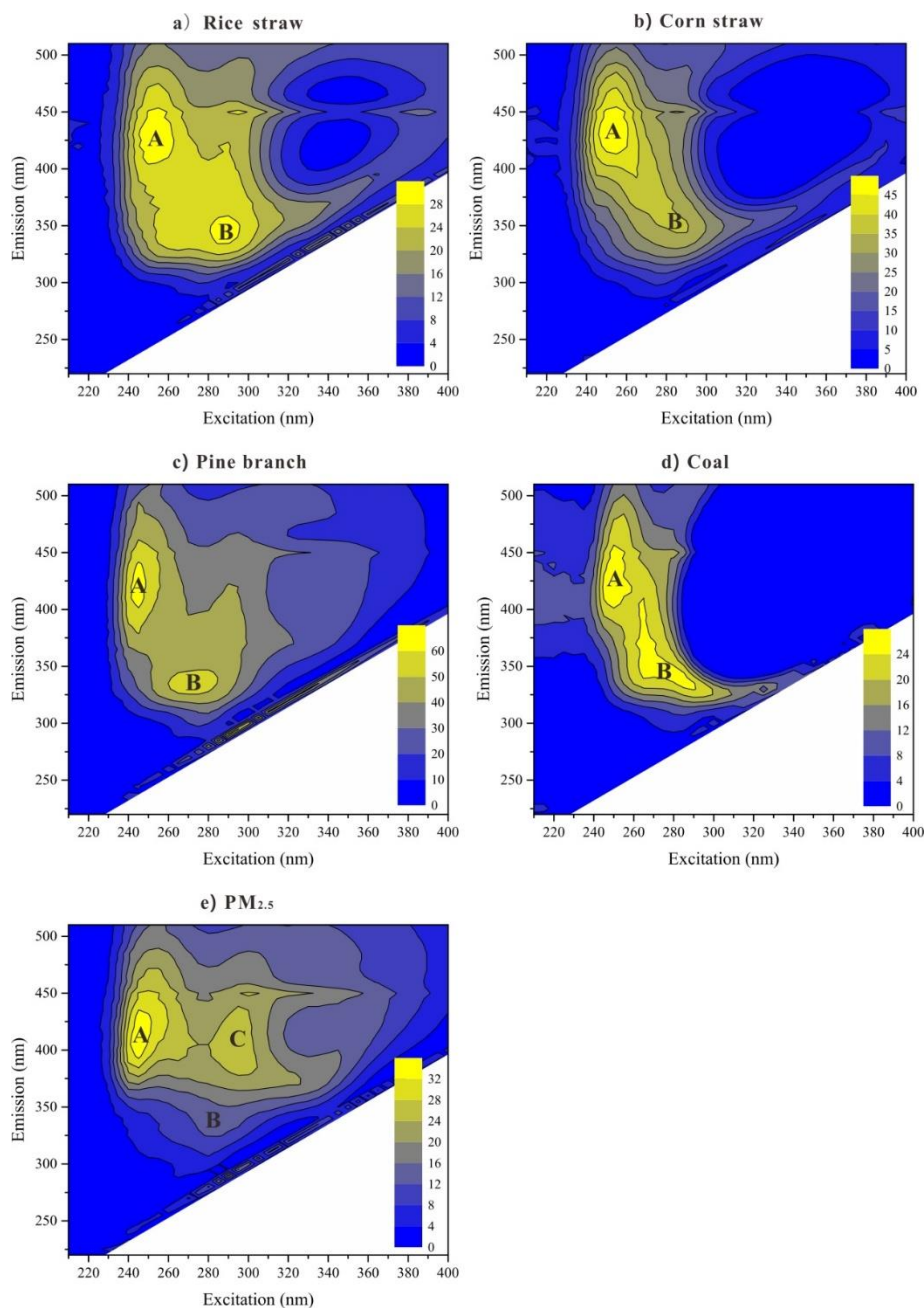
Figure 2. EEM spectra of HULIS in smoke $PM_{2.5}$ from combustion of rice straw (a), corn straw (b), pine branch (c), coal (d), and in ambient $PM_{2.5}$ (e), presented as specific intensity (a.u. L/(g C)).
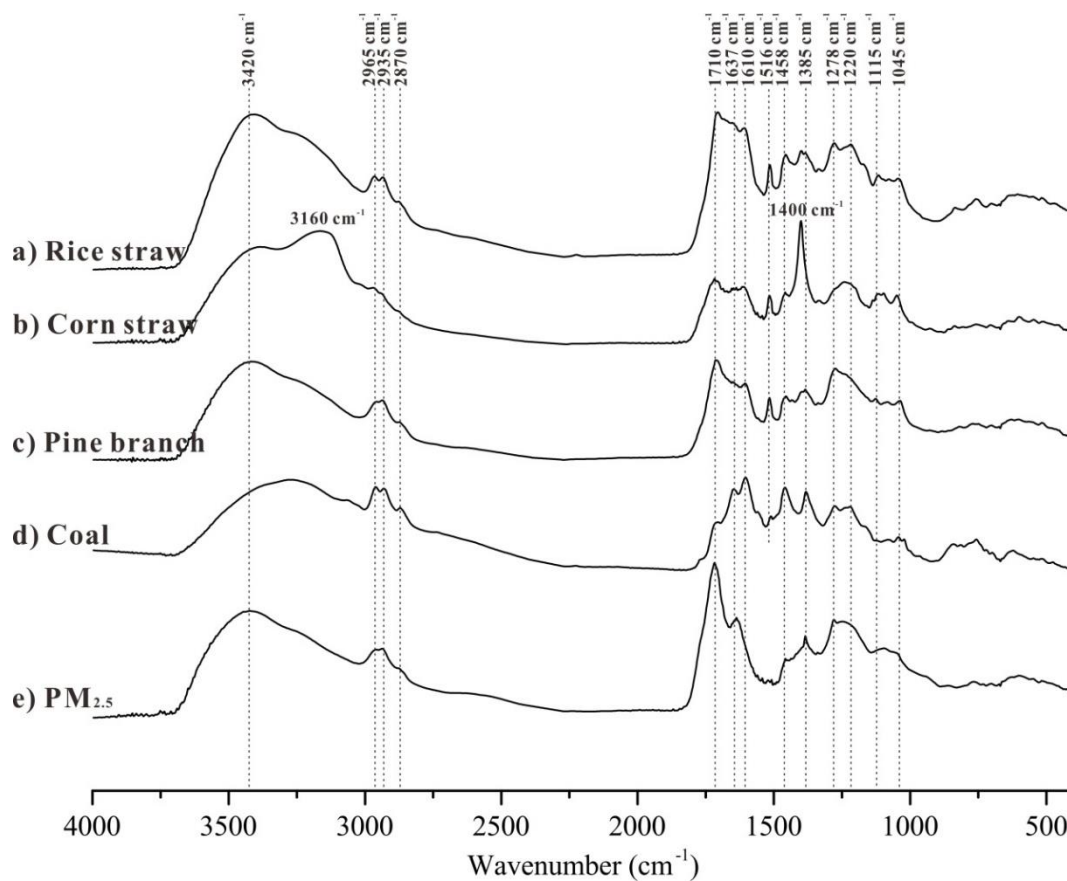
Figure 3. FTIR spectra of primary HULIS in smoke $PM_{2.5}$ from combustion of rice straw (a), corn straw (b), pine branch (c), coal (d), and in ambient $PM_{2.5}$ (e).

Atmospheric
Chemistry
and Physics
Discussions

Open Access

Figure 4. ^{1}H NMR spectra of HULIS in smoke $PM_{2.5}$ from combustion of rice straw (a), corn straw (b),
pine branch (c), coal (d), and in ambient $PM_{2.5}$ (e).

Atmospheric
Chemistry
and Physics
Discussions

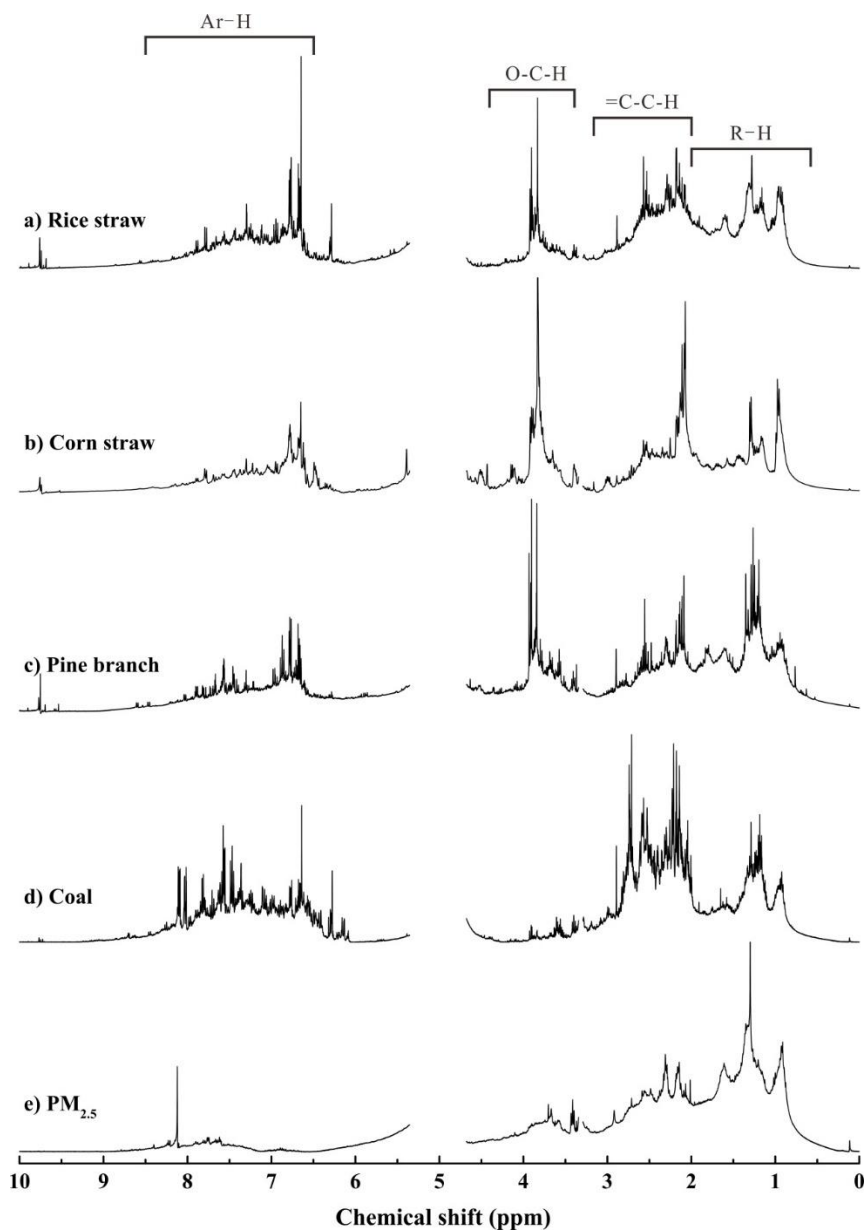Open Access

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Table 1. The contributions of HULIS to particular matters (PM), total carbon (TC), water soluble organic carbon (WSOC) in smoke $PM_{2.5}$ emitted from combustion of biomass materials and fossil fuels, and in ambient $PM_{2.5}$.

Samples	Types	HULIS-C/PM ($\mu gC/\mu g$, %)	HULIS/PM (%)	HULIS-C/OC (%)	HULIS-C/TC (%)	HULIS/WSOC (TOC, %)	HULIS/WSOC (UV250, %)	References
Rice straw	Smoke $PM_{2.5}$	13.5±3.1	23.4±5.5 [a]	-	21.7±4.0	66.1±2.4	79.5±1.5	
Corn straw	Smoke $PM_{2.5}$	5.9±4.0	11.2±7.5 [a]	-	14.7±6.9	59.2±2.4	75.4±2.9	
Pine branch	Smoke $PM_{2.5}$	6.4±2.2	11.4±3.8 [a]	-	8.0±2.9	56.9±3.1	68.1±5.5	
Coal	Smoke $PM_{2.5}$	3.5±0.3	5.3±0.4 [a]	-	5.2±0.3	45.5±2.1	64.4±3.9	Present work
Diesel soot	SRM 2975	0.5±0.01	0.8±0.02 [b]		0.7±0.0	62.3±3.7	58.3±3.5	
Urban aerosols	$PM_{2.5}$	5.2±0.4	10.7±0.8 [a]	26.8±3.3	22.6±3.7	60.7±1.0	70.7±2.1	
Leaf	Smoke PM_{10}	18.5-21.2	-	33.0-34.5	27.8-31.3	-	-	Schmidl et al. (2008a)
Wood	Smoke PM_{10}	0.6-5.8	-	1.0-12.0	0.9-9.2	-	-	Schmidl et al. (2008b)
Wood	Smoke PM_{10}	1.5-2.4	-	3.5-11.5	2.8-5.3	-	-	Goncalves et al. (2010)
Sugarcane	Smoke PM_{10}	-	7.6	14.3	-	33	-	Lin et al. (2010)
Rice straw	Smoke PM_{10}	-	12.4	14.7	-	30	-	Lin et al. (2010)
Vehicular exhaust	$PM_{2.5}$	0.6	-	2.9	1.0	18.4	-	I.El Haddad et al. (2009)
Vehicular exhaust	PM_{10}	0.8	-	3.4	1.3	20.7	-	I.El Haddad et al. (2009)
Roadway site aerosol	$PM_{2.5}$	5.2	-	34.5	26.6	59.8	-	Park et al. (2013)
Marine aerosol	PM_{10}	-	-	-	12	19	-	Krivacsy et al. (2008)
Rural aerosols	$PM_{1.5}$	-	-		39	57	-	Kiss et al. (2002)
Rural aerosols	$PM_{2.5}$	4.3	-	23.2	19.5	51.9	-	Duarte et al. (2007)
Urban aerosol	$PM_{2.5}$	6.0	11.7	29.5	-	60	-	Lin et al. (2010)
Urban aerosol	$PM_{2.5}$	-	6.7	18.3	10.6	62	-	Salma et al. (2007)
Urban aerosol	$PM_{2.5}$	-	-	26.6-28.9	18.4-20.8	45.8-49.7	-	Salma et al. (2008)
Urban aerosol	$PM_{2.5}$	-	-	35.4	27.6	63.0	-	Park et al. (2012)
Urban aerosol (dust)	$PM_{2.5}$	6.2	-	31.4	24.6	71.9	-	Park et al. (2013)
Urban aerosols	$PM_{2.5}$	2.8±1.3	5.4±2.7	16.9±4.9	13.0±4.5	49.5±5.9	68.3±4.7	Fan et al. (2016)

[a] HULIS mass are calculated by OM/OC ratios obtained by elemental analysis listed in Table 2.

[b] HULIS mass is calculated by the OM/OC ratio (1.51) of primary HULIS in coal smoke $PM_{2.5}$.

Table 2. Elemental composition and molar ratios of HULIS in smoke $PM_{2.5}$ from combustion of rice straw, corn straw, pine branch and coal and in ambient aerosols.

Samples	Types	Elemental composition (%)				Molar ratios			OM/OC	References
		N	C	H	O[a]	H/C	O/C	N/C		
Rice straw	Smoke $PM_{2.5}$	4.1	57.4	5.5	33.0	1.15	0.43	0.06	1.74	
Corn straw	Smoke $PM_{2.5}$	2.5	52.9	6.3	38.3	1.43	0.54	0.04	1.89	
Pine branch	Smoke $PM_{2.5}$	2.0	56.7	6.6	34.7	1.40	0.46	0.03	1.77	Present work
Coal	Smoke $PM_{2.5}$	3.3	66.1	7.1	23.6	1.28	0.27	0.04	1.51	
Urban aerosols	$PM_{2.5}$	2.9	48.5	6.4	42.1	1.59	0.65	0.05	2.06	
Alpine aerosol	$PM_{2.5}$	2.5	52	6.7	38	1.53	0.55	0.04	1.91	Krivacsy et al. (2001)
Rural aerosol	$PM_{1.5}$	2.5	52	6.2	39	1.43	0.58	0.04	1.93	Kiss et al. (2002)
Rural aerosol	$PM_{2.5}$	2.1-3.8	51-58	5.6-6.5	32-37	1.21-1.42	0.41-0.55	0.03-0.06	1.71-1.95	Duarte et al. (2007)
Urban aerosol	$PM_{2.5}$	3.1	55	7	35	1.49	0.47	0.05	1.82	Salma et al. (2007)
Urban aerosol	TSP	2.0-3.9	43-53	4.4-6.9	38-44	1.07-1.9	0.55-0.76	0.03-0.07	1.89-2.28	Song et al. (2012)
Urban aerosol	$PM_{2.5}$	3.1	54	5.9	38	1.31	0.53	0.05	1.86	Fan et al. (2013)

[a] Calculated as O(%) = 100%-C(%) -H(%) -N(%).

Atmospheric
Chemistry
and Physics
Discussions

Table 3. Absorptivity ratio between 250 nm and 365 nm (E_{250}/E_{365}), and the specific UV absorbance at 254 nm ($SUVA_{254}$) of HULIS in smoke $PM_{2.5}$ from combustion of rice straw, corn straw, pine branch and coal, and in ambient $PM_{2.5}$.

Samples	Type	E_{250}/E_{365}	$SUVA_{254}$	References
Rice straw	Smoke $PM_{2.5}$	5.8±0.5	3.7±0.5	
Corn straw	Smoke $PM_{2.5}$	4.5±0.2	3.9±0.7	
Pine branch	Smoke $PM_{2.5}$	4.4±0.3	3.7±0.4	Present work
Coal	Smoke $PM_{2.5}$	14.7±0.7	3.7±0.1	
Urban aerosols (Fall)	$PM_{2.5}$	7.2±0.3	2.5±0.1	
SRFA	-	4.86	3.94	
Urban aerosols	$PM_{2.5}$	4.7-5.2	2.6-4.6	Fan et al. (2012)
Rural aerosols	$PM_{2.5}$	5.5-6.2	2.7-2.8	
Urban aerosols	Annual $PM_{2.5}$	5.9±0.9	3.2±0.5	Fan et al. (2016)
Urban	Summer PM_{10}	7.3, 9.7		Krivacsy et al. (2008)
Urban	Winter PM_{10}	5.6, 5.7		
Rural aerosols	$PM_{1.5}$	8.0	-	Kiss et al. (2002)
Urban aerosols	Cold season $PM_{2.5}$	3.1-3.5	-	
Urban aerosols	Summer $PM_{2.5}$	4.6-5.9	-	
Urban aerosols	Mid season $PM_{2.5}$	3.4-3.6	-	Baduel et al. (2010)
Biomass burning background aerosols	Urban $PM_{2.5}$	2.9±0.2	-	
Rural aerosols	Summer $PM_{2.5}$	8.9	-	
Rural aerosols	Autumn $PM_{2.5}$	6.1	-	Duarte and Duarte (2005)
Urban/oceanic aerosols	$PM_{2.5}$	5.8	-	

Atmospheric
Chemistry
and Physics
Discussions

Open Access

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Table 4. Major band assignments for FT-IR spectra of HULIS in smoke $PM_{2.5}$ from biomass burning and coal combustion, and in ambient aerosols.

Wavenumber (cm^{-1})	Band assignments
3420	Stretching vibration of OH
2850-2980	Stretching vibrations of aliphatic C-H
1710	Stretching mainly of carboxyl-C and traces of ketones and esters C=O
1637	Stretching mainly of aromatic C=C and ketones, quinones and amides C=O
1610	Stretching vibration of aromatic rings
1516	Stretching vibrations of aromatic C=C
1458	Deformation of CH_2 and CH_3 bending
1385	Deformation of aliphatic C-H (some C-O stretching of phenolic OH)
1278	Stretching of aromatic C-O and phenolic OH
1220	Stretching vibrations of C-O and deformation of carboxylic O-H
1115	Stretching of ring breathing C-O
1045	Stretching of polysaccharide C-O or deformation of aromatic C-H

Atmospheric
Chemistry
and Physics
Discussions

Table 5. The proton species and corresponding content percentage of HULIS in smoke $PM_{2.5}$ from combustion of rice straw, corn straw, pine branch and coal, and in ambient $PM_{2.5}$.

Sources	Types/sites	Isolation methods	R-H [a] (0.6-2.0 ppm)	H-C-C= (2.0-3.2 ppm)	H-C-O (3.4-4.4 ppm)	Ar-H (6.5-8.5 ppm)	References
Rice straw	Burning emissions	HLB	34 [b]	30	10	27	
Corn straw	Burning emissions	HLB	31	26	19	24	
Pine branch	Burning emissions	HLB	45	22	14	19	Present work
Coal	Combustion emissions	HLB	27	40	2	31	
$PM_{2.5}$	Urban aerosol	HLB	51	31	11	6	
Rain water	Terrestrial/marine influenced	C18	51.4 (0.5-1.9)	32.1 (1.9-3.3)	15.0 (3.4-4.5)	1.4 (6.5-9.0)	Miller et al. (2009)
Rain water	Urban	DAX-8	45-51 (0.6-1.8)	22-29 (1.8-3.2)	17-24 (3.2-4.1)	2-7 (6.5-8.5)	Santos et al. (2012)
TSP	Urban aerosol	HLB	53.9-59.8 (0.7-2.0)	20.1-26.6 (2.0-3.2)	10.1-15.8 (3.3-4.5)	3.7-9.4 (6.5-8.3)	Song et al. (2010)
$PM_{2.5}$	Urban aerosol	ENVI-18, HLB, XAD-8 and DEAE	37-47 (0.6-1.9)	33-37 (1.9-3.2)	13-18 (3.4-4.4)	5.8-12 (6.5-8.5)	Fan et al. (2014)

[a] Investigation on the basis of the chemical shift assignments (unit: ppm)

[b] Relative abundance of each type of protons