Sources and oxidative potential of water-soluble humic-like substances (HULIS$_{WS}$) in fine particulate matter (PM$_{2.5}$) in Beijing

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Abstract. Water-soluble humic-like substances (HULIS$_{WS}$) are a major redox-active component of ambient fine particulate matter (PM$_{2.5}$); however, information on their sources and associated redox activity is limited. In this study, HULIS$_{WS}$ mass concentration, various HULIS$_{WS}$ species, and dithiothreitol (DTT) activity of HULIS$_{WS}$ were quantified in PM$_{2.5}$ samples collected during a 1-year period in Beijing. Strong correlation was observed between HULIS$_{WS}$ and DTT activity; both exhibited higher levels during the heating season than during the non-heating season. Positive matrix factorization analysis of both HULIS$_{WS}$ and DTT activity was performed. Four combustion-related sources, namely coal combustion, biomass burning, waste incineration, and vehicle exhaust, and one secondary factor were resolved. In particular, waste incineration was identified as a source of HULIS$_{WS}$ for the first time. Biomass burning and secondary aerosol formation were the major contributors (>59%) to both HULIS$_{WS}$ and associated DTT activity throughout the year. During the non-heating season, secondary aerosol formation was the most important source, whereas during the heating season, the predominant contributor was biomass burning. The four combustion-related sources accounted for >70% of HULIS$_{WS}$ and DTT activity, implying that future reduction in PM$_{2.5}$ emissions from combustion activities can substantially reduce the HULIS$_{WS}$ burden and their potential health impact in Beijing.

1 Introduction

Fine particulate matter (PM$_{2.5}$) pollution has caused both environmental and public health problems worldwide. PM$_{2.5}$ can travel deep into the human lung and lead to various respiratory diseases, such as respiratory tract infections, chronic cough, and asthma (Becker et al., 2005; Nel, 2005). Given the various sources and complex chemical composition of PM$_{2.5}$, the underlying mechanisms of PM$_{2.5}$ exposure-induced adverse health effects are not fully understood yet. However, it has been postulated that, the redox-active components on PM$_{2.5}$, such as transition metals and quinones (Charrier and Anastasio, 2012; Chung et al., 2006), can perturb the redox equilibrium in lung cell through the generation of excessive reactive oxygen species (ROS), and induce the subsequent oxidative stress.

Humic-like substances (HULIS$_{WS}$) are a mixture of compounds containing polycyclic ring structures with aliphatic side chains and multiple polar functional groups. They account for a significant proportion (30%–80%) of the water-soluble organic matter (WSOM) in PM$_{2.5}$ (Graber and Rudich, 2006; Kuang et al., 2015; Lin et al., 2010a). HULIS$_{WS}$ have recently been recognized to

39 be highly redox-active and they play a significant role in driving PM-associated ROS formation (Dou et al., 2015; Lin and Yu,

40 2011; Verma et al., 2015a). The reversible redox sites in $HULIS_{WS}$ fraction could serve as an electron transfer intermediate and

41 lead to continuous production of ROS (Lin and Yu, 2011). Dithiothreitol (DTT) assay have been widely used to evaluate the

42 oxidative capacity of $HULIS_{WS}$ and $PM_{2.5}$. Verma et al. (2015b) found that $HULIS_{WS}$ contributed approximately 45% of DTT

43 activity of the water extracts from $PM_{2.5}$ samples collected in Atlanta, USA, which was 5% higher than that induced by water-

44 soluble metals. Lin and Yu (2011) also found that $HULIS_{WS}$ accounted for 79%±12% of DTT activity caused by WSOM fraction

45 in $PM_{2.5}$ sampled in Pearl River Delta (PRD) region, China. Given the considerable amount of $HULIS_{WS}$ in $PM_{2.5}$ and their ROS

46 generation ability, both field measurements and smog chamber experiments have been conducted to determine their formation

47 pathways and origins in the atmosphere (Kautzman et al., 2010; Lin et al., 2010b; Sato et al., 2012). Biomass burning and secondary

48 formation have been suggested to be the major sources of atmospheric $HULIS_{WS}$ (Kautzman et al., 2010; Lin et al., 2010b).

49 However, studies on the quantitative source apportionment of $HULIS_{WS}$ are still limited (Kuang et al., 2015), and information on

50 the source-specific contribution to their redox activity is lacking.

51 Beijing, the capital of China located in the North China Plain, is a political and cultural center with an extremely dense population.

52 On the other hand, it has become one of the most polluted cities in the world, with an annual $PM_{2.5}$ concentration of up to 89.5 µg

53 m^{-3} in 2013 (Li et al., 2017). Therefore, it presents an ideal location to study the chemical characteristics of $HULIS_{WS}$ as well as

54 their sources and potential redox activity.

55 In this study, our major objective is to investigate the ROS-forming ability of $HULIS_{WS}$ in relation to different sources and

56 meteorological conditions. Thus, a total of 66 $PM_{2.5}$ samples collected in Beijing during a 1-year period were analyzed.

57 Concentrations of total $HULIS_{WS}$ were quantified, together with some characteristic individual $HULIS_{WS}$ species and the major

58 aerosol components. The redox activity of $HULIS_{WS}$ was determined using a DTT assay. Positive matrix factorization (PMF)

59 analysis was conducted to determine the sources of both $HULIS_{WS}$ and their associated redox activity. Such a comprehensive

60 source apportionment study of $HULIS_{WS}$-related ROS-generation potential has not been previously reported. Results from this

61 study could provide not only quantitative information regarding the sources and toxicity of $HULIS_{WS}$, but also a deeper

62 understanding of the source-specific oxidative potential of Chinese urban organic aerosols in general. This may be useful for the

63 future development of source-targeted air pollution control policies in Beijing and may provide public-health benefits.

64 **2 Material and methods**

65 **2.1 Sample collection**

66 $PM_{2.5}$ samples were collected at the Peking University Atmosphere Environment Monitoring Station (PKUERS) on the campus of

67 Peking University (39°59'21"N, 116°18'25'E, approximately 30 m above the ground), Beijing, China. A high-volume air sampler

68 coupled with a ≤2.5 µm inlet (HIVOL-CABLD, ThermoFisher Scientific, Waltham, MA, USA) was used to conduct sampling at

69 a flow rate of 1.13 m^3 min^{-1}. Samples were collected on quartz fiber filters (20.3×25.4 cm^2, prebaked at 550 °C for 5 h; Whatman,

70 Hillsboro, OR, USA) for 24 h every 6 days from 3 March 2012 to 1 March 2013. In addition, a four-channel mid-volume sampler

71 was operated synchronously (16.7 L min^{-1}, TH-16A, Wuhan Tianhong Instruments Co. Ltd, China) to collect $PM_{2.5}$ onto three 47-

72 mm Teflon filters and one quartz fiber filter for the determination of $PM_{2.5}$ mass, elemental carbon (EC) and organic carbon (OC),

73 and inorganic ionic species.

2.2 Chemical analysis

HULIS$_{WS}$ was isolated from PM$_{2.5}$ samples following the procedure described by Lin et al. (2010b). Briefly, a portion of sample filters (17.5 cm^2 for HULIS$_{WS}$ species identification and 3 cm^2 for HULIS$_{WS}$ mass measurement) was cut into small pieces and pollutants were extracted through sonication with distilled deionized (DDI) water for 30 min. The extracts were filtered with polytetrafluoroethylene (PTFE) filters (0.45-μm pore size; Grace, Houston TX, USA) and acidified to a pH of 2 with 2.4 M HCl. A solid phase extraction (SPE) cartridge (Oasis HLB, 3 mL/30 μm, 60 mg; Waters, Milford, MA, USA) was used to isolate HUILS$_{WS}$. The SPE cartridge was first activated using 1.0 mL of methanol and equilibrated using 1.0 mL of 0.01 M HCl. The extracts were then loaded onto an HLB cartridge. Because the majority of inorganic ions, low molecular weight organic acids, and sugar compounds could not be retained by the HLB cartridge, they were removed from the final effluent. For the analysis of individual HULIS$_{WS}$ species, the HLB cartridge was rinsed with two 1.0-mL portions of DDI water and then eluted with three 0.5-mL portions of basic methanol (2% ammonia, w/w). The effluent was dried with a gentle flow of ultrapure nitrogen at 40 °C, and then derivatized with 100 μL of N,O-bis(trimethylsilyl)trifluoroacetamide (BSTFA; with 1% trimethylchlorosilane; Sigma Aldrich, St. Louis, MO, USA) and 50 μL of pyridine (>99.5%; International Laboratory USA, CA, USA) at 70 °C for 2 h. When the mixture had cooled to room temperature, it was spiked with 30 μL of tetracosane-d$_{50}$ (50 μg mL^{-1} in n-hexane; Sigma Aldrich, St. Louis, MO, USA) as the internal standard for gas chromatography-mass spectrometry (GC-MS; 5975-7890A, Agilent, Santa Clara, CA, USA) analysis. Detailed information on this analysis is provided in the Supplementary Material.

For the quantification of HULIS$_{WS}$ mass concentration, 6.0 mL of pure methanol was used to elute HULIS$_{WS}$ from HLB cartridge instead of 1.5 mL of basic methanol (2% ammonia, w/w). This is to avoid possible influence of ammonia in the following DTT experiments (Lin and Yu, 2011), and larger volume of methanol was used to maintain the elution efficiency (Lin and Yu, 2011). Comparison on the GC-MS peak intensities of individual HULS$_{WS}$ species eluted by these two protocols was provided in the Supplementary Material (Figure S1). The effluent was dried with nitrogen, and restored in 1 mL of DDI water for quantification. An aliquot of 20 μL of aqueous solution was injected into a high-performance liquid chromatography system (HPLC, ThermoFisher Scientific, Waltham, MA, USA) coupled with an evaporative light scattering detector (Alltech ELSD 3300, Grace, Houston, TX, USA). Since ELSD is mass sensitive, the mass of HULIS$_{WS}$ instead of HULIS$_{WS\_carbon}$ was reported in this study. Detailed information on the HPLC-ELSD operation conditions is provided in the Supplementary Material.

Major water-soluble ions were identified and quantified using ion-chromatography (DIONEX, ICS-2500 for cations and ICS-2000 for anions, ThermoFisher Scientific, Waltham, MA, USA, Tang et al., 2011). EC and OC were analyzed by a thermal–optical carbon analyzer (Sunset Laboratory-Based Instrument, Tigard, OR, USA, Tang et al., 2011). Hopanes were measured by in-injection thermal desorption-gas chromatography mass spectrometry (GC-MS, Agilent 6890N-5975C, Santa Clara, CA, USA, Ho and Yu, 2004), while levoglucosan was measured using an Agilent 7890A- 5975C GC-MS (Hu et al., 2008). Concentrations of hopanes, levoglucosan, water-soluble ions, EC and OC were listed in Table S1 in the Supplementary Material.

2.3 DTT assay

We followed the procedure of Li et al. (2009) and Lin and Yu (2011) for DTT experiments. Briefly, a 120-μL portion of HULIS$_{WS}$ solution was transferred into an eppendorf tube. Then 920 μL of potassium phosphate buffer (pH = 7.4) containing 1 mM diethylene triamine pentaacetic acid (DTPA) and 50 μL of 0.5 mM DTT (both >99%; Sigma Aldrich, St. Louis, MO, USA) were added and mixed thoroughly. The samples were subsequently placed in a dry bath at 37 °C for 90 min and spiked with 100 μL of 1.0 mM 5,5'-dithiobis-2-nitrobenzoic acid (DTNB, 98%; Sigma Aldrich, USA) containing 1 mM DTPA. Considering the reaction between DTNB and DTT was very fast, the absorption could reach its maximum value immediately and stay stable for more than 2 hours (Li et al., 2009). So we followed the same protocol described in Li et al. (2009) with the elimination of quenching step described

113   in Cho et al.'s method (2005), and conduct measurement at 412 nm within 30 min using an ultraviolet-visible (UV-Vis)

114   spectrophotometer (8453, Hewlett Pakard, Palo Alto, CA, USA). Considering that some transition metals may still remain in the

115    $HULIS_{WS}$ fraction even after HLB purification, sufficient amount of DTPA was added in the procedure to chelate all the remaining

116   transition metals, such as Cu, Mn, and Fe, to eliminate the DTT consumption by these metals (Lin and Yu, 2011). For the control

117   samples, blank filters were used instead of real samples.

118   Previous study observed that the time-dependent consumption of DTT catalysed by $HULIS_{WS}$ was linear when DTT consumption

119   was less than 90% (Lin and Yu, 2011). We have also examined the $HULIS_{WS}$-catalysed DTT consumption as a function of time

120   and obtained a similar result as Lin and Yu (2011). In our study, the $HULIS_{WS}$-catalysed DTT consumption of all 66 samples were

121   between 3.6% and 77.0%, and the measured DTT activity was linearly proportional to $HULIS_{WS}$ mass concentration.

122   The $HULIS_{WS}$-catalysed DTT consumption of each sample was normalized by the volume of air sampled (DTT_V, defined as

123   extrinsic DTT activity and expressed in units of nmol min^{-1} m^{-3}) and the $HULIS_{WS}$ mass (DTT_m, defined as intrinsic DTT activity

124   and expressed in units of mol min^{-1} per µg $HULIS_{WS}$) (Dou et al., 2015; Verma et al., 2014), respectively. The mathematical

125   expressions of DTT_V and DTT_m are shown below.

126           $$Extrinsic\ DTT\ activity\ (DTT_V) = \frac{R_{DTT}(\%) \times n_{DTT}(nmol)}{t(min) \times Air\ volumn(m^{-3})}$$ E.q. (1)

127           $$Intrinsic\ DTT\ activity\ (DTT_m) = \frac{DTT_V\ (nmol\ min\ m^{-3})}{HULIS_{WS}\ (\mu g\ m^{-3})}$$ E.q. (2)

128   Since DTPA was added to suppress DTT consumption by metals ions throughout the incubation process and may affect the DTT

129   response of quinones (Dou et al., 2015), the DTT activity of $HULIS_{WS}$ measured here may be underestimated and is not directly

130   comparable to those studies conducting DTT assay experiments without DTPA.

131   **2.4 Source apportionment**

132   In this study, the United States Environmental Protection Agency PMF 5.0 was applied to identify the sources of $HULIS_{WS}$ and

133   apportion their contributions to both $HULIS_{WS}$ and the extrinsic DTT activity of $HULIS_{WS}$. As suggested by Henry et al. (1984),

134   the minimum sample size of N for PMF analysis was 30 + (V + 3)/2, where V is the number of input species. A total of 66 samples

135   and 13 species were included in PMF analysis, which was an adequate sample size to obtain a statistically reliable PMF result.

136   Details of PMF parameter settings are provided in the Supplementary Material.

137   **3 Results and discussion**

138   **3.1 $HULIS_{WS}$ mass concentration and the DTT activity of $HULIS_{WS}$**

139   In this study, the $HULIS_{WS}$ mass concentration and DTT activity of $HULIS_{WS}$ in 66 $PM_{2.5}$ samples were quantified. The annual

140   average concentration of total $HULIS_{WS}$ in Beijing measured in this study was 5.66 µg m^{-3} (median: 4.30, range: 1.08–22.36 µg

141   m^{-3}). This was approximately 20% higher than those measured in three other Chinese cities: 4.83 µg m^{-3} in Guangzhou (Kuang et

142   al., 2015), 4.71 µg m^{-3} in Nansha (Kuang et al., 2015), and 4.69 µg m^{-3} in Lanzhou (Tan et al., 2016). A clear temporal variation

143   of $HULIS_{WS}$ mass concentration was observed (Figures 1, 2), with significantly higher levels ($p < 0.05$, Mann–Whitney test) in the

144   heating season (November through March; average 7.93, median 6.15 µg m^{-3}) than in the non-heating season (April through

145   October; average 3.72, median 2.86 µg m^{-3}). This could be mostly attributed to the intensive coal and biomass burning activities

146   performed for residential heating during the heating season. In addition, the lower temperatures and mixing height during the

147   heating season could also favour the formation of particle-bound $HULIS_{WS}$ species. However, the contributions of total $HULIS_{WS}$

148   to organic matter (OM, calculated by multiplying OC with 1.98 and 1.50 for the heating and non-heating seasons, respectively,

149   Xing et al., 2013) in $PM_{2.5}$ are slightly lower during the heating season (21.8% ± 13.5%) than that during the non-heating season

150 (27.4% ± 12.0%, Figure 1), indicating higher levels of combustion-generated organic compounds other than $HULIS_{WS}$ were
151 emitted in the heating seasons as well.

152 The extrinsic DTT activity of $HULIS_{WS}$ exhibited similar temporal variation as $HULIS_{WS}$ (Figure 2), with significantly higher
153 levels in the heating season (average 0.073, median 0.063 nmol min^{-1} m^{-3}) than in the non-heating season (average 0.031, median
154 0.029 nmol min^{-1} m^{-3}). Because most of the inorganic ions were not retained by the HLB cartridge and the remaining metals in
155 the $HULIS_{WS}$ effluent were chelated by DTPA, the DTT activity measured here could be attributed entirely to the DTT active
156 moieties in $HULIS_{WS}$. The intrinsic DTT activity of $HULIS_{WS}$ describes the intrinsic ROS-generation ability of $HULIS_{WS}$, and the
157 average intrinsic DTT activity of $HULIS_{WS}$ in Beijing was 9.91 pmol min^{-1} per µg $HULIS_{WS}$ (median 9.02, range 2.74–25.8 pmol
158 min^{-1} per µg $HULIS_{WS}$), which was higher than the reported average DTT_m activity (6.4 ± 1.2 pmol min^{-1} per µg $HULIS_{WS}$) in six
159 $PM_{2.5}$ samples collected during winter in Guangdong, China (Dou et al., 2015). This difference might be attributed to the different
160 chemical components and sources of $HULIS_{WS}$ in these two regions.

3.2 Individual species of $HULIS_{WS}$

162 Because the main objective of this study was to identify the sources of $HULIS_{WS}$ and quantify the source-specific contributions to
163 both $HULIS_{WS}$ and their associated redox activity, we mainly focused on the identification of organic markers in the chemical
164 analysis. A total of 25 species were identified and quantified in the $HULIS_{WS}$ fraction of $PM_{2.5}$ using GC-MS, including 12 aromatic
165 acids, five nitrophenol analogues, three aliphatic acids, and five biogenic secondary organic aerosol (SOA) tracers (Table S2 in the
166 Supplementary Material, Hu et al., 2008)

167 All 12 aromatic acids, including three hydroxyl benzoic acids, three benzenedicarboxylic acids, three benzenetricarboxylic acids,
168 2-hydroxy-5-nitrobenzoic acid, vanillic acid, and syringic acid, exhibited higher levels during the heating season than during the
169 non-heating season (Figure S2 in the Supplementary Material). Among these acids, terephthalic acid (TPha) was the most abundant
170 (average 150.2 ng m^{-3} in the heating season, and 98.1 ng m^{-3} in the non-heating season), accounting for approximately 2% of the
171 $HULIS_{WS}$ mass concentration. Compared with other Chinese cities, the concentration of TPha in Beijing was substantially higher
172 than those in the southern cities, such as Hong Kong (19.9 ng m^{-3} in winter, Ho et al., 2011), and was similar to those in the
173 northern cities, such as Xi'an (54 ng m^{-3} in summer and 250 ng m^{-3} in winter, Cheng et al., 2013). TPha is mainly used to produce
174 polyethyleneterephthalate (PET) plastics, which are widely used for bottles and containers; therefore, it has been suggested as a
175 tracer for the pyrolysis of domestic waste (Kawamura and Pavuluri, 2010; Simoneit et al., 2005). Benzenetricarboxylic acids were
176 considered to be secondarily formed from the photodegradation of organic precursors, such as polycyclic aromatic hydrocarbons
177 (PAHs) (Kautzman et al., 2010). Therefore, 1,2,3-benzenetricarboxylic acid (123Ben) and 1,2,4-benzenetricarboxylic acid
178 (124Ben) were also included in the PMF analysis.

179 Similar to the aromatic acids, all five nitrophenol analogues, namely 4-nitrophenol, 2-nitrocatechol, 2-methyl-4-nitrophenol
180 (2M4NP), 4-methly-5-nitrocatechol (4M5NC), and 3-methly-6-nitrocatechol (3M6NC), exhibited 8–14 times higher
181 concentrations during the heating season than during the non-heating season (Table S1 in the Supplementary Material). In
182 particular, 4M5NC and 3M6NC not only showed similar temporal variations but also were strongly correlated ($R^2 = 0.87$), implying
183 that they may have similar sources. These two compounds have been suggested as tracers for the aging process of biomass burning
184 (Iinuma et al., 2010; Kahnt et al., 2013). However, Iinuma et al. (2010) pointed out that the photo-oxidation of vehicle exhaust
185 may be a more significant source for these two compounds in urban areas. Given that both 4M5NC and 3M6NC are good
186 anthropogenic SOA markers, they were also included in the PMF analysis.

187 Five biogenic SOA tracers including 3-hydroxyglutaric acid, 3-hydroxy-4,4-dimethylglutaric acid, 3-methyl-1,2,3-
188 butanetricarboxylic acid, 3-isopropylglutaric acid, and 3-acetylglutaric acid were identified and quantified. Because they were all
189 formed from the atmospheric oxidation of monoterpenes and had similar temporal variations, they were grouped as SOA markers
190 of monoterpenes (MonoT) in the PMF analysis (Hu et al., 2010). Briefly, MonoT showed higher concentrations during the non-
191 heating season (average 16.9, median 15.2 ng m^{-3}) than during the heating season (average 12.5, median 10.2 ng m^{-3}), which was
192 opposite to HULIS$_{WS}$ mass concentration. Because of the higher biogenic volatile organic compounds (VOCs) emissions, more
193 intense solar radiation, and higher temperature and humidity in the non-heating season, more active secondary formation could
194 lead to higher concentrations of biogenic SOA (Guo et al., 2012).

3.3 Source apportionment of HULIS$_{WS}$ and their extrinsic DTT activity

196 The optimal PMF solution was determined with five factors (A–E; Figure 3). The Q$_{robust}$ obtained was 62.9, which was exactly
197 equal to Q$_{true}$, and the scaled residues for all species were between −2 and +2, indicating no outliers for this solution. Constrained
198 model operation was adopted for a more reasonable interpretation (dQ$_{robust}$% = 0.32%) (Norris et al., 2014). The optimized solution
199 was bootstrapped 100 times, with 100% of the runs producing the same factors. A strong linear correlation between the measured
200 and PMF-predicted HULIS$_{WS}$ mass concentrations (R^2 = 0.76) also suggested a reliable PMF solution (Figure S4 in the
201 Supplementary Material).

202 As shown in Figure 3, factor A had a high percentage of non-sea salt Cl$^-$ (nss-Cl$^-$, [nss-Cl$^-$] = [Cl$^-$] − 1.17 × [Na$^+$]), and was
203 attributed to coal combustion (Tan et al., 2016; Tao et al., 2016; Zhang et al., 2013). Factor B had a high loading of levoglucosan
204 and was determined as biomass burning (Hu et al., 2010; Tao et al., 2016). Factor C was considered to be waste incineration, due
205 to the high level of TPha. Factor D was dominated by hopanes, tracers for fuel combustion, suggesting traffic related activities (Hu
206 et al., 2010). In particular, the two anthropogenic SOA markers, 4M5NC and 3M6NC, were mostly assigned to this factor (4M5NC
207 46%, and 3M6NC 33%) instead of factor C (4M5NC 14%, and 3M6NC 25%). These two species were mainly formed through the
208 photo-oxidation of cresols, which were directly emitted through wood combustion or produced from toluene through its reaction
209 with OH radicals in the presence of NO$_X$ (Iinuma et al., 2010). Traffic emissions were a significant source of single-ring aromatics,
210 especially toluene, in Chinese megacities (Huang et al., 2015). In this study, the sampling site was located in an urban area
211 influenced by considerable vehicular emissions of NO$_X$ and toluene, which may have led to subsequent secondary formation of
212 4M5NC and 3M6NC. Therefore, the fourth factor was considered as a mixed source including both primary emission and the aging
213 process of traffic exhaust. The fifth factor was characterized by a predominant loading of MonoT, SO$_4^{2-}$, and NH$_4^+$; thus, it was
214 considered as a secondary aerosol formation source.

3.4 Source-specific contributions to HULIS$_{WS}$

216 Source-specific contributions to HULIS$_{WS}$ during both non-heating and heating seasons were calculated based on PMF results.
217 The four combustion-related sources contributed >80% of HULIS$_{WS}$ in the heating season and 50% in the non-heating season
218 (Figure 4A), of which biomass burning was the most predominant. A strong correlation (R^2 = 0.51, Figure S5 in the Supplementary
219 Material) was observed between HULIS$_{WS}$ and levoglucosan, a marker of biomass burning, and this was consistent with previous
220 studies (Lin et al., 2010b). Approximately 33% of HULIS$_{WS}$ was attributed to biomass burning during the 1-year sampling period
221 in Beijing, higher than that observed in the PRD region (8%−28%, Kuang et al., 2015). The intensive wood and crop residue
222 burning activities in the Beijing−Tianjin−Hebei region during autumn and winter could emit a large amount of aerosols into the
223 atmosphere (Zhang et al., 2013). Thus, as shown in Figure 4A, the contribution of biomass burning to HULIS$_{WS}$ in the heating
224 season (2.96 μg m^{-3}) was 3.5 times that in the non-heating season (0.84 μg m^{-3}).

A previous study reported that refuse burning may contribute 1%–24% of organic particles in Asia (Simoneit et al., 2004). In this study, waste incineration was found for the first time as an important source of HULIS$_{WS}$ in Beijing, with a considerable and stable contribution to HULIS$_{WS}$ throughout the year (18.7% in the non-heating season and 17.1% in the heating season). According to the China Statistic Yearbook (2013), 6.33 million tons of domestic waste were produced in Beijing during 2012 (National Bureau of Statistics of China, 2013), among which 0.95 million tons were disposed through incineration. Given that nearly 24% of the urban waste was plastic (Wang and Wang, 2013), the incineration of such large amounts of domestic waste may explain the high levels of TPha in Beijing.

Coal has occupied the predominant position in China's energy consumption for a long time (Zhang and Yang, 2013). Therefore, coal combustion is an important source of PM$_{2.5}$ pollution in China, especially in northern Chinese cities. Tan et al. (2016) identified a strong correlation between HULIS$_{WS}$ and Cl$^-$ (R^2 = 0.89) in Lanzhou and suggested that coal burning was probably the major contributor to HULIS$_{WS}$ in winter. However, the contribution of coal combustion to HULIS$_{WS}$ was found to be minor (5.8%) in the present study. Similarly, a source apportionment analysis of PM$_{2.5}$-bound water-soluble organic carbon (WSOC) in Beijing found that less than 5% of WSOC was from coal combustion (Tao et al., 2016). This was because less oxidized compounds including PAHs were favourably produced from the aromatic fragments of coal under the fuel-rich incomplete combustion conditions; these less oxidized compounds are generally hydrophobic substances and not extracted into the HULIS$_{WS}$ fraction.

A correlation between HULIS$_{WS}$ and hopanes (R^2 = 0.46, Figure S5 in the Supplementary Material) might suggest direct emissions of HULIS$_{WS}$ from vehicle exhaust. As shown in Figure 4A, vehicle emissions are responsible for 13.7% of PM$_{2.5}$-bound HULIS$_{WS}$. Interestingly, the amount of HULIS$_{WS}$ assigned to vehicle exhaust was approximately three times higher in the heating season than in the non-heating season (Figure 4A). This could be attributed to the low temperature in winter, which favours the partition of semivolatile HULIS$_{WS}$ species into particle phases. Another explanation could be that more HULIS$_{WS}$ were formed from the aging process of traffic exhaust in the heating season. To evaluate this hypothesis, multilinear regression (MLR) analysis was conducted to assess the effects of NO$_X$, O$_3$, SO$_4^{2-}$, particle acidity (H$_p^+$), and particle-phase liquid water content (LWC$_p$) on HULIS$_{WS}$ resolved in the vehicle emissions factor (HULIS$_{WS\_VE}$; the calculation of H$_p^+$ and LWC$_p$, and the MLR analysis results are provided in the Supplementary Material). NO$_X$ was found as the only statistically significant factor that was positively correlated to HULIS$_{WS\_VE}$ with a regression coefficient of 0.012 (p < 0.01; Table S3 in the Supplementary Material), suggesting that a 1 μg m^{-3} increase in NO$_X$ was associated with a 0.012 μg m^{-3} increase in HULIS$_{WS\_VE}$, when holding other covariates unchanged. In fact, vehicle exhaust was the major source of ground level NO$_X$ (>60%) in Beijing, even in the heating season (Lin et al., 2011). A higher level of NO$_X$ was observed during the heating season than during the non-heating season due to a lower boundary layer and weaker vertical mixing (Figure S6 in the Supplementary Material). Kautzman et al. (2010) found that ring-opening oxygenated products with one benzyl group, which could be retained by the HLB cartridge and were considered as HULIS$_{WS}$ components, were predominantly formed from the photo-oxidation of PAHs under high NO$_X$ conditions. Thus, the higher levels of NO$_X$ in the heating season led to higher levels of secondarily produced HULIS$_{WS\_VE}$, indicating a synergistic effect of primary emission and the secondary aging process from vehicle exhaust. Furthermore, the presence of 4M5NC and 3M6NC, SOA markers of cresol, in this factor confirmed that a certain fraction of HULIS$_{WS\_VE}$ was secondarily formed.

In addition to the four combustion-related sources, one secondary source was apportioned by PMF, contributing 30.1% of HULIS$_{WS}$ throughout the year. MLR analysis was conducted to evaluate the effects of O$_3$, NO$_X$, SO$_4^{2-}$, H$_p^+$, and LWC$_p$ on the secondary formation of HULIS$_{WS}$ (HULIS$_{WS-SEC}$). Sulfate was found to be the most significant factor with a regression coefficient of 0.066 (Table S4 in the Supplementary Material). This may be due to the predominant role of sulfate in the particle-phase formation of organosulfates, one important HULIS$_{WS}$ component (Xu et al., 2015), through both nucleophilic addition reactions

and the salting-in effect (Lin et al., 2012; Riva et al., 2015). Results from the MLR analysis also indicated that an increase of 1 μg m^{-3} O_3 led to an increase of 0.028 μg m^{-3} $HULIS_{WS\_SEC}$. Gaseous highly oxidized multifunctional organic compounds (HOMs) were characterized in the ozonolysis of α-pinene in smog chamber experiments (Zhang et al., 2015). It was suggested that, after partitioning to the particle phase, these HOMs could undergo rapid accretion reactions to form oligomers containing multiple carboxylic acid and ester groups, which served as good $HULIS_{WS}$ candidates. Considering the higher concentrations of O_3 in the non-heating season (Figure S7 in the Supplementary Material), together with higher biogenic VOCs emissions and temperature as well as more intense solar radiation, a larger amount of $HULIS_{WS\_SEC}$ was produced in the non-heating season (2.01 μg m^{-3}) than in the heating season (1.41 μg m^{-3}).

3.5 Source-specific contributions to DTT activity of $HULIS_{WS}$

To gain quantitative insights into the potential health impacts of different $HULIS_{WS}$ sources, source-specific contributions to extrinsic DTT activity of $HULIS_{WS}$ were assessed using PMF. The strong correlation ($R^2 = 0.78$; Figure S4 in the Supplementary Material) between measured and predicted DTT activity suggested reliable predictions.

As shown in Figure 4B, the four combustion-related sources accounted for 75% of the extrinsic DTT activity of $HULIS_{WS}$ throughout the year, of which biomass burning contributed 33.6%, followed by vehicle emissions (18.5%), waste incineration (18.5%), and coal combustion (4.1%). The extrinsic DTT activity of $HULIS_{WS}$ describes the redox activity of $HULIS_{WS}$ on air volume basis (E.q.(1)), which is reflective of human exposure to $HULIS_{WS}$; while the intrinsic DTT activities of $HULIS_{WS}$ is on mass basis and is more important for assessing the intrinsic toxicity $HULIS_{WS}$ from various sources. The intrinsic DTT activities of the $HULIS_{WS}$ from the five identified sources were calculated (E.q.(2)). $HULIS_{WS}$ from vehicle emissions was found to be the most DTT-active (12.0 pmol min^{-1} per μg $HULIS_{WS\_VE}$), followed by waste incineration (9.25 pmol min^{-1} per μg $HULIS_{WS\_WI}$), biomass burning (9.10 pmol min^{-1} per μg $HULIS_{WS\_BB}$), secondary formation (7.45 pmol min^{-1} per μg $HULIS_{WS\_SEC}$), and coal combustion (6.22 pmol min^{-1} per μg $HULIS_{WS\_CC}$).

Similar to the source apportionment results of $HULIS_{WS}$, biomass burning was identified as the leading contributor to extrinsic DTT activity of $HULIS_{WS}$ in the heating season (39.4%, 0.015 nmol min^{-1} m^{-3}), and throughout the year (33.6%, 0.017 nmol min^{-1} m^{-3}). During biomass burning, highly oxidized organic compounds with quinone, hydroxyl, and carboxyl groups were directly produced (Fan et al., 2016). Moreover, some of the VOCs emitted from biomass burning could undergo further reactions and generate highly redox-active products, for example, hydroxyquinones formed through ●OH radical oxidation (McWhinney et al., 2013), which could be extracted into the $HULIS_{WS}$ fraction and lead to DTT consumption (Chung et al., 2006; Verma et al., 2015a). Moreover, Wang et al. (2017) found large amounts of nitrogen-containing organic compounds (NOCs) including nitroaromatics and nitrogen-containing bases in $HULIS_{WS}$ from biomass burning. The nitrite group next to aromatic ring in the nitroaromatics could promote electron transfer and lead to more DTT consumption and the nitrogen-containing bases emitted from biomass burning could also enhance the ROS-generation ability of $HULIS_{WS\_BB}$ (Dou et al., 2015), which may explain the observed intrinsic DTT activity of $HULIS_{WS\_BB}$.

Secondary formation was the most important source for the extrinsic DTT activity of $HULIS_{WS}$ in the non-heating season (44.1%, 0.015 nmol min^{-1} m^{-3}) and the second largest contributor throughout the year (25.3%, 0.013 nmol min^{-1} m^{-3}). A few smog chamber experiments have been carried out to investigate the ROS activity of SOA from various hydrocarbon precursors, and the intrinsic DTT activity values of several biogenic SOA systems (i.e. isoprene, α-pinene, and β-caryophyllene) were found to be within the range of 2 to 30 pmol min^{-1} per μg SOA (Kramer et al., 2016; Tuet et al., 2017). Tuet et al. (2017) also observed a much higher intrinsic DTT activity of naphthalene SOA than that of biogenic SOA, and suggested that this was probably due to the aromatic species, especially nitroaromatics, in naphthalene SOA. The intrinsic DTT activity of $HULIS_{WS\_SEC}$ measured in this study is 7.45

pmol min^{-1} per μg HULIS$_{WS\_SEC}$, which is within the reported intrinsic DTT activity range of biogenic SOA. Moreover, results from MLR analysis indicated that both sulfate and ozone were positively correlated with HULIS$_{WS\_SEC}$ (Table S4), suggesting that HULIS$_{WS}$ resolved in this factor could mainly consist of some less ROS-active SOA components, such as organosulfates (Chen et al., 2011; Lin et al., 2012). Although chamber experiments reported the formation of ROS-active HOMs or organic peroxides through the ozonolysis of biogenic VOCs (Docherty et al., 2005; Zhang et al., 2015), the production yields of these peroxides were generally low and thus could not have a major influence on the DTT activity of HULIS$_{WS\_SEC}$. However, since secondary formation predominated in HULIS$_{WS}$ formation (Figure 4A), especially in the non-heating season (50.1%), even with a lower intrinsic DTT activity, secondary aerosol formation still serves as a significant contributor to HULIS$_{WS}$-associated redox activity in Beijing. It should be noted that the contributions of secondary formation processes to both HULIS$_{WS}$ and DTT activity of HULIS$_{WS}$ could even have been underestimated in this study, because HULIS$_{WS}$ secondarily formed through the aging of biomass burning and vehicle emissions was resolved in factor B and D and could not be accurately quantified.

Although vehicle emission just contributed 18% to extrinsic DTT activity of HULIS$_{WS}$ throughout the year (18.5%, 0.009 nmol min^{-1} m^{-3}), HULIS$_{WS\_VE}$ has the highest intrinsic DTT activity among all sources (12.0 pmol min^{-1} per μg HULIS$_{WS\_VE}$). Similarly, Bates et al. (2015) revealed that the water-soluble PM$_{2.5}$ from gasoline vehicle emissions had the highest intrinsic DTT activity, probably due to the oxygenated OC and metals on gasoline particles. Verma et al. (2009) also observed a higher aerosol oxidative potential from the aged particles of traffic exhaust than those directly emitted, and a strong correlation was observed between oxygenated organic acids and vehicle-related redox activity. As shown in Figure 2D, most of the two methyl nitrocatechol markers were resolved in the vehicle emissions factor and HULIS$_{WS\_VE}$ was found to be significantly correlated with NO$_X$, therefore the high intrinsic ROS activity of HULIS$_{WS\_VE}$ is believed to be mostly due to the highly oxygenated OC content, especially the highly redox-active nitroaromatics (Tuet et al., 2017).

Waste incineration was also an important primary source of the extrinsic DTT activity of HULIS$_{WS}$ (20.5% in the non-heating season and 17.4% in the heating season), and its intrinsic HULIS$_{WS}$ ROS activity was slightly higher than that from biomass burning. Mohr et al. (2009) examined the elemental ratio of aerosols emitted from different sources. They found that particles from plastic burning had a higher O/C ratio (0.08) than those from diesel (0.03) and gasoline (0.04) combustion, indicating a more oxidized feature of aerosols emitted through refuse burning (Mohr et al., 2009). Considering that incineration will play an increasingly important role in waste treatment in Beijing in the following years (National Development and Reform Comission, 2016), concern should be directed to the potential threat of trash burning to public health.

In summary, four combustion-related sources and one secondary formation source of PM$_{2.5}$-bound HULIS$_{WS}$ and their associated ROS activity were identified by PMF. Biomass burning (32.7%) and secondary aerosol formation (30.1%) were the major contributors to HULIS$_{WS}$ in Beijing. For the first time, waste incineration was identified as an important source of HULIS$_{WS}$, with a considerable and stable contribution to HULIS$_{WS}$ throughout the year (17.7%). Regarding ROS-generation potential, HULIS$_{WS}$ from vehicle emissions was identified as the most ROS-active, and HULIS$_{WS}$ from secondary aerosol formation showed a lower intrinsic DTT ability than those of most primary sources except for coal combustion. Such variations in the ROS-generation ability of HULIS$_{WS}$ from different sources will be relevant for future inquiries into more detailed chemical speciation of HULIS$_{WS}$, their roles in ROS generation, and the possible oxidation mechanisms involved.

Supplementary Material. Information on chemical analysis; PMF source apportionment; MLR analysis together with Table S1-S4 and Figure S1-S7 are provided.

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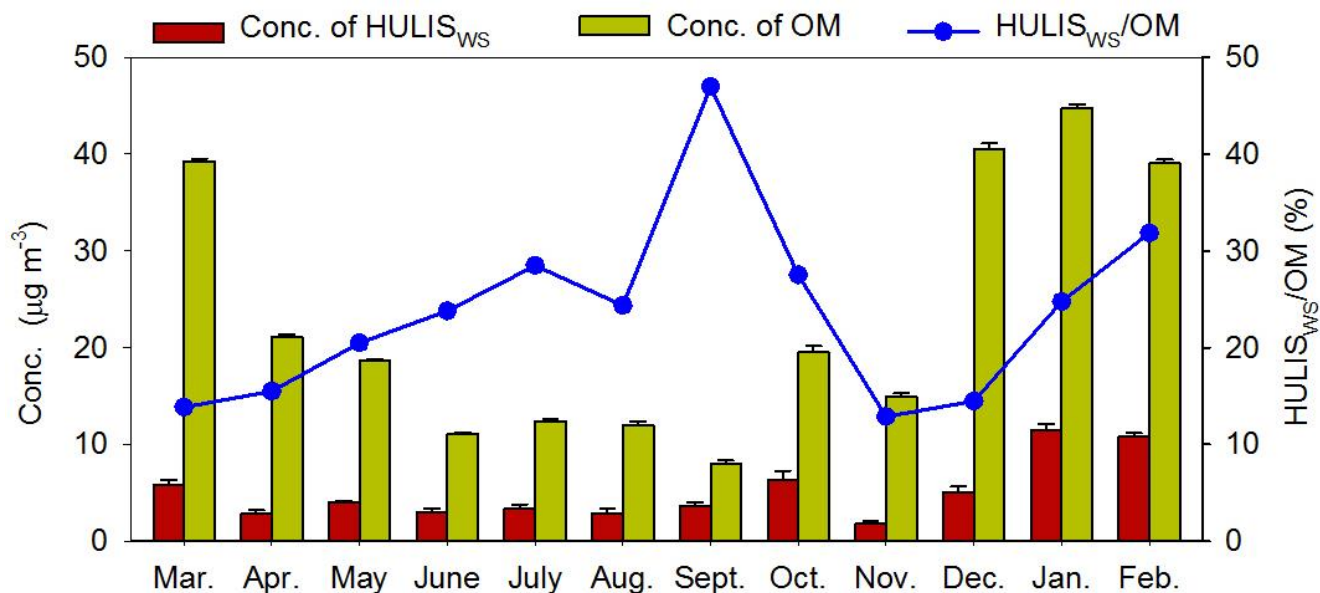
481 **Figure 1: Monthly average concentrations (average ± standard error) of HULIS_WS mass concentration and organic**
482 **matter (OM) in PM_{2.5} collected in Beijing. The monthly percentage contributions of HULIS_WS to OM are shown in the**
483 **blue line.**

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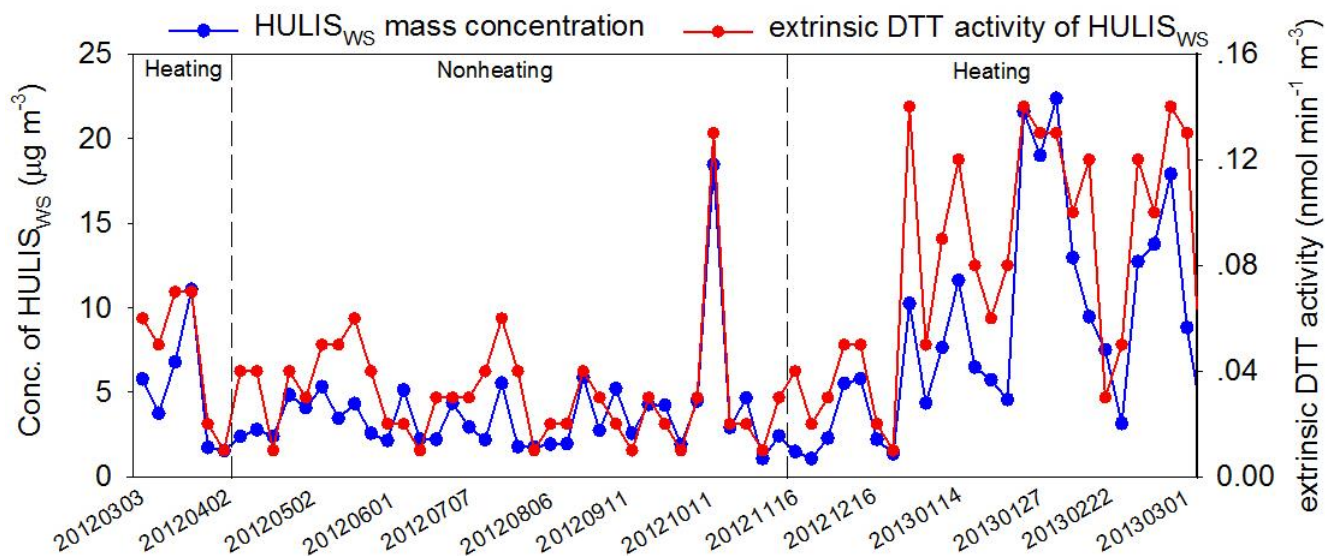
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486 **Figure 2: Temporal variation of HULIS_WS mass concentration and extrinsic DTT activity of HULIS_WS in Beijing.**

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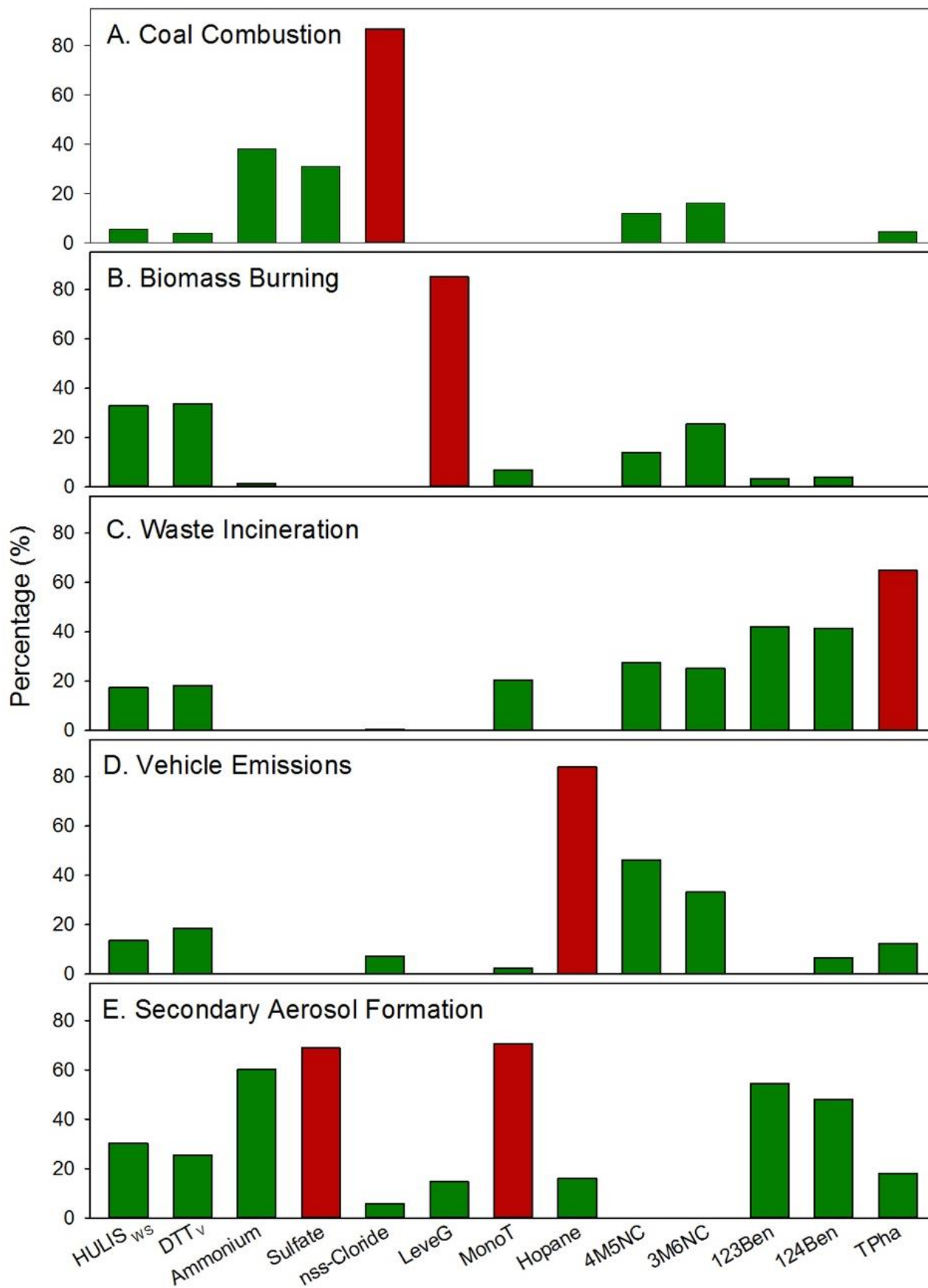
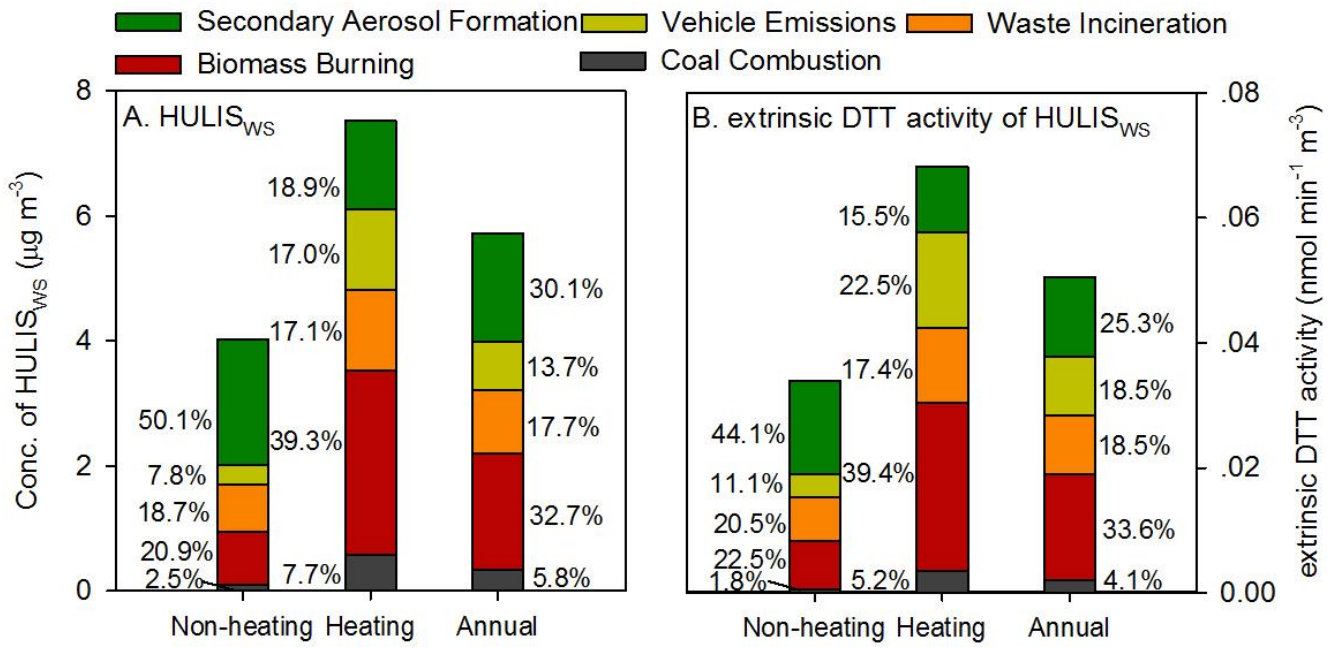


Figure 3: Distribution of HULISws, HULISws-associated DTT activity and other measured species in the five sources resolved by PMF.
Columns in dark red indicate characteristic tracers of each source.

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491 **Figure 4: Source-specific contributions to HULIS$_{WS}$ mass concentration (panel A) and extrinsic DTT activity of HULIS$_{WS}$ (panel B).**