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PM_{2.5} humic-like substances over Xi'an, China: Optical properties, chemical functional group, and source identification

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Abstract:

Humic-like substances (HULIS) in fine particulate matter (PM_{2.5}) were investigated during May 2015 to January 2016 in an urban environment in Xi'an, China. UV-VIS spectrometer and Fourier transform infrared spectroscopy (FTIR) were used to investigate optical properties and chemical structures of HULIS. Annual mean concentrations of HULIS-C (the carbon content of HULIS) was $2.9 \pm 2.1 \mu\text{g m}^{-3}$. On average, the contributions of HULIS-C to PM_{2.5}, TC, and OC were 6.1%, 27.2%, and 34.5%, respectively. Seasonal average of HULIS-C concentration followed a decreasing order of winter, spring, summer, and autumn. The UV absorption intensity of PM_{2.5} HULIS showed the highest in winter and the lowest in summer. The chemical functional groups for PM_{2.5} HULIS were highlighted with the presence of aliphatic C-H, hydroxy, carbonyl, carboxyl and aromatic rings structures. SUVA₂₅₄ and SUVA₂₈₀ values in autumn and winter exhibited more dispersive distribution than those in spring and summer, which indicated sources of HULIS in autumn and winter samples were relative complicated. The E₂/E₃ ratio showed a summer maximum and a winter minimum, indicating greater conjugation and aromaticity of HULIS in winter. In addition, strong correlations between HULIS-C with K⁺ and OC1+OP2 in spring, autumn and especially winter implied the important source of biomass burning to PM_{2.5} HULIS. The C-O stretching of COH, carbonyl groups (C=O) and O-H stretching of carboxylic acid were abundance both in winter and summer, implied that secondary organic aerosol (SOA) formation was found to be the dominant mechanism producing HULIS in Xi'an.

Keywords: Humic-like substances; optical properties; chemical groups; sources

1 Introduction

Organic carbon in atmosphere plays significant roles in atmospheric chemistry, e.g., promoting formation of reactive oxygen species (Dou et al., 2015; Duhl et al.,

2014; Lin and Yu, 2011), and climate, e.g., acting as cloud condensation nuclear (Dinar et al., 2007; Salma et al., 2006; Ziese et al., 2009). Humic-like substances (HULIS) account for a significant fraction of organic carbon and are ubiquitous in various environments, e.g., in atmospheric particles (Kiss et al., 2002; Feczko et al., 2007; Lin et al., 2010a; Lin et al., 2010b; Song et al., 2012; Kristensen et al., 2015; Lee et al., 2017), fog (Facchini et al., 1999; Krivacsy et al., 2000), cloud (Facchini et al., 1999), and precipitation (Yue et al., 2016). HULIS are complex compounds with average molecular weights in the range of 200-700 Da (Song et al., 2018). HULIS can be emitted directly from primary emission sources, e.g. biomass burning and coal combustion, or produced from secondary aerosol formation e.g., photosensitized reaction (Lin et al., 2010a; Song et al., 2018). HULIS contain many typical chemical functional groups including carbonyl, carboxyl, hydroxyl, aromatic, phenolic, and acidic (Graber and Rudich, 2006; Samburova et al., 2007; Chen et al., 2016).

HULIS were abundant in the atmosphere and can be measured conveniently based on carbon equivalent (HULIS-C) using total organic carbon (TOC) analyzer. Varga et al (2001) compared different packing solid phase extraction (SPE) columns and suggested that Oasis hydrophilic-lipophile balance (HLB) column is an optimal choice for measuring HULIS-C. In addition, Fan et al (2012) showed HLB column was suitable for isolating atmospheric HULIS. Salma et al (2007) investigated urban HULIS based on carbon equivalent (HULIS-C) and suggested that HULIS accounted for 20% of organic carbon (OC) in Budapest. Atmospheric HULIS-C was found to be an important fraction (e.g., 32-66%) of water-soluble organic carbon (WSOC) (Fan et al., 2016a; Zheng et al., 2013). HULIS concentrations as high as $22.4 \mu\text{g m}^{-3}$ were observed in Beijing, China and as low as $0.1 \mu\text{g m}^{-3}$ in Mace Head, Ireland (Krivácsy et al., 2008; Kiss et al., 2002; Emmenegger et al., 2007; Lin et al., 2010b; Ma et al., 2018).

Some kinds of organic matter in aerosols have light absorption in near ultraviolet and visible regions (300-700nm), which is called “brown carbon (BrC)”. Previous studies have shown that water-soluble BrC contains HULIS, and it was isolated from BrC and was recognized as an important components of BrC (Wu et al., 2018; Wu et

al., 2019; Park and Yu., 2016; Li et al., 2019; Andreae and Gelencsér., 2006). Laboratory studies have shown that AAE and MAE₃₆₅ of HULIS on PM_{2.5} by crop straw (wheat, rice and corn) combustion under different moisture contents and stacking modes were 5.3-8.8 and 0.9-1.9 m²g⁻¹ (Huo et al., 2018). Field experiments showed that AAE and MAC₃₆₅ of HULIS were 7.1-9.3 and 0.2-0.7 m²g⁻¹ in Tibetan Plateau TSP (Wu et al., 2018).

Xi'an is the largest city in Northwest of China with relatively high PM levels caused by coal combustion, rural biomass burning, vehicle emission and fugitive dust (Cao et al., 2012; Shen et al., 2009; Zhang et al., 2015; Xu et al., 2016; Sun et al., 2017). HULIS in this city have not been studied thoroughly and the knowledge of HULIS seasonal variations, sources, and formation mechanisms is needed in assessing their air quality and climate impacts. In this study, chemical and optical properties of PM_{2.5} HULIS in Xi'an were measured using the instruments of TOC analyzer, UV-VIS spectrometer and Fourier transform infrared spectroscopy (FTIR). The purposes of this study were to (1) determine the mass level of PM_{2.5} HULIS; (2) investigate the seasonal variations of chemical structures and optical properties of HULIS; and (3) identify the sources of PM_{2.5} HULIS in Xi'an.

2 Experiments

2.1 PM_{2.5} samples Collection

The sampling site is set on the rooftop of a 15-m high building inside the campus of Xi'an Jiaotong University in Xi'an (34°16'N, 108°54'E), and is surrounded by residential areas and traffic roads, as previously described in Shen et al (2014). One 24-hour sampling of ambient fine particles (PM_{2.5}) was collected in every 3 days from 12 May 2015 to 9 January 2016 on pre-baked (780°C for 7 hours) quartz fiber filters (203 mm × 254 mm, Whatman, QMA) using a high volume sampler (HVS-PM_{2.5}, Thermo-Anderson Inc.) with a flow rate of 1.13 m³ min⁻¹. A total of 81 samples were collected. These filters were equilibrated for 24 h at 20-23°C before and after PM sample collection in a chamber with a relative humidity of between 35% and 45%. They were weighed at least three times by a high-precision (±0.1 mg) microbalance

(ME-5, Sartorius Inc., USA) to determine PM mass. Quality assurance and control (QA/QC) measures were implemented including the use of blank filters as control and pre-treatment of the filters after baking and equilibrating to minimize particle evaporation and mass loss. After sampling, the samples were sealed and stored below 0 °C to avoid evaporative losses before analysis.

2.2 Chemical composition analysis

The concentrations of organic carbon (OC) and element carbon (EC) in PM_{2.5} were analyzed using Thermal and Optical Carbon Analyzer (DRI Model 2001A, Atmoslytic, Inc., US) with Interagency Monitoring of Protected Visual Environment (IMPROVE) thermal/optical reflectance (TOR) protocol. Both OC and EC were separated individually and were measured under different temperatures. OC and EC were defined as OC1+OC2+OC3+OC4+OPC and EC1+EC2+EC3-OPC, respectively. OC fractions (OC1, OC2, OC3, and OC4 at 140, 280, 480, and 580 °C, respectively) were volatilized in pure helium atmosphere, while EC fractions (EC1, EC2, and EC3 at 580, 740, and 840 °C, respectively) were released in the condition of 98% helium plus 2% oxygen. These released carbon fractions were totally converted into CO₂ and then converted to methane, which was then measured by flame ionization detector (FID). Total carbon (TC) is defined as the sum of OC and EC. Detailed description of OC and EC measurement method were presented in Cao et al (2004).

K⁺ in PM_{2.5} samples was determined by ion chromatography (Dionex 600, Dionex Corp, Sunnyvale, USA). A quarter of each filter was extracted by 10 ml distilled-deionized water for 1h in an ultrasonic bath. The extracts were filtered into a clear vial and stored in 4 °C freezer before analysis. The detailed process was described in Shen et al (2014).

Four filter punches (total about 2.0 cm²) were used to determine the water soluble HULIS levels in PM_{2.5} samples. Each punched filter was placed in about 10 ml distilled-deionized water with 18.3 MΩ resistivity and then extracted for 40 min in an ultrasonic bath. Subsequently, the extracts were filtered by a 0.45 μm syringe filter (Millipore, Billerica, MA, USA) into a clear vial in order to remove insoluble components. The filtrate was acidified to pH≈2.0 by HCl. Then it was loaded on a

SPE (Oasis HLB, 3cc, 60mg, Waters, USA) for desalting because of inorganic ions (e.g., NH_4^+ , SO_4^{2-} , NO_3^-). The cartridges need to be activated, rinsed and kept equilibrium using methanol, ultrapure water and HCl successively before using. Very hydrophilic fraction with strong polar functional groups passed into effluent, while relatively hydrophobic fractions were retained and then eluted by 1.5 ml methanol containing 2% ammonia (v/v) by about 1.0 ml/min. Eluents were evaporated to dryness under a gentle stream of nitrogen and dissolved with ultrapure water. The HULIS-C was qualified by TOC analyzer. HULIS is calculated as 1.76 times of HULIS-C, based on the known OM/OC ratio in $\text{PM}_{2.5}$ in Xi'an (Xing et al., 2013).

The TOC content of solution before loading on HLB column and HULIS aqueous solution was measured using a TOC analyzer (Shimadzu, Kyoto, Japan) based on high temperature catalytic oxidation method. 20 ml aqueous solution was measured by detecting CO_2 catalyzed to burn in oxygen at 680°C . Each sample was analyzed three times in parallel and TOC is the difference between water soluble total carbon (TC) and total inorganic carbon (IC). Triplicate measurements were done for each sample. The blank samples also went through the same experimental process. The blank concentrations of OC, FC, HULIS-C and K^+ were $0.18\mu\text{g}/\text{cm}^2$, $0.01\mu\text{g}/\text{cm}^2$, $0.09\mu\text{g}/\text{ml}$ and $0.013\mu\text{g}/\text{ml}$, respectively.

2.3 Measurements of optical properties and chemical functional groups for HULIS.

The light absorption of HULIS at UV-vis wavelengths were recorded using a USB2000+UV-VIS-LS spectrometer equipped with a 100 cm-long Liquid Waveguide Capillary Cell 3100 (LWCC-3100, World Precision Instruments, Sarasota, FL). Specific absorbance values at 250nm and 280nm (SUVA , $\text{L}(\text{mgC m}^{-1})^{-1}$) and E_2/E_3 were important parameters for analyzing chemical properties of HULIS derived from UV-VIS spectrum. E_2/E_3 ratio was the ratio of spectral absorbance measured at 250nm and 365nm. To eliminate the effect of concentration of HULIS samples, SUVA_{254} or SUVA_{280} were used in this study, calculated using equation (1):

$$\text{SUVA} = A / (C \cdot l) \quad (1)$$

Where A is the absorbance derived from the spectrophotometer at 254 or 280 nm, C is the concentration of WSOC of HULIS analyzed by TOC analyzer (g m^{-3}), and l was

optical path length (cm).

Chemical functional groups of HULIS were measured following the procedures described below. The HULIS extracts were first concentrated to about 0.5ml, and KBr powder (FT-IR grade, Sigma-Aldrich) was then added. The mixture of HULIS and KBr was entirely dried under mild nitrogen flow and was then ground in an agate mortar and pressured into a sheet (about 1 mm thickness). The chemical functional groups of HULIS were then analyzed using Fourier transform infrared spectroscopy with an attenuation total reflectance accessory (FTIR-ATR; Perkin Elmer, model Spectrum One). The FTIR spectrum was recorded in the 4000-400 cm^{-1} region at a resolution of 4 cm^{-1} . 32 scans were performed and averaged. The spectrum baseline was determined by analyzing pure KBr before analyzing samples.

3 Results and discussion

3.1 Levels and seasonal variations of $\text{PM}_{2.5}$ HULIS

The average concentrations of $\text{PM}_{2.5}$, TC, EC, OC, and HULIS are summarized in Table 1. Daily $\text{PM}_{2.5}$ HULIS ranged from 0.7 to 17.6 $\mu\text{g m}^{-3}$, with an annual mean value of 5.1 $\mu\text{g m}^{-3}$, accounting for $8.4 \pm 3.6\%$ of the $\text{PM}_{2.5}$ mass. Table 2 shows the HULIS levels observed worldwide for comparison with results obtained in the present study. The $\text{PM}_{2.5}$ HULIS concentration in Xi'an is similar to those measured in several Chinese cities such as Hong Kong, Guangzhou, and Lanzhou, lower than those in the Pearl River Delta region of China in the harvest season, and higher than those at the oceans and mountain sites (Lin et al., 2010a; Fan et al., 2016a; Tan et al., 2016; Ma et al., 2018).

Insert Table 1

Insert Table 2

Seasonal average HULIS concentration was the highest in winter, which was 2, 3, and 3.7 times of those in spring, summer and autumn, respectively, likely due to the

intensive primary emissions and poor dispersion conditions during the winter season in Xi'an (Shen et al., 2011). On the basis of the t-test at 95% confidence level, a statistically significant difference was observed ($p < 0.05$) in HULIS-C for winter with other seasons. In fact, biomass burning and coal combustion were very common for winter heating in this region (Shen et al., 2008; Sun et al., 2017), which should be importance sources for PM_{2.5} HULIS (Shen et al., 2017a, b; Lei et al., 2018). HULIS-C/OC ratios were higher in winter and spring than autumn and summer. This result was slightly different from that in Shanghai, which showed the summer HULIS concentrations was higher than spring and autumn (Qiao et al., 2015).

3.2 The UV-VIS absorbance of HULIS

UV-VIS absorption spectra of PM_{2.5} HULIS are depicted in Fig. 1. Strong absorbance was found in the UV range of 200-400 nm, and the absorption intensity decreased monotonically from the maximum with increasing wavelength in the UV range of 240-800 nm, which should be the typical characterization for double-bounded and aromatic chemical structures of humic substances (Salma et al., 2008). The absorption maximums of the spectra were located at 246 nm, 232 nm, 272 nm, and 273 nm, in spring, summer, fall and winter, respectively (Fig. 1). In the UV spectrum, an absorption region at 210-250 nm indicated that HULIS contained a conjugated system with two double bonds (Mistry, 2009). In addition, an absorption region at 250-300 nm was mainly caused by the π - π^* electronic transition of C=C or C=O in the aromatic compound (Fan et al., 2016; Baduel et al., 2009; Chen et al., 2002; Salma et al., 2008). Absorption at 270-350 nm is the R-band generated by the n - π^* transition, suggesting that HULIS might contain a simple non-conjugated chromophore group having n electrons, such as a carbonyl group of the aldehyde and ketone (Baduel et al., 2009). Baduel et al (2009) also showed that compounds with two or more rings, such as phenolic arenes, aniline derivatives, polyenes, and polycyclic aromatic hydrocarbons, can absorb UV at 270-280nm. Thus, HULIS measured in Xi'an likely contained conjugated systems and aromatic rings structures.

Insert Fig. 1

Seasonal average absorption intensity of PM_{2.5} HULIS followed a decreasing

order of winter, spring, autumn, and summer (Fig.1). Previous studies have shown higher absorbance for HULIS having higher aromaticity and/or larger molecules (Duarte et al., 2005; Fan et al., 2012; 2016). Therefore, there were likely more polyaromatic materials or compounds containing conjugated systems in HULIS in winter than other seasons in this city. Seasonal patterns of aromaticity of PM_{2.5} HULIS were consistent with those of the concentrations of particulate-bound polycyclic aromatic hydrocarbons (PAHs) in Xi'an (Huang et al., 2018; Zeng et al., 2018).

3.3 Identification of chemical functional groups in HULIS

The FTIR spectra of HULIS among the four seasons were shown in Fig. 2. Based on the peak positions in the FTIR spectra, different functional groups were assigned and listed in Table 3.

In all of the four seasons, the O-H stretching of phenol, alcohol or/and carboxylic acid was seen at 3420-3250 cm⁻¹, which was consistent to the previous literature of Zhong et al (2014). Hawthorne et al (1998) suggested that the phenols and methoxy phenols contributed 20-40% to PM from hardwood and softwood burning. These chemical groups were also similar to the composition of lignin and other carbohydrates in vegetative materials (Bianchi et al., 1993; Cass, 1998). In addition, the C-H asymmetric stretching of methyl and methylene groups of aliphatic chains occurred at 2990-2850 cm⁻¹. The methyl and methylene groups can be found in long-chain plant cuticle waxes and other detritus (Hawkins and Russell, 2010; Zhong et al., 2014). In addition, these peaks were similar to the spectra reported for emissions at Hyytiälä, Finland that were transported from the large wildfires burning near Moscow, Russia, and northern Ukraine (Corrigan et al., 2013). As a result, these absorptive bands clearly indicated the important contribution of biomass burning to HULIS.

It was noticed that the absorption intensities of methyl and methylene groups in winter HULIS sample were about 2 times of those in summer samples, indicating that long-chain hydrocarbons associated with biomass burning were more abundance in winter. In addition, some bands were also displayed near 1617 cm⁻¹ and 1460 cm⁻¹

which were attributed to C = C stretching vibrations of aromatic rings (Fan et al., 2016), indicating the presence of aromatic groups. Furthermore, the absorbance peak value at 1088 cm^{-1} in winter was nearly 4 times of that in summer, due to C–O stretching of carbohydrate moieties and ethers from syringyl or guaiacyl units as aromatic phenols, and these were taken as the tracer of biomass burning in winter (Fan et al., 2016; Duarte et al., 2007). In fact, winter $\text{PM}_{2.5}$ levoglucosan level was above 2.5 time higher than summer, implying the important contribution from biomass burning to winter $\text{PM}_{2.5}$ (Wang et al., 2018).

Insert Fig. 2

Insert Table. 3

The C–O stretching of COH, carbonyl groups (C=O) and O–H stretching of carboxylic acid were identified at 1386 cm^{-1} , $1640\text{--}1850\text{ cm}^{-1}$ and $3420\text{--}3250\text{ cm}^{-1}$, respectively, emphasizing the existence of carboxylic acid in four seasons. Previous studies pointed out that carboxylic acid was a significant tracer of secondary particulate matter, which can be induced by an increase in aromatic precursors (i.e., benzene and ethylbenzene), most likely through photochemical reactions (Liu et al., 2011; Zhong et al., 2014; Ma and Xu, 2014). In this study, the relative intensity of C=O peak was the highest among all peaks in summer, indicated that carboxylic acids were much abundant than other compounds. This result emphasized that the secondary-HULIS was dominated in summer from the photochemical reactions under the conditions of high ozone level and strong sunlight (Ofner et al, 2011). In fact, high O_3 level ($>100\text{ ppb}$; Feng et al., 2016) and strong sunlight (Wang et al., 2012) are were observed in summer compared to other seasons over Xi'an. In contrast, the intensity of C=O bond of carboxylic acid in winter was a slightly lower than that in summer, which implied that secondary-HULIS was also abundance in winter over Xi'an. In view of winter heating activities, the production of secondary-HULIS was estimated to be higher than other seasons and was derived from aqueous reactions with high anthropogenic combustion precursors from biomass burning (such as catechol, guaiacol and glyoxal) in high relative humidity condition (Ofner et al, 2011;

Li et al., 2018; Zhang et al., 2015). As supported, previous studies also confirmed that aqueous oxidation reaction between OH radical and glyoxal and similar substances can form carboxylic acid (Carlton et al. 2007; Tan et al. 2009; Lim et al. 2010).

3.4 Source identification of HULIS

SUVA₂₅₄ was often chosen to represent the content of aromatic structures in humic substances (Peuravuori and Pihlaja, 1997; Vione et al., 2014), and SUVA₂₈₀ to represent aromaticity and molecular weight in HULIS (Voliotis et al., 2017). These parameters were also used in the present study to identify chromophores in PM_{2.5} HULIS. In this study, SUVA₂₅₄ and SUVA₂₈₀ were in the range of 0.09-5.28 and 0.08-5.68 L (mgC m)⁻¹, with the average values of 0.8 and 0.7 L (mgC m)⁻¹ (Table 1).

The dependence of SUVA₂₅₄ or SUVA₂₈₀ on HULIS-C concentration is shown in Fig. 3. Similar distribution patterns were found for SUVA₂₅₄ and SUVA₂₈₀ with HULIS-C levels, and both of them showed a strong negative correlation ($R^2=0.539$, $P<0.01$ and $R^2=0.443$, $P<0.01$). Note that the absorbance data of UV-VIS spectra were normalized by HULIS concentration, and the seasonal differences shown in Fig. 3 should mainly due to the seasonal variations in emission sources. The ranges of SUVA values are small in spring and summer, but are relatively large in autumn and winter, suggesting more complicated source of HULIS in autumn and winter than spring and summer. It was noticed that most of the high SUVA₂₅₄ and SUVA₂₈₀ values were occurred in winter and autumn samples (As shown in Figure 3), suggesting that higher contents of UV-absorbance compounds containing C=C and C=O unsaturated bonds in PM_{2.5} HULIS collected in these two seasons (Salma et al., 2008).

Insert Fig. 3

Previous studies reported that the E₂/E₃ ratio is inversely proportional to the molecular weight and aromaticity of HULIS in atmosphere (Chin et al. 1994; Chen et al., 2002; Peuravuori and Pihlaja, 1997; Duarte et al., 2005; Fan et al., 2012; Wu et al., 2018). E₂/E₃ ratios for four seasons were shown in Fig. 4. The average E₂/E₃ ratio of HULIS in PM_{2.5} in Xi'an followed the order of summer > spring > autumn > winter, indicating that winter HULIS samples had a greater conjugation and aromaticity than those in the other seasons. A statistically difference of E₂/E₃ ratios were found

between winter with other seasons ($p < 0.05$, t-test). In addition, Duarte et al (2005) founded that low E_2/E_3 ratio represented the abundance of aromatic compounds in winter from wood burning. Therefore, the lowest seasonal average E_2/E_3 ratio in HULIS in autumn and winter inferred the important contribution of biomass burning to $PM_{2.5}$ HULIS in Xi'an. In fact, maize straw smoldering burning in Chinese "heated Kang" for autumn cooking and winter heating was popular in rural areas surrounding Xi'an, which was also the major sources of polycyclic aromatic hydrocarbons (PAHs) in urban $PM_{2.5}$ (Sun et al., 2019; Zeng et al., 2018). In addition, slow degradation and volatilization of aromatic compounds under low temperatures also enhanced concentration levels of aromatics materials in winter (Samburova et al., 2007; Wang et al., 2018). Moreover, good correlations between HULIS-C with K^+ and OC1+OP2 were observed both in spring, autumn and winter (Fig. 5), further highlighting the important contributions of biomass burning to HULIS in these seasons considering that K^+ and OC1+OP2 were good markers for biomass burning (Shen et al., 2017; Sun et al., 2017). In contrast, relatively high E_2/E_3 ratios and poor correlations HULIS-C with K^+ and OC1+OP2 were observed in summer, suggesting the limited contributions of biomass burning to summer HULIS.

Insert Fig. 4

Insert Fig. 5

Differing from the case in winter, the FTIR results showed that the intensity of carboxylic acid was very high in summer, indicating secondary aerosol processes is the major source of HULIS formation. For example, photosensitized reactions, which yield more aliphatic non-conjugated components, played a major role in producing HULIS in summer (Laskin et al., 2015). A laboratory study by Vione et al (2014) also showed that photosensitized reactions, which involved triplet sensitizers or photogenerated oxidants like $\bullet OH$, produced compounds that are closely resemble to HULIS occurring in atmospheric aerosols in both gas-solid systems and the aqueous phase. Triplet sensitizers, such as benzophenones, anthraquinones and nitroaromatic

compounds, can yield reactive triplet states after sunlight absorption. Thus, secondary HULIS from strong photosensitized reactions was dominated in summer in comparison with other seasons.

4 Conclusions

Seasonal variations in optical and chemical properties of HULIS in PM_{2.5} samples have been monitored in urban Xi'an. Winter HULIS-C level was several times higher than other seasons. Water-soluble HULIS-C contributed significantly to OC, illustrating the important roles of HULIS in organic aerosols. The high UV-VIS absorption by HULIS, high SUVA₂₅₄ and SUVA₂₈₀ values, and low E₂/E₃ ratio in autumn and winter indicated abundant polyaromatic compounds or compounds containing conjugated systems and high aromaticity. The high intensity of aliphatic C-H bands of HULIS combined with good correlations of HULIS-C with K⁺ and OC1+OP2 in spring, autumn and winter revealed the contribution from biomass burning emissions, especially in winter. In contrast, relative low aromaticity in HULIS and poor correlations between HULIS-C with biomass burning markers implied the limited contributions of biomass burning to summer HULIS. The high intensity peak of carboxylic acid was existed in Xi'an, implied the dominance of secondary processes for HULIS formation, especially in summer. Future studies can focus on exploring specific chemical species in HULIS and their functional groups that dominate the optical absorption of HULIS.

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Figure Captions

Fig. 1. UV-VIS spectra of atmospheric HULIS in $PM_{2.5}$ (The absorbance of HULIS for each season's samples in same spectrum were averaged and then to plot its seasonal variation.).

Fig. 2. FTIR spectra of HULIS in four seasons.

Fig. 3. Variation of $SUVA_{254}$ and $SUVA_{280}$ with HULIS-C concentration in four seasons.

Fig. 4. Variation of E_2/E_3 ratio in four seasons.

Fig. 5. The correlations between HULIS and K^+ (a) or OC1+OP2 (b).

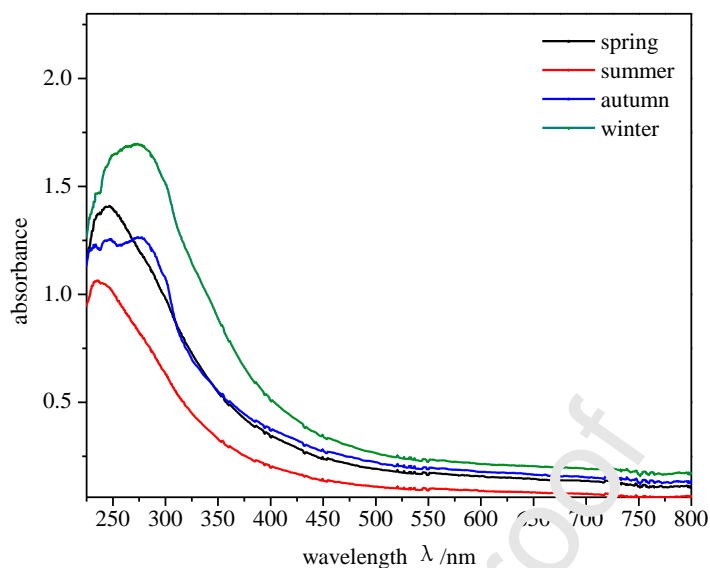


Fig. 1. UV-VIS spectra of atmospheric HULIS in PM_{2.5}. (The absorbance of HULIS for each season's samples in same spectrum were averaged and then to plot its seasonal variation.)

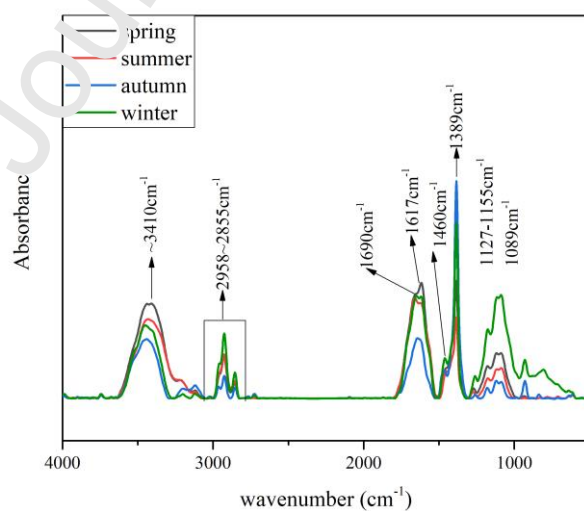


Fig. 2. FTIR spectra of HULIS for four seasons

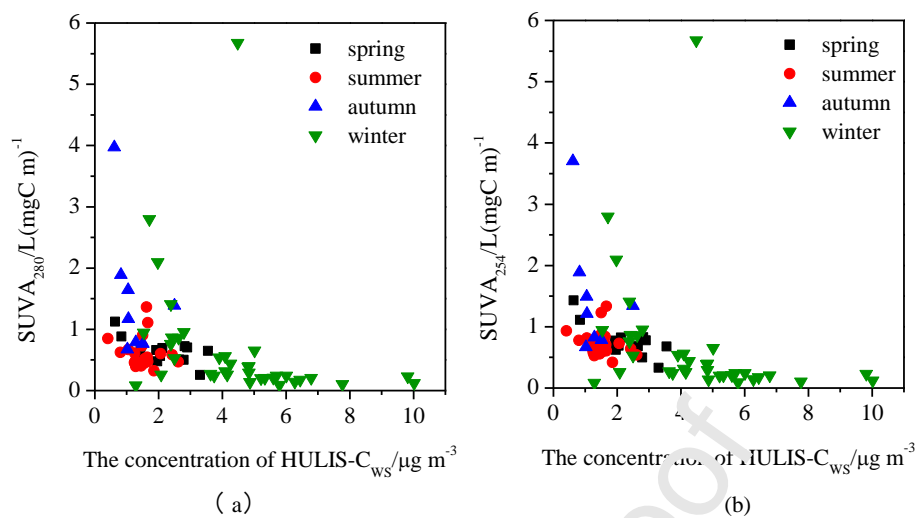


Fig. 3. Variation of $SUVA_{280}$ (a) and $SUVA_{254}$ (b) with HULIS-C concentration for four seasons

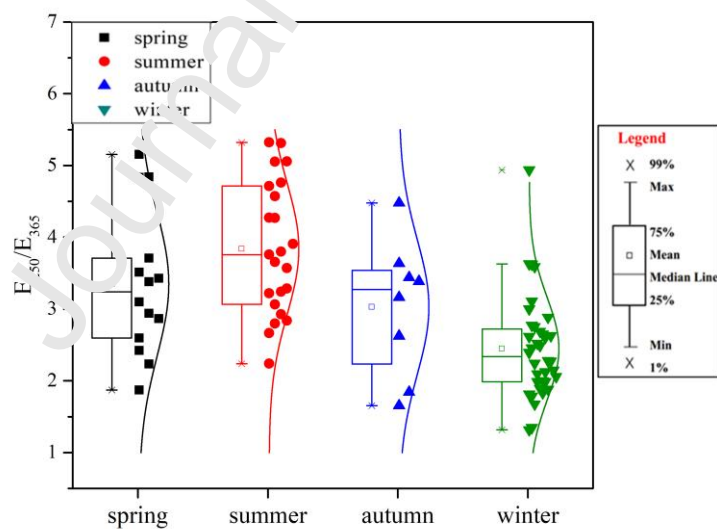


Fig. 4. Variation of E_2/E_3 ratio for four seasons

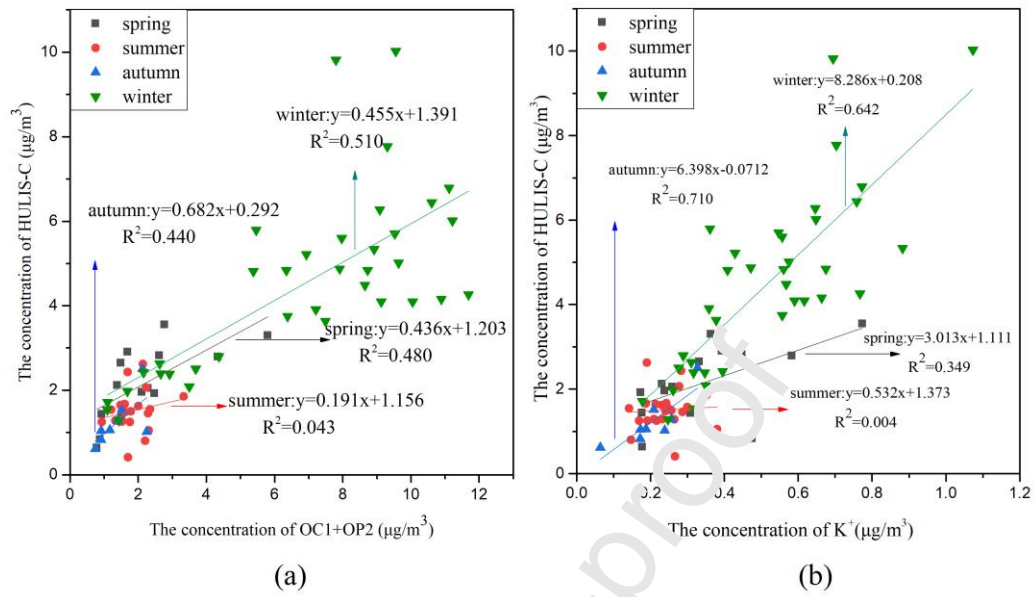


Fig. 5 The correlations between HULIS and K^+ (a) and OC1+OP2 (b)

Table Captions

Table 1. Annual and seasonal average of mass concentrations of PM_{2.5}, carbonaceous species, and HULIS (HULIS-C), HULIS/OC ratio, and UV parameters of HULIS.

Table 2. Concentrations of HULIS or HULIS-C in aerosols monitored in other cities

Table 3. Major band assignments for FTIR spectra of HULIS in ambient aerosols.

Table 1. Annual and seasonal average of mass concentrations of PM_{2.5}, carbonaceous species, and HULIS (HULIS-C), HULIS/OC ratio, and UV parameters of HULIS.

| Species | Unit | Spring | Summer | Autumn | Winter | Annual |
|--------------------------------|------------------------|-----------|-----------|-----------|-----------|-----------|
| # of Samples | / | 14 | 23 | 8 | 36 | 81 |
| PM _{2.5} | μg m ⁻³ | 48.3±27.4 | 49.1±13.9 | 42.4±41.5 | 76.4±28.2 | 61.6±29.9 |
| TC | μg m ⁻³ | 7.8±3.3 | 7.9±2.2 | 5.7±2.4 | 16.8±6.2 | 11.8±6.5 |
| OC | μg m ⁻³ | 6.2±2.9 | 6.2±1.9 | 4.6±2.0 | 13.4±5.2 | 9.4±5.3 |
| EC | μg m ⁻³ | 1.6±0.5 | 1.7±0.4 | 1.2±0.7 | 3.4±1.1 | 2.4±1.2 |
| HULIS-C | μgC m ⁻³ | 2.0±0.9 | 1.5±0.5 | 1.2±0.6 | 4.5±2.1 | 2.9±2.1 |
| K ⁺ | μg m ⁻³ | 0.3±0.2 | 0.24±0.1 | 0.20±0.1 | 0.5±0.2 | 0.4±0.2 |
| HULIS ^a | μg m ⁻³ | 3.6±1.6 | 2.6±0.8 | 2.2±1.0 | 7.9±3.7 | 5.1±3.6 |
| HULIS-C/OC | % | 33.6±8.3 | 25.9±8.6 | 28.0±6.7 | 34.5±10.8 | 30.9±10.0 |
| SUVA ₂₅₄ | L(mgC m) ⁻¹ | 0.8±0.3 | 0.7±0.2 | 1.5±1.0 | 0.7±1.0 | 0.8±0.8 |
| SUVA ₂₈₀ | L(mgC m) ⁻¹ | 0.6±0.2 | 0.6±0.3 | 1.5±1.1 | 0.7±1.0 | 0.7±0.8 |
| E ₂ /E ₃ | / | 3.4±1.0 | 3.8±0.9 | 3.0±0.9 | 2.5±0.7 | 3.1±1.0 |

a. HULIS-C was measured by the TOC analyzer and HULIS is calculated as 1.76 times of HULIS-C.

Table 2. Concentrations of HULIS or HULIS-C in aerosols monitored in other cities

| Sites | Time | Samples type/Isolation/Analysis | HULIS($\mu\text{g m}^{-3}$) | Citations |
|--------------------------------|----------------------|--|-------------------------------------|-------------------------|
| Mace Head, Ireland, marine | 2001.8-9 | PM _{1.5} /HLB/UV-VIS+TOC | 0.1 | Krivácsy et al.(2008) |
| Gwangju, Korea, urban | 2015.1-2 | PM _{2.5} /HLB(60mg)/TOC | 1.7 (0.5–5.1) | Park and Son.(2017) |
| Anmyeon Island, Korea | 2015.7-2016.4 | PM _{2.5} /HLB(60mg)/TOC | 1.0-2.5 | Lee et al.(2017) |
| Budapest, Hungary, urban | 2002.4-5 | PM _{2.5} /HLB/TOC | 2 | Salma et al. (2006) |
| Budapest, Hungary, urban | 2006.5 and 2006.7 | PM _{2.5} /HLB/TOC | 4.7(spring) 3.8(summer) | Salma et al. (2008) |
| K-puszt, Hungary, rural | 2000.1-9 | PM _{1.5} /HLB/TOC | 4.4(winter) 3.2(summer) | Kiss et al.(2002) |
| Zurich, Switzerland, suburban | 2005.12-2006.1 | PM ₁ /C18-SEC/UV+ELSD | 1.1 | Emmenegger et al.(2007) |
| TW, Hong Kong, urban | 2007.7-2008.8 | PM _{2.5} /HLB(60mg)/HPLC+ELSD | 4.9 | Lin et al. (2010a) |
| NS, Guangzhou, China, suburban | 2007.7-2008.8 | PM _{2.5} /HLB(60mg)/HPLC+ELSD | 7.1 | Lin et al. (2010a) |
| PRD, China | 2007.11 | PM _{2.5} /HLB(60mg)/HPLC+ELSD | 11.8(5.9-18.1) | Lin et al. (2010b) |
| MFS, Guangzhou, China | 2006.7 and 2007.1 | TSP/HLB(500mg)/TOC | 5.7(summer) 3.3(winter) | Song et al. (2012) |
| UT, Guangzhou, China, suburban | 2006.7 and 2007.1 | TSP/HLB(500mg)/TOC | 4.3(summer) 7.8(winter) | Song et al. (2012) |
| WS, Guangzhou, China, urban | 2006.7 and 2007.1 | TSP/HLB(500mg)/TOC | 5.8(summer) 13.4(winter) | Song et al. (2012) |
| Guangzhou, China, urban | 2010.2-2011.1 | PM _{2.5} /ENVI-18/TOC+UV-Vis | 4.6 | Fan et al. (2016a) |
| Lanzhou, China, urban | 2012.12 and 2013.6-7 | PM _{2.5} /HLB(60mg)/HPLC+ELSD | 7.2(winter) 2.1(summer) 4.7(annual) | Tan et al. (2016) |

TW: Tsuen Wan; NS: Nansha; MFS: Maofengshan Mountain Forest Park; UT: Universities Town; WS: Wushan.

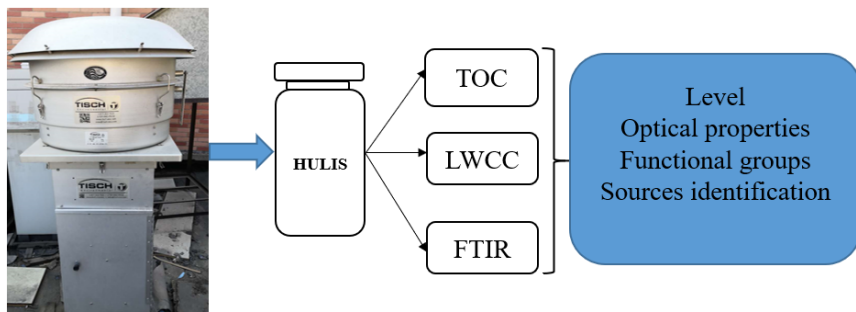
Table 3. Major band assignments for FTIR spectra of HULIS in ambient aerosols.

| Wavenumber/cm ⁻¹ | Band assignments |
|-----------------------------|--|
| 3410 | Stretching vibration of alcohols and phenolic O-H |
| 2990-2850 | Stretching vibration of C-H in aliphatic -CH ₃ and -CH ₂ - |
| 1690 | Stretching vibration of carbonylic C=O |
| 1617 | Stretching vibration of aromatic C=C |
| 1460 | Stretching vibration of aromatic rings |
| 1386 | Stretching vibration of C-O of COH of carboxylic group |
| 1272-1155 and 1088 | In-plane deformation of aromatic C-H or deformation of phenolic O-H |

Declaration of interests

☒ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

☐ The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:



Highlights

- The UV-VIS absorption of winter HULIS is obviously higher than summer.
- HULIS contain aliphatic C-H, hydroxy, carbonyl, carboxyl and aromatic rings structures.
- Biomass burning was an important source for winter HULIS, while secondary formation prevailed in summer HULIS source.