Chemical characterization of humic-like substances (HULIS) in PM_{2.5} in Lanzhou, China

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HIGHLIGHTS

- HULIS are important components of WSOC and PM_{2.5} in Lanzhou.
- HULIS were low and stable in summer while high and varied dramatically in winter.
- Residential coal burning was probably dominant HULIS source in winter.
- The contribution of HULIS from dust could be neglect.
- Adverse weather conditions play important effects on the accumulation of HULIS.

GRAPHICAL ABSTRACT

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ABSTRACT

Evaporative light scattering detection (ELSD) was applied to quantify HULIS (humic-like substances) for the first time in 2012 winter and 2013 summer at an urban site in Lanzhou. Water soluble organic carbon (WSOC), water soluble inorganic ions, and carbonaceous species (OC/EC) were also analyzed. The results show that OM (Organic Matter = OC × 1.6, constituting 45.8% to PM_{2.5}) was the most abundant species, followed by SNA (SO₄²⁻ + NO₃⁻ + NH₄⁺, constituting 23.4% to PM_{2.5}). The chemical species were in the order of: OC > EC > SO₄²⁻ > NO₃⁻ > NH₄⁺ > Cl⁻ > Ca²⁺ > K⁺. The annual average concentration of HULIS was 4.70 µg/m³ and HULIS_C (carbon content of HULIS) contributed 6.19% to PM_{2.5} and 45.6% to WSOC, indicating that HULIS was the most important components of WSOC. The concentration of HULIS was 2.14 ± 0.80 µg/m³ in summer and 7.24 ± 2.77 µg/m³ in winter, respectively. The concentrations of HULIS were relatively low and stable in summer, while high and varied dramatically in winter. The abundance of HULIS_C in WSOC shows a more concentrated distribution in Lanzhou, with a range between 0.28–0.57. The ratios of HULIS/K⁺ were 6.25 ± 1.41 and 6.14 ± 1.96 in summer and winter, respectively, suggesting there were other significant sources in addition to biomass burning emissions. HULIS and WSOC exhibited similar seasonal variation and had a strong positive correlation. In addition to the good relationship (0.89) between HULIS and Cl⁻ in winter, the great enhancement of HULIS with significantly high Cl⁻ and relatively low K⁺ in winter indicated that residential coal burning was probably an important HULIS source in

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winter. Correlation and back trajectory analysis suggested that biomass burning and secondary formation were also important HULIS sources and the contribution of HULIS from dust could be neglected. Adverse meteorological conditions were also important factors for the accumulation of HULIS in winter.

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1. Introduction

Humic-like substances (HULIS) are ubiquitous high molecular weight organic compounds in atmospheric environments (Havers et al., 1998; Zappoli et al., 1999; Kiss et al., 2002; Graber and Rudich, 2006; Duarte et al., 2007). This kind of high molecular compounds could be found in atmospheric particle, fog and cloud water, and retained term (HULIS) for its similarity with terrestrial/aquatic humic substances, especially in ultraviolet and fluorescence spectral characteristics (Zheng et al., 2013). HULIS are important species of water soluble organic compounds (~50%) and organic matter (~30%) (Havers et al., 1998; Zappoli et al., 1999; Kiss et al., 2002; Limbeck et al., 2005; Krivácsy et al., 2008; Stone et al., 2009; Zheng et al., 2013). HULIS are of special interest because of their ubiquity, high level, surface activity, light-absorbing capability and photochemical activity. HULIS can affect aerosol properties, such as hygroscopicity, cloud condensation nucleus, surface tension, and optical property (Kiss et al., 2005; Dinar et al., 2007; Fan et al., 2012; Chen et al., 2016). Because of their aqueous solubility and surface activity, HULIS also play an important role on the activation of aerosol particle into cloud droplets, and thereby have important impacts on climate change (Facchini et al., 2000; Kiss et al., 2005; Dinar et al., 2007). Moreover, recent study found HULIS may have significant adverse health effect (Lin and Yu, 2011). So, studies on HULIS are greatly helpful to understand the complexity of atmospheric organic aerosols.

The level, chemical characteristics, source, and formation pathways of HULIS have been widely studied (Havers et al., 1998; Decesari et al., 2000; Krivácsy et al., 2000; Lin and Yu, 2011; Qiao et al., 2015; Fan et al., 2012, 2016). HULIS have been quantified in bulk aerosols with quantification methods of gravimetric measurement, UV–vis detection, Total Organic Carbon analyzer (TOC) and Evaporative Light-Scattering Detection (ELSD). ELSD is especially suitable for the quantification of HULIS (Zheng et al., 2013). Measurement methods of HULIS have been reported in many sorts of places, such as ocean environments (Cavalli et al., 2004), background areas (Samburova et al., 2005; Lukács et al., 2007), rural areas (Decesari et al., 2001; Kiss et al., 2002), and urban areas (Krivácsy et al., 2008; Baduel et al., 2010). The concentrations of HULIS varied from 0.15 to 25.6 $\mu\text{g}/\text{m}^3$, with HULIS_c consisting of 9–72% of WSOC (Zheng et al., 2013). In addition, the methods of UV–vis, fluorescence, Raman spectroscopy, elemental compositions and molecular weight analysis of HULIS are also widely used to provide further information on functional group, molecular weight distribution of atmospheric HULIS (Graber and Rudich, 2006; Duarte et al., 2007; Lin et al., 2012).

Previous studies have confirmed biomass burning and secondary formation are dominant sources of HULIS (Lin et al., 2010; Zheng et al., 2013). Lin et al. (2010) found atmospheric HULIS were abundant in both ambient (~60% of WSOC), and fresh biomass burning emission (~30% of WSOC) in South China. Facchini et al. (1999) found a good relationship between HULIS and levoglucosan, suggesting biomass burning is a significant source of HULIS. As for secondary formation, there are several pathways for the formation of HULIS. Plume processes (including the aging of fresh HULIS or new HULIS formation) and ambient atmospheric secondary HULIS formation (heterogeneous reaction and aqueous phase oligomerization) contribute most of the secondary HULIS. Although there have been numerous studies on atmospheric HULIS, no information has been published about chemical characteristics of HULIS in PM_{2.5} in Lanzhou.

Lanzhou is the capital and largest city of Gansu Province in North-west China, with a population of about 3.6 million, and also a center for heavy industry and petrochemical industry. Lanzhou ranks as one of the cities with the worst air quality in China and the world, due to industrial pollution and its situation in a narrow river trough-shaped valley surrounded by mountains. The topography of Lanzhou forms a stable atmosphere, weak wind and strong inversion layer, which hinder the dispersion of air pollutants (Zhang et al., 2014). It ranked as the most polluted city among the provincial capital cities in China and the levels of air pollution were 6 times higher than the WHO annual average guide value (20 $\mu\text{g}/\text{m}^3$) in 2009 (Zhang et al., 2014). There have been several studies about chemical species of PM_{2.5} in Lanzhou (Pathak et al., 2009; Wang et al., 2009; Yang et al., 2011; Fan et al., 2014). Until now, no measurements of atmospheric HULIS have been reported in Lanzhou. The objective of this work, which based on the field sampling, laboratory experiment, and mathematical analysis, was to investigate the chemical characteristics, sources and formation mechanisms of HULIS in Lanzhou. The results would be helpful to understand HULIS in organic aerosol in the North China.

2. Experimental

Lanzhou city is situated at the intersection of Qinghai–Tibet Plateau, the inner Mongolian Plateau and Loess Plateau. It is surrounded by mountains rise to 200 ~ 600 m. The sampling site (36.046°N, 103.833°E) was located at the roof of Lanzhou Environmental Protection Bureau (EPB) office building (a 4-storey building). Fig. 1 shows the location of the sampling site, which is located in the eastern of urban Lanzhou. The sampling location is about 25 m above the ground and located in a primarily residential and commercial area without obvious industrial sources. There are two major roads with busy traffic, Jinchang Road and Minzhu west road, which lie 50 m west and 300 m south of the sampling site, respectively.

24-h samples of PM_{2.5} were collected with a high volume air sampler (Graseby-Andersen, GMW High Volume Air Sampler) at a flow rate of 1.13 $\text{m}^3 \text{min}^{-1}$. A total of 80 samples were collected from 1 December 2012 to 31 December 2012 (winter), and 23 June 2013 to 25 July 2013 (summer). Whatman quartz fiber filters (20.3 × 25.4 cm) were heated at 500 °C to remove organic species and used to collect bulk aerosol samples. The loaded filters were wrapped in aluminum foil after sampling, and stored in a refrigerator at –20 °C before analysis to prevent the evaporation of volatile components. Meteorological data during the sampling period were obtained from <http://www.wunderground.com>.

2.1. Chemical analyses

2.1.1. Water soluble inorganic ions

An ultrasonic method was used to extract water soluble inorganic ions from filter, and over 98% of ions can dissolve into water. The filter was submerged in a vial with 10 mL ultrapure water, and ultrasonicated for 15 min for each time. The extraction was repeated twice and was filtered with a 0.45 μm Teflon filter, and then analyzed by ion chromatography (Dionex ICS 900 and 1100). The recoveries of each ion (SO_4^{2-} , NO_3^- , NH_4^+ , Cl^- , K^+ , Ca^{2+} , Na^+ and Mg^{2+}) were in the range of 90%–110%. The relative standard deviation of each ion was

Fig. 1. The sampling map of Lanzhou.

<5% in reproducibility tests. The details are given elsewhere (Tan et al., 2009, 2016).

2.1.2. OC/EC

A DRI Thermal/Optical Carbon Analyzer was used to analyze OC and EC and the thermal evolution protocol IMPROVE (Interagency Monitoring of Protected Visual Environments) was adopted. A punch of quartz filter was heated stepwise at temperatures of 120 °C (OC1), 250 °C (OC2), 450 °C (OC3), and 550 °C (OC4) in a non-oxidizing helium (He) atmosphere, and 550 °C (EC1), 700 °C (EC2) and 800 °C (EC3) in an oxidizing atmosphere of 2% oxygen in a balance of helium. The carbon is quantified with a flame ionization detector. The instrument was calibrated daily with CH₄. The limits of detection of OC and EC are below 1.0 µg/m³. Replicate analyses were performed per 10 samples. The determined repeatability was better than 5% (Cheng et al., 2009; Tan et al., 2014).

2.1.3. WSOC

Each filter was ultrasonically extracted with 30 mL of ultrapure water for 15 min. The extraction was filtered with a 0.22 µm membrane filter (PVDF, German Sciences). WSOC were measured by a TOC Analyzer (Analyticjena AG multi N/C 3100, Germany) using high temperature (680 °C) Pt-catalyzed oxidation coupled to non-dispersive infrared gas detection of CO₂. Calibration curves for WSOC were created using a potassium hydrogen phthalate standard. All samples were acidified to remove inorganic carbon with 2 M hydrochloric acid.

2.1.4. Isolation and detection of HULIS

The isolation of HULIS is based on the method established by Lin et al. (2010). Hydrophilic low weight molecular organic acids and inorganic ions will pass through the SPE cartridge (Oasis HLB, 30 µm, 60 mg/cartridge, Waters, USA) and appear in the effluent, while the protonated hydrophobic HULIS are retained on the SPE cartridge. Portions of the filters were extracted with Milli-Q water in an ultrasonic bath for 20 min. The extraction was filtered with a 0.22 µm membrane filter to remove debris and suspended insoluble particle, and then acidified to pH 2 with HCl (2 M) before it was loaded on a SPE cartridge. The loaded cartridge was subsequently rinsed with 1 mL water and 1 mL methanol containing 2% (w/w) ammonia. The eluate was evaporated to dryness

under a gentle stream of N₂ and re-dissolved in 4 mL water and then analyzed by an ELSD (Model 3300, Alltech, USA).

A PEEK tube (polyaryletheretherketone, Alltech, Dearfield, IL, USA, 15 m long and 0.127 mm) was used to connect the HPLC injector port and ELSD detector to provide a proper level of back pressure to maintain a stable baseline. Operating conditions of HPLC were as follows: isocratic elution with a mobile phase of 20% acetonitrile (HPLC grade) and 80% water (above 18 MΩ-cm) at a flow rate of 0.6 mL min⁻¹. N₂ was operated at a flow rate of 1.5 L min⁻¹ for the nebulizer and a drift tubing temperature (90 °C). The analyzer was calibrated with NAFA (Nordic Aqueous Fulvic Acid), SRFA (Suwannee River Fulvic Acid, International Humic Substances Society), and sucrose. The instrument calibration was performed by using standard solutions of SRFA at the concentrations of 0, 10, 25, 50, 100 and 250 µg/mL. Detection limit of the analytical method was based on three times signal to noise ratio plus the average blank, and was 0.19 µg/m³ in this study. The uncertainty of the HULIS was estimated to be about 10%. To verify the reliability of the sampling procedure and analysis procedure, field blanks were performed per 10 samples to determine the background contamination. Solvent blanks and spiked blanks (standards spiked into solvent) were also analyzed.

2.1.5. Back trajectory calculation

In order to better understand the transport of airborne particles from distant sources, the HYSPLIT model (HYbrid Single-Particle Lagrangian Integrated Trajectory, Version 4.9, windows-based version), a comprehensive modelling system developed by the National Oceanic and Atmospheric Administration (NOAA) Air Resource Laboratory (Draxler and Rolph, 2003), was used to generate 72-h back trajectories during typical episodes. The relative ground height was 500 m and every trajectory was colored with the concentration of HULIS.

3. Results and discussion

3.1. Chemical composition of PM_{2.5}

The seasonal distribution and the time series of major chemical species of PM_{2.5} were illustrated in Figs. 2 and 3, respectively. The conversion factor of 1.6 was assumed to calculate OM from OC (Cheng et al., 2009). The concentrations of PM_{2.5} were reconstructed from the

Fig. 2. The chemical composition of major chemical species in PM_{2.5}.

measured chemical species, including OM, EC and water soluble inorganic ions (Cl⁻, NO₃⁻, SO₄²⁻, NH₄⁺, Na⁺, K⁺, Ca²⁺ and Mg²⁺). Although chemical species were significantly higher in winter than those in summer, the contribution of OC to PM_{2.5} was relatively stable through the entire sampling period (Fig. 2). Consistent with the previous results in China (Yang et al., 2011), carbonaceous species and SNA were the largest component. The chemical species were in the order of: OC > EC > sulfate > nitrate > ammonium > chloride > calcium > potassium (Table 1). It is worth to note that EC usually exceeded sulfate and nitrate, except during no-haze period.

Fig. 2 clearly indicated that OC was the most abundant constituent of PM_{2.5}. OM accounted for $45.1 \pm 6.7\%$ and $46.5 \pm 7.1\%$ of PM_{2.5} in summer and winter, respectively. OC ranged from 3.1 to 59.5 $\mu\text{g}/\text{m}^3$, with an average of $22.56 \pm 12.35 \mu\text{g}/\text{m}^3$, and was significantly higher in winter than that in summer. OC ($35.39 \pm 13.89 \mu\text{g}/\text{m}^3$) in winter was about 3.63 times that ($9.73 \pm 3.30 \mu\text{g}/\text{m}^3$) in summer. EC ranged from 1.54 to

24.48 $\mu\text{g}/\text{m}^3$, with an average of $9.12 \pm 6.2 \mu\text{g}/\text{m}^3$, and was also an important component of PM_{2.5} and well correlated with OC, which indicated that they might have a similar primary source. The average level of carbonaceous species in Lanzhou is higher than those in recent results from European and Chinese urban cities (Viana et al., 2008; Huang et al., 2012; Du et al., 2014; Tan et al., 2016).

The concentration of WSOC was low in summer ($2.67 \pm 0.77 \mu\text{g}/\text{m}^3$) and high in winter ($8.58 \pm 2.84 \mu\text{g}/\text{m}^3$), ranging from 1.14 to 13.24 $\mu\text{g}/\text{m}^3$, with an annual average of $5.61 \pm 3.54 \mu\text{g}/\text{m}^3$. Atmospheric WSOC in winter in Lanzhou was much higher than those in other European cities, such as Barcelona, Amsterdam, and Netherlands (Viana et al., 2008). It is obvious that WSOC varied significantly in different seasons and was always well correlated with OC (Fig. 4). The ratios of WSOC/OC exhibited slightly temporal variations with a slightly higher value in summer ($29.3 \pm 5.3\%$) than that ($25.6 \pm 5.9\%$) in winter, consistent with the results of previous studies (Huang et al., 2012). The WSOC/OC ratio is

Fig. 3. Time series of chemical species of PM_{2.5} in Lanzhou.

Table 1 The seasonal variation of HULIS and other species in Lanzhou ($\mu\text{g}/\text{m}^3$).

Sampling Periods	PM _{2.5}	HULIS	WSOC	WSOM	OC	EC	SO ₄ ²⁻	NO ₃ ⁻	NH ₄ ⁺	Cl ⁻	Ca ²⁺	K ⁺
Winter	120.47	7.24	8.55	26.84	35.39	13.80	11.82	7.21	6.70	5.20	2.18	1.10
Summer	34.12	2.15	2.68	7.06	9.74	4.44	4.30	1.88	1.93	0.67	1.30	0.38
Annual	77.29	4.70	5.61	16.95	22.56	9.12	8.06	4.55	4.31	2.94	1.74	0.79
Haze	182.08	10.06	12.05	40.14	52.19	19.67	15.98	14.13	11.74	9.33	2.21	1.82
No-haze	51.65	3.49	4.58	8.20	12.78	5.77	7.85	3.10	3.90	1.84	1.24	0.58
Snow	80.69	4.62	5.71	18.69	24.40	8.82	8.64	3.69	3.45	2.70	2.77	0.73

usually used as an indicator of the formation of secondary organic aerosol (SOA) (Huang et al., 2012; Du et al., 2014). The enhancement of WSOC/OC in summer was likely due to the transformation of primary organic compounds to WSOC.

SNA accounted for 23.3% of PM_{2.5} and 71.5% of water soluble inorganic ions, and exhibited high value ($25.73 \pm 11.33 \mu\text{g}/\text{m}^3$) in winter, while low value ($8.10 \pm 3.01 \mu\text{g}/\text{m}^3$) and slightly daily variation in summer. Sulfate, nitrate, ammonium, chloride and calcium were the most important water soluble inorganic ions both in summer and winter (Table 1). The concentrations of sulfate, nitrate, and ammonium in winter were 2.7, 3.8 and 3.5 times of those in summer, respectively. Nitrate is more sensitive to temperature, and higher temperature do not favor the formation of nitrate in summer. The seasonal trend of NH₄⁺ is similar to that of NO₃⁻.

Non-sea-salt (nss) Cl⁻ is believed to be associated with coal combustion, and greatly elevated nss-Cl⁻ level in winter ($5.21 \pm 2.57 \mu\text{g}/\text{m}^3$) is consistent with a high contribution from coal combustion, coupled with low atmospheric mixing layer. Cl⁻ experienced the largest variation in two seasons and its level in winter was 7.8 times of that in summer. K⁺ can be derived from sea-salt, dust, coal combustion as well as biomass burning. However, biomass burning is regarded as the most important source for K⁺ and it is usually used as an indicator of biomass burning (Cheng et al., 2013). Compared with other cities, the average concentration of K⁺ was relatively low in summer ($0.38 \pm 0.17 \mu\text{g}/\text{m}^3$) and winter ($1.10 \pm 0.51 \mu\text{g}/\text{m}^3$), suggesting biomass burning is not the most important source for PM_{2.5} and other chemical species (Pathak et al., 2009). Ca²⁺ originates from sea salt, soil particle, and traffic dust. Even Lanzhou is located in loess plateau, the yellow sand storm has not been observed during the sampling period and the

concentration of Ca²⁺ was only slightly higher than those in other cities (Pathak et al., 2009; Yang et al., 2011).

3.2. The abundance of HULIS

As shown in Table 1, the average concentration of HULIS ranged from 0.93 ~ 11.61 $\mu\text{g}/\text{m}^3$ with the average concentration of $4.69 \pm 3.27 \mu\text{g}/\text{m}^3$. Zheng et al. (2013) summarized the levels of HULIS in field investigations with different qualification methods, and HULIS was in the range of 1–2 $\mu\text{g}/\text{m}^3$ in most studies. HULIS was most intensively studied in Europe, where its level <0.1 $\mu\text{g}/\text{m}^3$ for marine environments, ~4.7 $\mu\text{g}/\text{m}^3$ in urban areas (Salma et al., 2007). In those previous studies, TOC and HPLC-ELSD are both common quantification methods. Thus, for the convenience of the comparison, the concentration of HULIS is always estimated by dividing HULIS with a conversion factor. For HULIS isolated by SPE method, the factor ranged from 1.8 to 2.3, with 1.81 for urban HULIS (Salma et al., 2007), 1.93 for rural aerosol (Kiss et al., 2002), 1.94 for a rural site during a harvest season (Lin et al., 2010), 2.04 for biomass burning (Salma et al., 2010), and 1.89–2.28 in Guangzhou (Song et al., 2012). 1.81 was used as a conversion factor of HULIS/HULISc in this study. The comparison of HULISc in Lanzhou with other studies was showed in Fig. 5. The highest concentration of HULISc was 6.45 $\mu\text{g}/\text{m}^3$ in urban Lanzhou. Compared with previous studies, HULISc was higher in Lanzhou city than those in rural areas, and consistent with those in urban area. HULISc was intensively studied and significantly higher (13.4 $\mu\text{g}/\text{m}^3$) in the South China (Song et al., 2012).

In previous studies, HULISc/WSOC was generally within the range of 0.24–0.72, while HULIS and HULISc/WSOC were both low (0.09–0.23)

Fig. 4. The time series of HULIS and WSOC in Lanzhou city.

Fig. 5. The comparison of the level of HULIS in Lanzhou with other studies.

from marine and highland aerosol (Feczeko et al., 2007; Lukács et al., 2007; Krivácsy et al., 2008). The ratio of HULIS/WSOC shows a more concentrated distribution in Lanzhou, with a range between 0.28–0.57. The average ratio of HULIS/WSOC was 0.45 ± 0.06 , with slightly high value (0.47 ± 0.05) in winter, and low value (0.44 ± 0.06) in summer, which less than those such as ~ 0.60 in South China (Lin et al., 2010), ~ 0.62 in Hungary (Salma et al., 2007), and consistent with that in Shanghai (Qiao et al., 2015). The high ratio of HULIS/WSOC illustrated that HULIS was the most important components of WSOC in Lanzhou.

3.3. Temporal variations of HULIS

The time series of HULIS and WSOC was illustrated in Fig. 4. The average concentration of HULIS was $4.81 \pm 3.54 \mu\text{g}/\text{m}^3$, accounting for $6.2 \pm 1.3\%$ of $\text{PM}_{2.5}$, with high concentration ($7.24 \pm 2.77 \mu\text{g}/\text{m}^3$) in winter, low concentration ($2.14 \pm 0.80 \mu\text{g}/\text{m}^3$) in summer. HULIS exhibited similar seasonal variation with WSOC, and varied dramatically day by day in winter, with the maximum ($11.60 \mu\text{g}/\text{m}^3$) in winter 12.6 times of the minimum ($0.90 \mu\text{g}/\text{m}^3$) in summer. The seasonal variation of HULIS resulted from weather conditions, secondary processes and primary source emissions. The high concentrations of HULIS in winter were mainly caused by the large amount of local emission due to warm-heating, poor diffusion condition, and slow degradation rate. Further evidence about the possible source of HULIS would be presented in Section 3.5. Lanzhou is located at a narrow (2–8 km width), long (40 km) and deep (200–600 m) valley basin with the Baita (~ 1700 m) and Gaolan Mountain (~ 1900 m) in the north and south. The special topographic features make air pollution very difficult to diffuse in winter (Chu et al., 2008). However, temperature inversion phenomenon is reduced in summer, coupled with strong convective activity, so air pollutants can be easily diffused.

The ratio of HULIS/WSOC was relatively stable (0.34–0.51) in different countries, despite the large variation of HULIS (0.4 – $10 \mu\text{g}/\text{m}^3$) (Krivácsy et al., 2008). In this study, we can also find the ratios of HULIS/WSOC were stable (0.30–0.50) and HULIS (0.90 – $11.62 \mu\text{g}/\text{m}^3$) experienced large variation during the sampling period in Lanzhou (Fig. 6). The ratio of HULIS/WSOC has a relatively good positive relationship with HULIS in summer. However, when HULIS are higher than $6.0 \mu\text{g}/\text{m}^3$, which all of those samples are found in winter, the ratio of HULIS/WSOC is between 0.40–0.50 and has a weak relationship with HULIS. In addition, HULIS was found to represent 4.0%–19% of OC, with the average value of 12.3%. HULIS/OC ratios were 11.9% and 12.3% in summer and winter, respectively. Thus, even though most of

chemical species were significantly higher in winter than those in summer, for example, Cl^- , NO_3^- , HULIS, OC and EC in winter were 7.8, 3.8, 3.4, 3.4 and 3.1 times of those in summer. The contributions of most of chemical species to $\text{PM}_{2.5}$ and some diagnostic ratios (HULIS/ K^+ , HULIS/OC, HULIS/WSOC) were relatively stable in summer and winter, suggesting local source emissions were dominant through the sampling period in Lanzhou.

3.4. Relationship between HULIS and meteorology

HULIS can be formed by photochemical reactions of primary precursors as well as their oxidation products. Thus, meteorological parameters, such as temperature, wind speed, wind direction, can influence atmospheric chemistry processes and diffusion conditions, consequently affecting the concentration of HULIS. In order to evaluate the effects of meteorological conditions on HULIS, correlations between HULIS and ambient temperature, relative humidity (RH), and wind speed were determined (Fig. 7). The correlation between HULIS and temperature is weak, and the concentrations of HULIS were low under warm conditions ($> 10^\circ\text{C}$), which are generally considered favorable for their formation. However, high level of HULIS occurred under cold conditions ($< 0^\circ\text{C}$), indicating that the concentration of HULIS is strongly dependent upon atmospheric dynamics and local dispersion conditions, and these factors are not necessarily related to temperature. The ratio of HULIS/WSOC exhibited a weak relationship with temperature in summer, which further suggested that high temperature in summer may not favor the formation of HULIS.

Fig. 6. The relationship between HULIS and the ratio of HULIS/WSOC.

Fig. 7. The relationship between temperature, RH, wind speed and HULIS.

A substantial number of studies have highlighted the importance of aerosol liquid water to the formation of SOA. However, no significantly relationship was found between HULIS and RH in summer, and they are negatively correlated in winter. The negative correlation of HULIS and RH is not consistent with the hypothesis that HULIS formation is linked with aqueous processes, which indicates the importance of photo-oxidation reaction to the formation of HULIS. The depletion of oxidant might accelerate and hinder the reaction between VOCs and the oxidant under high RH. An exponential decrease of HULIS and HULIS/OC occurred with the increase of wind speed. Thus, it is apparent most of air pollutants were diluted in strong wind speed.

Fig. 8 presented the typical back trajectories ending at Lanzhou city during the sampling period. The model results indicated that the concentration of HULIS had a good relationship with the path air masses passed. The HYSPLIT model illustrated that air mass with high level of HULIS during haze periods (starting with a circle) came from south or west passing through the south of Lanzhou, where is greatly influenced by air pollution from Yuzhong industrial park. This type of air masses had the highest concentration of $\text{PM}_{2.5}$ and chemical species, especial for HULIS and Cl^- . The results showed that significant amounts of air pollutants were possibly transported from the south polluted areas. On the contrary, the cleaner air mass (starting with a triangle or rectangle) came from the north of Lanzhou with the lower chemical species. It's also interesting to note that polluted air masses originated from Tarim basin in Xinjiang province, characterized with the highest concentration of most chemical species (colored with red), passed the trough-shaped valley from Xining (the capital city of Qinghai province), and then arrived in Lanzhou. Its pathway covered relatively densely populated areas of the Qinghai province and emissions from those regions would be transported to Lanzhou. The topography also favors the accumulation of the air pollutants.

3.5. Possible sources of HULIS

3.5.1. HULIS associated with biomass burning

Biomass burning was now generally regarded as a dominant primary source of HULIS (Zheng et al., 2013). Relationships between HULIS and tracers (such as K and levoglucosan, etc.) can provide evidence with respect to the formation of HULIS. Biomass burning is regarded as the most important source for K^+ , which it's acceptable to be adopted as an indicator of biomass burning (Cheng et al., 2013). Compared with other cities, the average concentration of K^+ was pretty low both in summer ($0.38 \pm 0.17 \mu\text{g}/\text{m}^3$), and winter ($1.20 \pm 0.51 \mu\text{g}/\text{m}^3$) in Lanzhou. Good positive correlations were revealed between HULIS and K^+ both in winter ($R^2 = 0.82$) and summer ($R^2 = 0.60$), which may indicate HULIS and K^+ had a similar source during the entire period.

The HULIS/ K^+ ratio can be used to indicate the magnitude of the accumulation of HULIS during atmospheric aging. The HULIS/ K^+ ratio in the ambient aerosols (5.27 ± 0.7) were 4–9 times of that from fresh biomass burning emission (Lin et al., 2010), suggesting there were significant sources in addition to biomass burning. The ratios of HULIS/ K^+ were 6.25 ± 1.41 and 6.14 ± 1.96 in summer and winter, respectively, suggesting there were significant sources other than biomass burning, which are consistent with the correlation analysis results.

3.5.2. HULIS associated with coal combustion

Field observation investigations have related HULIS with biomass burning, vehicle emissions and atmospheric secondary processes (Zheng et al., 2013). HULIS related with vehicular exhaust in road tunnel (El Haddad et al., 2009) and kerbside (Salma et al., 2007) was found to constitute 5% to $\text{PM}_{2.5}$. However, no direct evidence of HULIS was presented from vehicular exhaust, and thus it was more likely due to ambient background contamination. Until now, no field observation has

Fig. 8. Back trajectories of air masses arriving at the sampling site.

been reported to investigate HULIS from coal combustion emissions. However, previous studies found brown to yellowish organic carbon could be observed from smoldering coal combustion, especially in low temperature combustion condition and inferred that the light absorbing organic carbon was probably oxygenated or multifunctional with very high molecular weight, which related with HULIS and brown carbon (Bond, 2001). It is emitted just after coal addition, when coal devolatilizes and the combustion chamber is not hot enough to oxidize particles (Bond, 2001). Thus, coal combustion, especial briquettes for heating purpose in winter, could be an important source of HULIS.

Strong positive correlation was revealed between HULIS and Cl^- in winter ($R^2 = 0.89$) and the correlation was relatively weak in summer ($R^2 = 0.17$), indicating HULIS and Cl^- might have a similar source in winter. Cl^- could not have been presented as sea salt particle since Lanzhou is far away from sea, and it is directly emitted from coal combustion, since the Cl^- depletion reaction with nitric acid and hydrochloric acid would be favored at high temperature (Wei et al., 2015). Cl^- is known to be a minor component of particle from coal combustion and a major constituent from the briquettes used in Chinese cities. Residential coal combustion (briquettes) is one of the major sources of air pollution during winter heating period in Lanzhou. Duan (unpublished) found coal combustion was major source of $\text{PM}_{2.5}$ in winter (29%) and only 6% in summer in Lanzhou. High contributions of WSOC and Cl^- were also found from coal combustion in our unpublished results. So, the high concentration of HULIS during winter heating period was probably related with coal combustion.

3.5.3. HULIS associated with secondary formation

Laboratory studies showed that certain atmospheric organic compounds were oxidized in simulated cloud water to high molecular weight compounds, which exhibited similar properties to HULIS (Gelencser et al., 2003). The correlations of HULIS with secondary inorganic ions were also investigated (Table 2 and Fig. 9). Weak correlation between HULIS and sulfate in summer ($R^2 = 0.25$) possibly indicated that they didn't have similar sources or formation pathways, and photochemical reaction wasn't an important source of HULIS. In this case, the

good correlation between HULIS and sulfate in winter ($R^2 = 0.74$) could indicate the importance of secondary formation of HULIS.

HULIS also correlated well with NO_3^- ($R^2 = 0.83$) and NH_4^+ ($R^2 = 0.82$) in winter. NH_4^+ is mainly from the conversion of atmospheric emissions significantly affected by local sources. Different Seasonal correlation between HULIS and NO_3^- , SO_4^{2-} , NH_4^+ showed a more important primary source of HULIS. The correlation between HULIS and Ca^{2+} was poor and varied slightly throughout the year; suggesting dust or soil should not be an important source of HULIS.

In order to further evaluate the secondary formation of HULIS, correlations between HULIS and, SOC and WSOC were determined. The OC/EC ratio is widely used to identify the presence of SOA when the value exceeds 2.0 (Du et al., 2014). In this study, secondary organic carbon (SOC) was calculated based on EC-tracer method:

$$\text{SOC} = \text{OC} - (\text{OC}/\text{EC}_{\text{pri}}) * \text{EC}$$

where (OC/EC)_{pri} is the ratio of OC to EC for primary emission; Slope and intercept of the linear regression of OC on EC for a subset of samples with lowest OC/EC ratio have been suggested as an estimation of (OC/EC)_{pri}. Correlation between HULIS and SOC was $R^2 = 0.49$, suggesting secondary formation might contribute to HULIS. HULIS and WSOC have a strong correlation both in summer and winter, suggesting HULIS is an important component of OC and they have a common origin.

Table 2

Correlation coefficient (R^2) between water soluble inorganic ions and HULIS.

	Annual	Summer	Winter
Na^+	0.89	0.50	0.72
NH_4^+	0.88	−0.01	0.82
K^+	0.85	0.60	0.82
Mg^{2+}	0.68	0.39	0.18
Ca^{2+}	0.41	0.42	−0.04
Cl^-	0.93	0.17	0.89
NO_3^-	0.89	0.13	0.83
SO_4^{2-}	0.85	0.25	0.74

Fig. 9. The relationship between water soluble inorganic species and HULIS.

4. Conclusions

HULIS are an important macromolecular compound and only a little has been known about HULIS in Lanzhou. PM_{2.5} filter sampling was consecutively conducted on a daily basis in 2012 winter and 2013 summer at an urban site in Lanzhou, North China. PM_{2.5} samples were subjected to chemical analysis including HULIS, WSOC, water soluble inorganic ions, OC and EC. HULIS was quantified with Evaporative Light-Scattering Detection. The results showed that OM was the most abundant species, followed by SNA. The chemical species were in the order of: OC > EC > sulfate > nitrate > ammonium > chloride > calcium > potassium. It is worthy to point out the contribution of EC exceed sulfate and nitrate, except during no-haze period. HULIS ranged from 0.93–11.61 $\mu\text{g}/\text{m}^3$ with the average concentration of $4.69 \pm 3.27 \mu\text{g}/\text{m}^3$. HULIS-C contributed 6.19% to PM_{2.5} and 45.6% to WSOC. Compared with previous studies, the average concentration of HULIS in Lanzhou was higher than those in rural areas, and consistent with those in urban areas; however, HULIS ($< 2 \mu\text{g}/\text{m}^3$) was pretty low in summer. HULIS exhibited similar seasonal variation with WSOC and the average concentration of HULIS was low ($2.14 \pm 0.80 \mu\text{g}/\text{m}^3$) in summer and high ($7.24 \pm 2.77 \mu\text{g}/\text{m}^3$) in winter, respectively. The concentrations of HULIS were relatively low and stable in summer, while high and varied dramatically in winter. The average ratio of HULIS/WSOC was 0.45 ± 0.06 and HULIS/WSOC showed a more concentrated distribution, with a range between 0.2–0.57 in Lanzhou. HULIS were positively correlated with Cl^- , K^+ , WSOC, SOC, and secondary water soluble inorganic ions (SO_4^{2-} , NO_3^- , and NH_4^+), suggesting that biomass burning and secondary organic aerosols both contributed to HULIS. The weak negative relationship between HULIS and Ca^{2+} suggested the contribution of HULIS from dust could be neglect. In addition to the good relationship between HULIS and Cl^- in winter, the great enhancement of HULIS with significantly high Cl^- and relatively low K^+ in winter also indicated that residential coal burning was probably a dominant HULIS source in winter. Adverse meteorological conditions (such as weak wind) were also the important causes for the accumulation of HULIS in winter.

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References

- Baduel, C., Voisin, D., Jaffrezou, J.L., 2010. Seasonal variations of concentrations and optical properties of water soluble HULIS collected in urban environments. *Atmos. Chem. Phys.* 10, 4085–4095.
- Bond, T.C., 2001. Spectral dependence of visible light absorption by carbonaceous particles emitted from coal combustion. *Geophys. Res. Lett.* 28 (21), 4075–4078.
- Cavalli, F., Facchini, M.C., Decesari, S., et al., 2004. Advances in characterization of size-resolved organic matter in marine aerosol over the North Atlantic. *J. Geophys. Res. D Atmos.* 109, 1–14.
- Chen, Q., Ikemori, F., Higo, H., et al., 2016. Chemical structural characteristics of HULIS and other fractionated organic matter in urban aerosols: results from mass spectral and FT-IR analysis. *Environ. Sci. Technol.* 50, 1721–1730.
- Cheng, Y., He, K.B., Duan, F.K., et al., 2009. Measurement of semivolatile carbonaceous aerosols and its implications: a review. *Environ. Int.* 35, 674–681.
- Cheng, Y., Engling, G., He, K.B., et al., 2013. Biomass burning contribution to Beijing aerosol. *Atmos. Chem. Phys.* 13, 7765–7781.
- Chu, P.C., Chen, Y., Lu, S., 2008. Atmospheric effects on winter SO_2 pollution in Lanzhou, China. *Atmos. Res.* 89, 365–373.
- Decesari, S., Facchini, M.C., Fuzzi, S., et al., 2000. Characterization of water-soluble organic compounds in atmospheric aerosol: a new approach. *J. Geophys. Res. D Atmos.* 105, 1481–1489.
- Decesari, S., Facchini, M.C., Matta, E., et al., 2001. Chemical features and seasonal variation of fine aerosol water-soluble organic compounds in the Po Valley, Italy. *Atmos. Environ.* 35, 3691–3699.
- Dinar, E., Taraniuk, I., Graber, E.R., et al., 2007. Hygroscopic growth of atmospheric and model humic-like substances. *J. Geophys. Res. D Atmos.* 112.
- Draxler, R.R., Rolph, G.D., 2003. HYSPLIT (HYbrid Single-Particle Lagrangian Integrated Trajectory). NOAA Air Resources Laboratory, Silver Spring, MD.
- Du, Z., He, K., Cheng, Y., et al., 2014. A year-long study of water-soluble organic carbon in Beijing I: sources and its primary vs. secondary nature. *Atmos. Environ.* 92, 514–521.
- Duarte, R.M.B.O., Santos, E.B.H., Pio, C.A., et al., 2007. Comparison of structural features of water-soluble organic matter from atmospheric aerosols with those of aquatic humic substances. *Atmos. Environ.* 41, 8100–8113.
- El Haddad, I., Marchand, N., Dron, J., et al., 2009. Comprehensive primary particulate organic fraction characterization of vehicular exhaust emissions in France. *Atmos. Environ.* 43, 6190–6198.

- Facchini, M.C., Fuzzi, S., Zappoli, S., et al., 1999. Partitioning of the organic aerosol component between fog droplets and interstitial air. *J. Geophys. Res. Atmos.* 104, 26821–26832.
- Facchini, M.C., Decesari, S., Mircea, M., et al., 2000. Surface tension of atmospheric wet aerosol and cloud/fog droplets in relation to their organic carbon content and chemical composition. *Atmos. Environ.* 34, 4853–4857.
- Fan, X., Song, J., Peng, P., 2012. Comparison of isolation and quantification methods to measure humic-like substances (HULIS) in atmospheric particles. *Atmos. Environ.* 60, 366–374.
- Fan, J., Yue, X., Jing, Y., et al., 2014. Online monitoring of water-soluble ionic composition of PM₁₀ during early summer over Lanzhou City. *J. Environ. Sci.* 26, 353–361.
- Fan, X., Song, J., Peng, P., 2016. Temporal variations of the abundance and optical properties of water soluble humic-like substances (HULIS) in PM_{2.5} at Guangzhou, China. *Atmos. Res.* 172–173, 8–15.
- Feczko, T., Puxbaum, H., Kasper-Giebl, A., et al., 2007. Determination of water and alkaline extractable atmospheric humic-like substances with the TU Vienna HULIS analyzer in samples from six background sites in Europe. *J. Geophys. Res. D Atmos.* 112.
- Gelencser, A., Hoffer, A., Kiss, G., et al., 2003. In-situ formation of light-absorbing organic matter in cloud water. *J. Atmos. Chem.* 45, 25–33.
- Graber, E.R., Rudich, Y., 2006. How humic-like are they: a comprehensive and critical review. *Atmos. Chem. Phys.* 729–753.
- Havers, N., Burba, P., Lambert, J., et al., 1998. Spectroscopic characterization of humic-like substances in airborne particulate matter. *J. Atmos. Chem.* 29, 45–54.
- Huang, H., Ho, K.F., Lee, S.C., et al., 2012. Characteristics of carbonaceous aerosol in PM_{2.5}: Pearl Delta River region, China. *Atmos. Res.* 104, 227–236.
- Kiss, G., Varga, B., Galambos, I., et al., 2002. Characterization of water-soluble organic matter isolated from atmospheric fine aerosol. *J. Geophys. Res. D Atmos.* 107.
- Kiss, G., Tombacz, E., Hansson, H.C., 2005. Surface tension effects of humic-like substances in the aqueous extract of tropospheric fine aerosol. *J. Atmos. Chem.* 50, 279–294.
- Krivácsy, Z., Kiss, G., Varga, B., et al., 2000. Study of humic-like substances in fog and interstitial aerosol by size-exclusion chromatography and capillary electrophoresis. *Atmos. Environ.* 34, 4273–4281.
- Krivácsy, Z., Kiss, G., Ceburnis, D., et al., 2008. Study of water-soluble atmospheric humic matter in urban and marine environments. *Atmos. Res.* 87, 1–12.
- Limbeck, A., Handler, M., Neuburger, B., et al., 2005. Carbon-specific analysis of humic-like substances in atmospheric aerosol and precipitation samples. *Anal. Chem.* 77, 7288–7293.
- Lin, P., Yu, J.Z., 2011. Generation of reactive oxygen species mediated by humic-like substances in atmospheric aerosols. *Environ. Sci. Technol.* 45, 10362–10368.
- Lin, P., Engling, G., Yu, J.Z., 2010. Humic-like substances in fresh emissions of rice straw burning and in ambient aerosols in the Pearl River Delta region, China. *Atmos. Chem. Phys.* 10, 6487–6500.
- Lin, P., Yu, J.Z., Engling, G., et al., 2012. Organosulfates in humic-like substance fraction isolated from aerosols at seven locations in East Asia: a study by ultra-high-resolution mass spectrometry. *Environ. Sci. Technol.* 46, 13118–13127.
- Lukács, H., Gelencsér, A., Hammer, S., et al., 2007. Seasonal trends and possible sources of brown carbon based on 2-year aerosol measurements at six sites in Europe. *J. Geophys. Res. Atmos.* 112.
- Pathak, R.K., Wu, W.S., Wang, T., 2009. Summertime PM_{2.5} ionic species in four major cities of China: nitrate formation in an ammonia-deficient atmosphere. *Atmos. Chem. Phys.* 9, 1711–1722.
- Qiao, T., Zhao, M., Xiu, G., et al., 2015. Seasonal variations of water soluble composition (WSOC, HULIS and WSILs) in PM₁ and its implications on haze pollution in urban Shanghai, China. *Atmos. Environ.* 123, 306–314.
- Salma, I., Ocskay, R., Chi, X., et al., 2007. Sampling artefacts, concentration and chemical composition of fine water-soluble organic carbon and humic-like substances in a continental urban atmospheric environment. *Atmos. Environ.* 41, 4106–4118.
- Salma, I., Mészáros, T., Maenhaut, W., et al., 2010. Chirality and the origin of atmospheric humic-like substances. *Atmos. Chem. Phys.* 10, 1315–1327.
- Samburova, V., Szidat, S., Hueglin, C., et al., 2005. Seasonal variation of high-molecular-weight compounds in the water-soluble fraction of organic urban aerosols. *J. Geophys. Res. D Atmos.* 110.
- Song, J.Z., He, L.L., Peng, P.A., et al., 2012. Chemical and isotopic composition of humic-like substances (HULIS) in ambient aerosols in Guangzhou, South China. *Aerosol Sci. Technol.* 46, 533–546.
- Stone, E.A., Hedman, C.J., Sheesley, R.J., et al., 2009. Investigating the chemical nature of humic-like substances (HULIS) in North American atmospheric aerosols by liquid chromatography tandem mass spectrometry. *Atmos. Environ.* 43, 4205–4213.
- Tan, J.H., Duan, J.C., Chen, D.H., et al., 2009. Chemical characteristics of haze during summer and winter in Guangzhou. *Atmos. Res.* 94, 238–245.
- Tan, J.H., Duan, J.C., Ma, Y.L., et al., 2014. Source of atmospheric heavy metals in winter in Foshan, China. *Sci. Total Environ.* 493, 262–270.
- Tan, J.H., Duan, J.C., Ma, Y.L., et al., 2016. Long-term trends of chemical characteristics and sources of fine particle in Foshan City, Pearl River Delta: 2008–2014. *Sci. Total Environ.* 565, 519–528.
- Viana, M., López, J.M., Querol, X., et al., 2008. Tracers and impact of open burning of rice straw residues on PM in Eastern Spain. *Atmos. Environ.* 42, 1941–1957.
- Wang, S., Feng, X., Zeng, X., et al., 2009. A study on variations of concentrations of particulate matter with different sizes in Lanzhou, China. *Atmos. Environ.* 43, 2823–2828.
- Wei, L.F., Duan, J.C., Tan, J.H., et al., 2015. Gas-to-particle conversion of atmospheric ammonia and sampling artifacts of ammonium in spring of Beijing. *Sci. China* 58, 345–355.
- Yang, F., Tan, J., Zhao, Q., et al., 2011. Characteristics of PM_{2.5} speciation in representative megacities and across China. *Atmos. Chem. Phys.* 11, 5207–5219.
- Zappoli, S., Andracchio, A., Fuzzi, S., et al., 1999. Inorganic, organic and macromolecular components of fine aerosol in different areas of Europe in relation to their water solubility. *Atmos. Environ.* 33, 2733–2743.
- Zhang, Y., Li, M., Bravo, M.A., et al., 2014. Air quality in Lanzhou, a major industrial city in China: characteristics of air pollution and review of existing evidence from air pollution and health studies. *Water Air Soil Pollut.* 225, 1–17.
- Zheng, G.J., He, K.B., Duan, F.K., et al., 2013. Measurement of humic-like substances in aerosols: a review. *Environ. Pollut.* 181, 301–314.