Characterization of Seasonal Difference of HULIS-C Sources from Water Soluble PM_{2.5} in Seoul, Korea: Probing Secondary Processes

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ABSTRACT

HUMic-Like Substances (HULIS) consists of a significant fraction of water-soluble organic carbon (WSOC) and optically active brown carbon. Understanding seasonality in their abundance and sources is an important step to quantifying their impacts on air quality and climate. In this study, we characterized the seasonal variation of HULIS-C (the carbon component of HULIS) and identified primary and secondary sources contributing to HULIS-C at an urban site in Seoul, Korea by analyzing 131 PM_{2.5} samples collected over a year from October 2012 to September 2013. The HULIS-C in Seoul had an annual average of 2.0 $\mu\text{g m}^{-3}$, and displayed a seasonality of highest abundance in the winter ($2.7 \pm 1.3 \mu\text{g m}^{-3}$) and the lowest in the summer ($1.7 \pm 0.8 \mu\text{g m}^{-3}$). Its fraction in WSOC reached up to 0.96 in the summer while remained relatively constant in the range of 0.4–0.6 in other seasons. Sources of HULIS-C were resolved using Positive Matrix Factorization (PMF) and checked using inter-species relationships between HULIS-C and aerosol components. Specifically, secondary processes including aging and heterogeneous reaction (26%) contributes to the year-round background concentration of HULIS-C and fresh biomass burning (38%) and incomplete combustion (16%) were the major sources of underlying seasonal variation. We also found aging process in the secondary process had an important role in HULIS-C formation and was a dominant contributor in the summer while heterogeneous reaction contributed considerably in other seasons. It implies that the different secondary processes in forming HULIS should be considered when the radiative forcing of brown carbon is estimated. Because these processes can lead the different physicochemical properties of HULIS in aerosols.

Keywords: Seasonal variation, Aging, Heterogeneous reaction, Positive matrix factorization

1 INTRODUCTION

HUMic-Like Substances (HULIS), often referred as a hydrophobic part of water soluble organic carbon (WSOC), is a class of organic molecules found in ambient aerosols that have a polyacidic nature analogous to terrestrial and aquatic humic substances (Graber and Rudich, 2006; Lin *et al.*, 2010). Key features distinguishing HULIS from terrestrial and aquatic humic substances are smaller average molecular weight, lower aromatic moiety content, greater surface activity, and better droplet activation ability (Graber and Rudich, 2006). HULIS has been ubiquitously found in aerosol, fog, and cloud.

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HULIS typically accounts for more than 10% of $\text{PM}_{2.5}$ mass (Lin *et al.*, 2010) and a significant portion (9–72%) of WSOC (Krivacsy *et al.*, 2008; Lin *et al.*, 2010; Zheng *et al.*, 2013; Zhao *et al.*, 2016). HULIS has both direct and indirect impacts on the radiative forcing of the atmosphere. As a precursor of cloud droplets (Dinar *et al.*, 2006; Graber and Rudich, 2006), HULIS can contribute to climate cooling indirectly by stimulating cloud formation, while its light absorbing property due to its orange to brown color can contribute directly to warm the air (Hoffer *et al.*, 2006; Feng *et al.*, 2013). Also, the primary and secondary fraction of organic aerosols has been found to be important in determining number of cloud droplet (Trivitayanurak and Adams, 2014) and light absorption enhancement (Wu *et al.*, 2018).

Sources of HULIS are thought to be size dependent. For the fine mode aerosols that we focus in this study, both primary emissions and secondary processes have been suggested (Graber and Rudich, 2006; Zheng *et al.*, 2013; Zhao *et al.*, 2016; Win *et al.*, 2020). Primary sources are relatively well identified. For example, emissions from marine (Cini *et al.*, 1996), biomass burning (Feczko *et al.*, 2007, Schmidl *et al.*, 2008), and biofuel combustion (Mayol-Bracero *et al.*, 2002; Kuang *et al.*, 2015). It is generally accepted that biomass burning is the major primary source (Zheng *et al.*, 2013). Secondary processes include condensation (Zheng *et al.*, 2013; Kuang *et al.*, 2015), aging (Lin *et al.*, 2010; Kirillova *et al.*, 2013), and heterogeneous reaction on liquid aerosol surfaces (Baduel *et al.*, 2011). However, it is difficult to specify secondary process or sources of precursors due in part to uncertainty in splitting primary and secondary organic carbon (Wu and Yu, 2016).

Since HULIS is an operationally defined rather than analytically identified, using carbon component of HULIS (HULIS-C) is a good choice for direct comparison with other studies (Zheng *et al.*, 2013). HULIS is often estimated from HULIS-C by multiplying a conversion factor in various range derived from different analyzing method and sampling environment (Lin *et al.*, 2010, Zheng *et al.*, 2013).

There have been several studies on HULIS but year-long measurement studies with source identification are rather scarce (see, for example, Zheng *et al.*, 2013). Pio *et al.* (2007) and Feczko *et al.* (2007) reported seasonal variation of HULIS-C from 2-year long sampling in six non-urban sites in Europe under the framework of European CARBOSOL project (Present and Retrospective State of Organic versus Inorganic Aerosol over Europe: Implications for Climate). Zhao *et al.* (2016) investigated a year-long HULIS measurements from an urban site in Shanghai, China. Recently, Li *et al.* (2019) analyzed a year-long HULIS observation from an urban site in Beijing, China, utilizing source-oriented atmospheric chemical transport model. In Korea, there are only a few studies on characterization of HULIS and they were for short time periods (Park and Son, 2016) or limited to optical properties (Lee *et al.*, 2017; Han *et al.*, 2020).

Positive matrix factorization (PMF) is a multivariate factor analysis model that has been widely used for source apportionment of air pollutants (e.g., Hu *et al.*, 2010; Chan *et al.*, 2011; Wagener *et al.*, 2012) including HULIS-C (Kuang *et al.*, 2015; Ma *et al.*, 2018; Srivastava *et al.*, 2018; Ma *et al.*, 2019; Li *et al.*, 2019). The PMF enables quantification of source contribution based on user defined source profile.

Relating to its geographical position, Korea is under the influence of China for the mixed air pollutants (Choi *et al.*, 2019) and North Korea for the enhanced biomass burning emissions (Kim *et al.*, 2013). At the same time, intensive local emissions contribute to high concentration of organic aerosols in Seoul where is one of megacities in Northeast region (Nault *et al.*, 2018). Understanding for the characteristics of HULIS-C concentration in $\text{PM}_{2.5}$ measured from Seoul can be useful to give the information about the relative significance and roles of primary emissions and secondary processes in forming HULIS in Northeast region. In this study, we provided the first mass-based analysis and source apportionment on a year-long data of HULIS-C using daily $\text{PM}_{2.5}$ measurements in Seoul, Korea. We aimed to seasonally identify sources of HULIS-C with specified secondary processes. Findings from this study give insights of how biomass burning, aging, and heterogeneous reactions make up HULIS seasonality at a site having local emissions and transported mixed pollutants in Northeast Asia region.

2 SAMPLING AND ANALYSIS

2.1 $\text{PM}_{2.5}$ Sampling

$\text{PM}_{2.5}$ samples were collected daily for 24 hours from October to November 2012, January to

February, March to April, and August to September 2013 at the Korea Institute of Science and Technology (KIST, 127.046°E, 37.602°N) located in a mixed commercial and residential area, about 400 m from a major road in an urban setting (Fig. 1). A PM_{2.5} high-volume air sampler (1,000 L min⁻¹) was used with a quartz microfiber filter (203 mm × 254 mm, Whatman, 1851-865) to analyze HULIS-C and other organic compounds. The filters were heated at 550°C for more than 12 hours before sampling and stored in the freezer at -20°C after sampling. PM_{2.5} samples for mass concentrations and inorganic species analyses were collected on pre-weighed 47-mm Teon filters (ZeuorTM, Pall Corp., Port Washington, NY, USA) using a Teflon-coated aluminum cyclone with a cut size of 2.5 µm and a flow rate of 16.7 L min⁻¹ (URG Corp., Chapel Hill, NC, USA). The statistical summary of 131 total samples is shown in Table 1.

2.2 Chemical Analysis

2.2.1 WSOC and HULIS-C

A portion (3 cm × 5 cm) of the filter was extracted by sonication in 40 mL of ultra-pure water (18 M) twice for 30 minutes each time. Iced ultra-pure water was used to minimize loss of volatile organic compounds. The extracts were filtered using a PTFE (Polytetrafluoroethylene) 0.2 µm membrane filter (Advantec) to remove insoluble materials and fibers before analysis. Half of the extracted water (20 mL) was used for WSOC, and the rest was used for HULIS-C analysis. To isolate HULIS from the water we used solid phase extraction method (SPE) using Hydrophilic-Lipophilic-Balanced (HLB) cartridge (Oasis HLB, 30 µm, 60 mg/cartridge, Waters, USA) following Lin *et al.* (2010). Then the cartridge was rinsed with methanol containing 2% ammonia (w/w). The eluate was evaporated under the gentle stream of N₂ and the solute was re-dissolved in ultra-pure water for subsequent analysis. Finally, the carbon amount from each 20 mL extract were quantified using total organic carbon (TOC) analyzer (General Electric Power & Water) and resulted in WSOC and HULIS-C, respectively.

2.2.2 Evaluation of HULIS-C analysis method

To evaluate the isolation of HULIS by the HLB cartridge, several known organic substances were quantified using their standard solution following Lin *et al.* (2010). Tested organic substances included SRFA (Suwannee River Fulvic Acid), NAFA (Nordic Aquatic Fulvic Acid), volatile organic acids (acetic acid, oxalic acid, succinic acid, malic acid, suberic acid, azelaic acid, phthalic acid), and non-volatile anhydrosugars (levoglucosan, xylose, sucrose). SRFA and NAFA are two types of aquatic humic substances being used as surrogates for HULIS-C (Zheng *et al.*, 2013).

Table S1 lists recovery rates of the substances which is the fraction of known substance that is measured as HULIS-C. SRFA and NAFA showed high recovery rates which is reasonable and consistent with Lin *et al.* (2010). However, unexpected high recovery rates of suberic acid (C₈H₁₄O₄), azelaic acid (C₉H₁₆O₄), and phthalic acid (C₈H₆O₄) which should be not considered as HULIS-C were observed. By applying determined recovery rates to our samples, the contributions of carbon component of these compounds to HULIS-C were calculated as shown in Table S2.

Fig. 1. Map of sampling site located in Seoul, Korea.

Table 1. Summary of seasonal average meteorological factors and mass concentrations of PM_{2.5} and components used in this study (mean $\pm 1\sigma$).

Season	Fall	Winter	Spring	Summer	Whole period
Date	2012.10.04–11.03	2013.01.09–02.28	03.01–04.30	08.12–09.10	
T (°C)	15.3	−3.4	5.7	27.7	10.4
RH (%)	58	57	54	69	58
# of samples	29	32	43	27	131
Aerosol and carbon fractions ($\mu\text{g m}^{-3}$)					
PM _{2.5}	26.8 $\pm$ 10.3	55.7 $\pm$ 33.0	46.5 $\pm$ 26.9	23.1 $\pm$ 12.9	40.3 $\pm$ 27.2
OC	7.5 $\pm$ 2.6	12.0 $\pm$ 5.4	8.3 $\pm$ 3.6	4.5 $\pm$ 1.6	8.4 $\pm$ 4.5
EC	2.1 $\pm$ 0.6	1.6 $\pm$ 0.5	1.5 $\pm$ 0.7	1.3 $\pm$ 0.3	1.6 $\pm$ 0.7
WSOC	3.1 $\pm$ 1.5	5.0 $\pm$ 2.0	3.7 $\pm$ 1.8	2.5 $\pm$ 1.3	3.6 $\pm$ 1.9
HULIS-C	1.7 $\pm$ 0.8	2.7 $\pm$ 1.3	1.9 $\pm$ 1.0	1.7 $\pm$ 0.8	2.0 $\pm$ 1.1
Ratio					
OC/EC	3.6 $\pm$ 1.1	7.7 $\pm$ 2.4	5.5 $\pm$ 1.3	3.5 $\pm$ 0.8	5.2 $\pm$ 2.2
WSOC/OC	0.4 $\pm$ 0.1	0.4 $\pm$ 0.1	0.4 $\pm$ 0.1	0.6 $\pm$ 0.1	0.4 $\pm$ 0.1
HULIS-C/WSOC	0.5 $\pm$ 0.1	0.5 $\pm$ 0.1	0.5 $\pm$ 0.1	0.7 $\pm$ 0.1	0.6 $\pm$ 0.1
Ions ($\mu\text{g m}^{-3}$)					
NO ₃ [−]	3.8 $\pm$ 2.5	11.9 $\pm$ 8.8	10.3 $\pm$ 9.4	0.8 $\pm$ 1.6	8.2 $\pm$ 8.6
SO ₄ ^{2−}	4.5 $\pm$ 2.1	9.3 $\pm$ 7.2	7.8 $\pm$ 6.1	6.8 $\pm$ 6.0	7.5 $\pm$ 6.1
Ca ²⁺	0.1 $\pm$ 0.1	0.2 $\pm$ 0.1	0.2 $\pm$ 0.1	0.1 $\pm$ 0.1	0.2 $\pm$ 0.1
K ⁺	0.3 $\pm$ 0.1	0.6 $\pm$ 0.4	0.4 $\pm$ 0.2	0.2 $\pm$ 0.1	0.4 $\pm$ 0.3
NH ₄ ⁺	2.2 $\pm$ 0.9	6.8 $\pm$ 5.1	5.5 $\pm$ 4.4	2.7 $\pm$ 2.5	4.9 $\pm$ 4.4
n-Alkanes ($\mu\text{g m}^{-3}$)					
ΣC20-C25	0.9 $\pm$ 1.0	2.6 $\pm$ 1.9	1.8 $\pm$ 1.4	0.2 $\pm$ 0.2	1.3 $\pm$ 1.6
ΣC26-C34	1.4 $\pm$ 1.2	1.4 $\pm$ 1.3	2.1 $\pm$ 2.0	0.8 $\pm$ 0.7	1.5 $\pm$ 1.5
PAHs ($\mu\text{g m}^{-3}$)					
Phenanthrene (3-ring)	0.2 $\pm$ 0.2	1.2 $\pm$ 0.7	0.5 $\pm$ 0.3	0.1 $\pm$ 0.0	0.5 $\pm$ 0.6
Fluoranthene (4-ring)	0.4 $\pm$ 0.4	1.7 $\pm$ 0.9	0.8 $\pm$ 0.5	0.1 $\pm$ 0.1	0.8 $\pm$ 0.8
Benzo[b+k]fluoranthene (5-ring)	1.9 $\pm$ 1.9	5.5 $\pm$ 4.7	2.4 $\pm$ 3.7	0.4 $\pm$ 0.2	2.5 $\pm$ 3.6
Indeno[1,2,3-cd]pyrene (6-ring)	0.3 $\pm$ 0.2	1.2 $\pm$ 1.9	0.5 $\pm$ 0.2	0.2 $\pm$ 0.1	0.5 $\pm$ 1.0
n-Alkanoic acids (ng m ^{−3})					
Palmitic acid	54.6 $\pm$ 33.5	73.5 $\pm$ 54.0	62.7 $\pm$ 44.2	44.4 $\pm$ 19.5	58.0 $\pm$ 39.9
Stearic acid	32.3 $\pm$ 21.0	34.3 $\pm$ 34.1	47.8 $\pm$ 62.1	17.0 $\pm$ 11.7	33.2 $\pm$ 39.9
Elaidic acid	6.2 $\pm$ 2.5	7.0 $\pm$ 3.0	5.0 $\pm$ 1.5	5.3 $\pm$ 1.8	5.9 $\pm$ 2.4
Dicarboxylic acids (ng m ^{−3})					
Succinic acid	31.7 $\pm$ 34.2	48.5 $\pm$ 27.5	47.3 $\pm$ 32.1	20.9 $\pm$ 15.4	36.7 $\pm$ 30.1
D-Malic acid	10.8 $\pm$ 8.0	27.8 $\pm$ 18.1	9.1 $\pm$ 4.6	5.8 $\pm$ 3.2	13.1 $\pm$ 13.0
Phthalic acid	22.9 $\pm$ 12.8	52.5 $\pm$ 37.6	25.9 $\pm$ 13.3	18.1 $\pm$ 6.2	29.4 $\pm$ 24.3
Azelaic acid	26.9 $\pm$ 19.5	20.6 $\pm$ 17.8	27.9 $\pm$ 18.7	16.4 $\pm$ 5.0	22.8 $\pm$ 16.7
Anhydrosugar (ng m ^{−3})					
Levogluconan	198 $\pm$ 102	356 $\pm$ 153	226 $\pm$ 165	64 $\pm$ 41	207 $\pm$ 160

Although the recovery rates for suberic acid, azelaic acid and phthalic acid were high in SPE extraction method, their contribution to HULIS-C concentrations were minor (from 0.2% to 0.5% for each compounds). Thus, we considered the impact of other components to the measured HULIS-C concentration is negligible.

2.2.3 Other components

Details for analysis of inorganic species, organic carbon (OC), and elemental carbon (EC) in PM_{2.5} samples were reported by Kim *et al.* (2018), we only give a brief description here. Water soluble ionic species were extracted from the Teon filter samples, sonicated in a mixture of 0.5 mL ethanol and 14.5 mL deionized water for 30 minutes, and analyzed using the Dionex 2000i/SP ion chromatograph (Dionex, Sunnyvale, CA, USA). OC and EC were analyzed using a

thermal/optical carbon aerosol analyzer (Sunset Laboratory, Tigard, OR, USA) based on the NIOSH (National Institute for Occupational Safety and Health) Method 5040 (Birch and Cary, 1996). Organic markers such as 15 n-alkanes, 14 PAHs, 19 n-alkanoic acids, 19 dicarboxylic acids, and 10 anhydrosugars were analyzed using GC-MS (Choi *et al.*, 2015). For organic speciation GC/MS analysis was carried out on a Hewlett Packard 7890A GC equipped with a 5975 mass selective detector (Agilent Technologies) in synchronous selected ion monitoring (SIM)/scan mode.

2.3 Positive Matrix Factorization Analysis

Positive matrix factorization (PMF) analysis is performed using EPA PMF 5.0 (Norris *et al.*, 2014). Factor numbers are determined by two methods and details are given in supplementary material. As a result of factor number determination, 87 samples out of 131 were selected for source apportionment. Some organic species were regrouped and filtered from the original dataset for the PMF. Odd_Alkane is the sum of odd carbon alkanes with carbon number 29 to 33 while Even_Alkane is the sum of even carbon alkanes with carbon number 28 to 32. Odd_Alkanes and Even_Alkanes are used to differentiate the aerosols from either terrestrial plant emission or anthropogenic and petrogenic emissions. Odd_Alkanes are found to be dominant in background soil and plants less influenced by anthropogenic emissions (Kuhn *et al.*, 2010, Cabrerizo *et al.*, 2016). Two groups of heavy PAH compounds are used to track the incomplete combustion: PAH 252 (benzo[b+k]fluoranthene, benzo[e]pyrene and benzo[a]pyrene) and PAH 276 (indeno[1,2,3-cd]pyrene). Palmitric acid (Palm), Stearic acid (Stear), products of oxidation of fatty acids in cooking activities, are considered separately. Phthalic acid (Phth) originates from secondary formation or aging of organic compounds. Three more dicarboxylic acids, succinic acid, glutaric acid and adipic acid, are included individually to track SOA formation processes. We note that bulk OC was broken into three parts by solid phase extraction, that is, HULIS-C, water insoluble organic carbon (WISOC) and hydrophilic organic carbon (HPI).

2.4 Splitting Primary and Secondary Organic Carbons

Quantification of primary organic carbon (POC) and secondary organic carbon (SOC) is essential to understand sources of organic aerosols but challenging as direct SOC measurement is not yet feasible. Seasonal variation of POC and SOC combined with PMF and inter-species relationships can be informative to differentiate primary and secondary sources of HULIS-C.

Using EC as a tracer to track the co-emitted POC portion and further to determine SOC is called EC tracer method and has been widely used (Turpin and Huntzicker, 1991; Kunwar and Kawamura, 2014). Conventionally, OC/EC ratio that represents primary combustion emission sources (i.e., $(OC/EC)_{pri}$) is determined by regressing OC and EC within a fixed range (about 5–20%) of the lowest OC/EC ratio data. The drawback of these approaches is a lack of clear quantitative criteria in the selection of data subsets (Wu and Yu, 2016). Therefore, we adopt minimum r (coefficient of correlation) squared (MRS) method (Millet *et al.*, 2005; Wu and Yu, 2016) that generates the minimum r^2 (SOC, EC) then represents the actual $(OC/EC)_{pri}$ ratio if variations of EC and SOC are independent and $(OC/EC)_{pri}$ is relatively constant in the study period. SOC estimated by this method is less biased than other methods and not disturbed by sample size, sampling period, and number of primary sources (Wu and Yu, 2016). In the end, SOC can be estimated using Eq. (1) given $(OC/EC)_{pri}$ from MRS method.

$$\begin{aligned} POC &= EC \times (OC/EC)_{pri} \\ SOC &= OC - POC \end{aligned} \quad (1)$$

Both fresh and aged aerosols having combustion origin will be recognized as POC in this method by nature, secondary aerosols formed by condensation and heterogeneous reactions not involving combustion sources will be classified into SOC.

Among primary emissions, OC/EC is higher for biomass burning and biofuel combustion, while the ratio is lower for fossil fuel (coal and vehicular exhausts) emissions (Zhu *et al.*, 2010; Pio *et al.*, 2011; Ram *et al.*, 2012). On the other hand, EC concentration varies in broad range depending on the measurement method, i.e., EC measured by NIOSH protocol as our case tends to be less

than half of that measured by the IMPROVE protocol (Chow *et al.*, 2001). Thus, the care is needed when compare OC/EC in between different studies because for the same sample the results will be NIOSH > IMPROVE (Zhu *et al.*, 2010; Pio *et al.*, 2011; Srinivas and Sarin, 2014). Therefore, we only considered inter-seasonal variation of EC/OC, POC, and SOC in this study.

3. RESULTS AND DISCUSSION

3.1 Overview of Seasonality

3.1.1 HULIS-C concentration comparison with other studies

We compared seasonal average HULIS-C concentrations to previously reported values from other cities in the world (Fig. 2). HULIS-C has been measured by a broad range of analyzing methods for different particle sizes and the values can vary significantly among the methods. Therefore, we filtered only HULIS-C from PM_{2.5} measured using SPE (HLB or C18) extraction and TOC quantification methods. Also, we exclude studies report HULIS-C converted from HULIS measurements because of the uncertainty in HULIS-C/HULIS conversion factor (Zheng *et al.*, 2013). Result shows higher levels of HULIS-C in urban sites than in mountain, remote, and rural sites. This suggests anthropogenic emissions as the important sources of HULIS, but difference between the sites are within the same order of magnitude and not large enough to ignore the importance of natural sources.

Seasonal average HULIS-C concentrations in Seoul are at a comparable level with those of other urban cities (e.g., Shanghai, China (Zhao *et al.*, 2015, 2016) and Budapest, Hungary (Salma *et al.*, 2007; Krivácsy *et al.*, 2008; Salma *et al.*, 2008)) embracing their seasonal mean within one-standard deviation range except for two out of 52 cases compared. Our result shows seasonality of the winter maximum and the summer minimum. This seasonal pattern of HULIS-C has also been observed in other urban cities as shown in Fig. 2. An opposite pattern of summer maximum and winter minimum of HULIS has reported from sites where biogenic emissions are dominant (Zheng *et al.*, 2013) such as a mountain site in Austria (Feczko *et al.*, 2007).

3.1.2 Related organic carbon and their ratios

Statistically summarized seasonal mean of measured species are provided in Table 1. The annual average WSOC concentration was $3.6 \pm 1.9 \mu\text{g m}^{-3}$, and the HULIS-C concentration was $2.0 \pm 1.1 \mu\text{g m}^{-3}$ occupying about 56% of WSOC. Seasonality of winter maximum and summer minimum was also observed for WSOC, OC, and PM_{2.5}.

^aKrivácsy *et al.* (2001), ^bFeczko *et al.* (2007), ^cSalma *et al.* (2010), ^dSalma *et al.* (2008), ^eKrivácsy *et al.* (2008), ^fSalma *et al.* (2007), ^gZhao *et al.* (2016), ^hZhao *et al.* (2015)

Fig. 2. Comparison of HULIS-C from this study with previous studies from other cities in the world. For the consistency, HULIS-C from PM_{2.5}, measured using SPE and TOC quantification methods are compared. Open markers for less-polluted sites including mountain, remote, and rural settings and closed markers for urban sites. Error bars for this study indicate one standard deviation.

Fig. 3 shows discontinuous time series of all data points of OC, WSOC, HULIS-C, and their ratios. HULIS-C becomes a dominant component of WSOC occupying up to 96% (average 70%) in the summer while in other seasons it occupies about 40 to 60%. At the same time, WSOC/OC ratio also peaks in the summer (~56%) while remaining fairly constant (~40%) in other seasons. It suggests increased WSOC fraction of OC in the summer is mainly due to the HULIS-C. Organic species of high volatility are unlikely to be present in aerosols, and the fraction of semi-volatile organic species present in PM_{2.5} was lower in the summer due to increased temperature (Yang *et al.*, 2003; Schnelle-Kreis *et al.*, 2007). Thus, the HULIS-C/WSOC ratio in the summer can be attributed to the low volatility of HULIS-C or promoted photochemical production with increased solar radiation (Zheng *et al.*, 2013). The latter is the way of WSOC/OC is increased in the summer (Aggarwal and Kawamura, 2008).

Fig. 3. Temporal variations of OC, WSOC, HULIS-C, WSOC/OC, and HULIS-C/WSOC. Scatters indicate each daily measurement and box-plots indicate first and third quartiles with median (orange) of each season. Bars show the range of $1.5 \times (\text{third quartile} - \text{first quartile})$. Days without measurement are not shown thus the x-axis is discontinuous.

3.2 Source Identification and Apportionment by PMF Analysis

3.2.1 Overall result for whole period

Fig. 4 shows the 7-factor source profile, displaying speciation contribution in each factor. Explanations will be in order of HULIS-C loadings: Factor 1 is biomass burning (BB), identified by high loading of levoglucosan as well as K^+ . Forty percent of HULIS-C was attributed in BB. It is consistent with previous studies suggested BB as important source of HULIS-C (Zheng *et al.*, 2013; Kuang *et al.*, 2015). Factor 2 is secondary sulfate formation processes, characterized by high loading of ammonium and sulfate ions. Twenty percent of HULIS-C was found associated with this factor. In addition, 20% of phthalic acid coexist in this factor which represents aging or secondary organic formation. Due to the limited tracer species included in this study, mixing effect may occur in the secondary formation factors. More organic species are required to fully characterize different SOA processes (Wang *et al.*, 2017). Factor 3 is assigned as incomplete combustion (IC) due to high abundance of PAHs. Less than 20% of HULIS-C is in this factor. It is reasonable that incomplete combustion promotes the formation of PAH as well as some brown carbon like HULIS. To be noted, around 20% of levoglucosan and 40% of palmitic acid were also found in this factor. The mixing of multiple sources could be due to the similar transport route shared by these species.

Rest factors are showing much lower HULIS-C loading. Factor 4 is named secondary nitrate formation processes. This factor is characterized by a high abundance of nitrate and ammonium ions. A small presence of HULIS-C (~5%) was found in this factor while more WISOC (~20%) was associated. Factor 5 is identified as a secondary organic aerosols (SOA) factor, indicated by strong presence of dicarboxylic acids. HPI is the major OC component in this factor (~20%) compared with the hydrophobic carbon and HULIS-C (< 5%). Factor 6 is sea salt, recognized by high concentration of Na^+ . HULIS-C loading in this factor is also limited (< 5%). Factor 7 is cooking emission, identified by higher contribution of palmitic acid and stearic acid. HULIS-C is hardly present in this factor, but some WISOC and HPI were detected. It is the evidence for different formation pathways for different organic components.

Here, the difference between HULIS-C loadings in factor 2 (secondary sulfate formation) versus

Fig. 4. Source profile by speciation contribution. Factor numbers are used in referring each factor in text.

4 (secondary nitrate formation) and 5 (secondary organic aerosol) should be noted. Secondary sulfate formation can be promoted by more oxidation of SO_2 when high level of oxidants and day-lights exist (i.e., typical summer) or active heterogeneous reactions occur when RH is high even in winter (Wang *et al.*, 2014). On the other hand, secondary nitrate formation is high when temperature is low as nitric acid is semi-volatile (opposite to HULIS-C) and there is enough NH_3 remained after neutralizing H_2SO_4 . This factor is not solely applicable to the nitrate but for other secondary aerosols (note considerable loadings of SO_4^{2-} , Ca_2^+ , K^+ , and Na^+). It has been found that during the time in Seoul, there were sufficient NH_3 to neutralize HNO_3 year-round and RH was high enough to promote heterogeneous reaction in the winter (Kim *et al.*, 2018). Thus, the PMF result showing high HULIS-C load with factor 2 but low with factor 4 and 5 implies that the HULIS-C formation was favored by oxidative atmosphere (aging) or heterogeneous reactions but less related with condensation of inorganic and organic gases, i.e., secondary aerosol formation.

Based on the identified factor contributions to HULIS-C, time series of each factors in HULIS-C is calculated and shown in Fig. S2.

3.2.2 PMF result evaluation and seasonal variation of sources

In Fig. 5, scatter plot of measured vs. reconstructed HULIS-C and seasonal variation of HULIS-C with source composition are shown. HULIS-C shows good predication by PMF, with $R^2 > 0.6$ but underestimation (i.e., slopes less than 1) is noticed. The numbers of factor are limited by the numbers of tracer species input. Thus, without more source-indicative compounds for inclusion in PMF to capture the full source spectrum, underestimation is expected. From the annual average pie chart, BB contributes most to HULIS-C (38%) and secondary sulfate is the second largest factor (26%) followed by incomplete combustion (16%). Factors like secondary nitrate, cooking, secondary organic formation and sea salt account for the rest 20% to HULIS-C with roughly 2 to 7% from each.

In the right column, seasonal contributions of individual sources to the reconstructed HULIS-C are summarized. It is clear from the top figure that the seasonality of HULIS-C is determined by the sum of biomass burning and incomplete combustion. Secondary sulfate (factor 2) composition exists as background throughout the year. That is, as found in overall analysis of PMF result, combination or either of aging or heterogeneous reaction impacts year-round. From the bottom figure, we can see the seasonality of secondary sulfate formation contribution is similar to the

Fig. 5. Scatter plots of measured HULIS-C vs. reconstructed HULIS-C (left), seasonal variation of reconstructed HULIS-C with source composition (right top), and relative source apportionment (right bottom).

HULIS-C/WSOC ratio (Fig. 3). Yet, it is difficult to separate contribution from aging of carbonaceous aerosol and heterogeneous reaction from this result.

3.3 Specifying Secondary Processes from Inter-species Relationship

To delve into the mechanism determining background HULIS-C concentration largely occupied by secondary sulfate formation (factor 2), we looked at the correlations of HULIS-C with individual PM_{2.5} components in each season as shown in Fig. 6. The correlation coefficient (*r*) of HULIS-C with levoglucosan (a biomass burning marker) shows expected seasonality having maximum in the spring (fall: 0.47, winter: 0.36, spring: 0.80, summer: 0.48). However, another well-known biomass burning marker K⁺ shows high correlations with HULIS-C except for the summer (fall: 0.68, winter: 0.78, spring: 0.88, summer: 0.40). K⁺ is not only a marker of biomass burning, but also representative of aging process that could happen within an hour when highly correlated with NO₃⁻ and/or SO₄²⁻ (Gao *et al.*, 2003). K⁺ used as a proxy for aged aerosols is often reported elsewhere (e.g., Li *et al.*, 2000, Diapouli *et al.*, 2014). This is the case except for the summer. In addition, dicarboxylic acids (phthalic, succinic, and malic acids) showed considerable correlations in the winter, spring, and summer. Increase of dicarboxylic acids has been observed with aging of biomass burning plumes (Pratt *et al.*, 2011). Thus, the evidences of aging process have found in all seasons but the origin of aerosols being aged could be different.

Correlation with EC was highest in the summer, which means they shared a large portion of primary emissions. This result is consistent with the high correlation of HULIS-C with POC estimated by the MRS method (Fig. 7). Fig. 7 shows correlations of POC and SOC with HULIS-C, respectively. For each HULIS-C data, corresponding total OC is the sum of blue and orange values. Aged OC as well as fresh emitted OC from combustion is accounted as POC by MRS method, and SOC represents OC formed by the processes of condensation and heterogeneous reactions. HULIS-C shows higher correlation with SOC in all seasons except in the summer. As we have found that condensation is unlikely the source of HULIS-C from the PMF, heterogeneous reaction is thought to be the major source of HULIS-C in the fall, winter, and spring. The dominant fraction of POC and its very high correlation with HULIS-C are taken as evidence of aging process as the major source in the summer.

Fig. 6. Correlation coefficient (*r*) of major tracers with HULIS-C in each season. Values greater than 0.4 are shown (no negative *r* less than 0.4 were observed). Full-name of tracers are in Table 1.

Fig. 7. Correlations of HULIS-C vs. POC (blue) and HULIS-C vs. SOC (orange) in each season. The sum of blue and orange values can be regarded as total OC at each point.

Another measure of aging of aerosol is the elaidic acid (trans-C18:1, unsaturated fatty acid with 18 carbons and 1 double bond) to stearic acid (C18, saturated fatty acid with 18 carbons) ratio. Since saturated fatty acids (e.g., stearic acid) are more stable than unsaturated fatty acids (e.g., elaidic acid) in the atmosphere, lower value represents more aged aerosol (Wang *et al.*, 2006; Wu *et al.*, 2015). The seasonal averages of this ratio are 3.5 (summer), 4.4 (winter), 6.1 (fall), and 8.8 (spring). The lowest ratio in the summer indicates that the aged fraction of aerosols is largest in the summer.

4 CONCLUSIONS AND IMPLICATION

In this study, we measured one-year HULIS-C mass concentration at Seoul, Korea to evaluate average concentration of HULIS-C and its general characteristics in the whole year. Seasonal variations and sources of HULIS-C were analyzed using organic and inorganic $\text{PM}_{2.5}$ components by PMF model and inter-species correlations. HULIS-C concentration from our study shows comparable level with previous values reported from urban cities. It shows seasonal variation of winter maximum and summer minimum similar to those observed in urban sites.

From the PMF model, we found year-round background concentration of HULIS-C having secondary sulfate formation as the fairly constant source and fluctuations in biomass burning and incomplete combustion determines the seasonal variation. Contribution from secondary formation (condensation) of inorganic and organic gasses showed inconsiderable contribution. Here the secondary sulfate formation refers aging or heterogeneous reaction of aerosols. Although the background concentration was stable throughout the year, the contribution from aging and heterogeneous reaction could vary and have seasonality.

Using inter-species correlations and POC and SOC separation, we found the aging process is the dominant source of HULIS-C in the summer. This is also thought to be the reason of increased HULIS-C/WSOC ratio in the summer. In other seasons, heterogeneous reaction is found to be the major source of the background HULIS-C because of higher correlation with SOC than POC. As condensation of inorganic and organic gases were ruled out from the PMF analysis we concluded heterogeneous reaction makes higher correlation with SOC. These different formation pathways can lead the different physicochemical properties of HULIS in aerosols. Therefore, more study on

the origin of aerosols being aged and heterogeneous reaction mechanism to form HULIS will be needed for better estimate of radiative forcing of brown carbons.

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SUPPLEMENTARY MATERIAL

Supplementary data associated with this article can be found in the online version at <https://doi.org/10.4209/aaqr.2020.05.0233>

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