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1 **Speciation of Carboxylic Components in Humic-like Substances (HULIS) and Source Apportionment**  
2 **of HULIS in Ambient Fine Aerosols (PM<sub>2.5</sub>) Collected in Hong Kong**

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17

18 **Abstract**

19 Humic-like substances (HULIS) are an important mixture of organic compounds, which account for a  
20 great part of water-soluble organic compounds in ambient aerosols. In this study, individual carboxylic and  
21 hydroxylic species in HULIS extracts of PM<sub>2.5</sub> samples collected in Hong Kong during summer were  
22 measured by gas chromatography mass spectrometry with prior chemical derivatization. Significantly higher  
23 levels of HULIS was observed on days mainly impacted by regional pollution (regional days,  $4.11 \pm 1.76 \mu\text{g}$   
24  $\text{m}^{-3}$ ) than on days under local emission influences (local days,  $0.56 \pm 0.30 \mu\text{g m}^{-3}$ ). Positive matrix  
25 factorization was applied to identify the major sources and apportion their contributions to HULIS.  
26 Simultaneous monitoring and analysis data from four different sampling sites showed that sources of HULIS  
27 in Hong Kong were mainly regional with small spatial variations. Secondary aerosol formation (both organic  
28 and inorganic) had a predominant contribution (52.7%) to HULIS during the whole sampling period. It  
29 accounted for  $1.88 \pm 0.91 \mu\text{g m}^{-3}$  of HULIS on regional days, which was about 5 times higher than its  
30 contribution ( $0.39 \pm 0.34 \mu\text{g m}^{-3}$ ) on local days. Of the three identified primary sources, biomass burning had  
31 the largest contribution on both regional (34.9%) and local days (24.6%). Marine vessels were also a  
32 significant contributor, especially on local days (20.3%). Vehicle exhaust, on the other hand, showed a  
33 negligible contribution to HULIS (2.1%) in Hong Kong in this study.

34 **Keywords**

35 fine particulate matter (PM<sub>2.5</sub>); Humic-like substances (HULIS); source apportionment; speciation of  
36 atmospheric HULIS; water-soluble organic compounds

## 37 1. Introduction

38 Humic-like substances (HULIS) are an important constituent of atmospheric aerosols. The carbon  
39 fraction of HULIS accounts for 36-57% of aerosol phase water soluble organic carbon (WSOC) in the Pearl  
40 River Delta (PRD) region (Lin et al. 2010b; Song et al. 2012; Kuang et al. 2015), 9-62% of WSOC in Europe  
41 (Krivácsy et al. 2000; Feczko et al. 2007; Salma et al. 2010), and 25-55% of WSOC in North America  
42 (Pavlovic and Hopke 2012).

43 HULIS are structurally similar to aquatic and terrestrial fulvic acid, but with lower aromaticity and  
44 molecular weight (MW) (Graber and Rudich 2006). Laboratory studies have been carried out to examine the  
45 physical properties of HULIS. Studies found that HULIS play an important role in global energy budget  
46 directly by its strong absorption of ultraviolet (UV) and visible light, and indirectly by acting efficiently as  
47 the cloud condensation nuclei (CCN) (Dinar et al. 2006). It can also enhance the oxidation of certain organic  
48 pollutants in aqueous-phase and mediate the generation of reactive oxygen species (Lin and Yu 2011; Dou  
49 et al. 2015). Several techniques have been applied to determine the MW distribution of HULIS, and it is  
50 found that most HULIS compounds have MW ranging from 200 to 600 Da and the average MW of HULIS  
51 is estimated to be in the range of 215-345 Da (Graber and Rudich 2006). Lin et al. (2012a, b) used ultrahigh  
52 resolution mass spectrometer to explore the chemical structures and elemental compositions of HULIS.  
53 Thousands of molecular formulas were identified, with some analogous to aquatic fulvic acids (e.g.  
54 carboxylic acids) and some unique in atmospheric HULIS fraction (e.g. nitrooxy-organosulfates and  
55 organosulfates). They suggested that both secondary aerosol formation and biomass burning are important  
56 sources of HULIS in PRD region. Kuang et al. (2015) performed source apportionment of HULIS collected

57 at Nansha (NS) and Guangzhou (GZ) in the PRD region, and found that besides secondary formation process  
58 and biomass burning, residual oil burning is also an important contributor to HULIS in the PRD region.

59 Given the highly complex composition of atmospheric HULIS, we focused on the determination of  
60 carboxylic and hydroxylic components in HULIS in current study, especially those with characteristic source  
61 origins. We then conducted source analysis of HULIS mass using positive matrix factorization (PMF). Thirty  
62 eight PM<sub>2.5</sub> samples collected at four sampling sites in Hong Kong during summer were analyzed. With  
63 results obtained from this study, we aimed to have an improved understanding of both the speciation and  
64 origins of carboxylic components in HULIS, the major sources of HULIS, and their spatial variations and  
65 relative contributions to atmospheric HULIS in Hong Kong.

66

## 67 **2. Analytical Methods**

### 68 **2.1. Sample Collection**

69 The fine aerosol samples were simultaneously collected at four different sites in Hong Kong, which  
70 were the Hong Kong University of Science and Technology (HKUST), Yuen Long (YL), Tung Chung (TC),  
71 and Tsuen Wan (TW). Of the four sampling sites, HKUST is a suburban site with commercial and industrial  
72 areas located more than 5 km away, YL and TW are two densely populated urban sites, and TC is an emerging  
73 area close to airport with less residents. The geographical feature of Hong Kong was illustrated in detail in  
74 our previous study (Hu et al. 2008).

75 Samples were collected from 07:00 in the morning and sustained for 24 h from 8 July to 3 August 2006.  
76 PM<sub>2.5</sub> aerosol samples were collected on 20×25 cm<sup>2</sup> quartz fiber filters (Whatman, Clifton, USA) with a high

77 volume PM<sub>2.5</sub> sampler (TE-6070V-BL, Tisch Environmental Inc., USA). The flow rate was maintained at  
78 1.13 m<sup>3</sup> min<sup>-1</sup>. The quartz fiber filters were pre-baked at 550°C for 12 h before sampling to avoid possible  
79 organic contaminants. Simultaneously, parallel PM<sub>2.5</sub> samples were collected on 47-mm Teflon filters (Pall  
80 Life Sciences, Ann Arbor, MI) by a R&P Partisol Model 2000 sampler (Rupprecht and Patashnick, Albany,  
81 NY, USA) for PM<sub>2.5</sub> mass determination, and analysis of ionic species and metals. Field blanks of both Teflon  
82 and quartz fiber filters were collected at each site. On each sampling day, the start and end time, the flow rate  
83 chart, and environmental conditions, such as temperature, humidity, and precipitation etc., were carefully  
84 recorded. After sampling, filters were wrapped with aluminum foil, sealed in a zip bag, transported back to  
85 the lab in a cooler with ice packs, put into a sealed container and immediately stored in refrigerator at -18°C  
86 for further analysis.

## 87 **2.2. Chemical Analysis**

88 Elemental carbon (EC) and organic carbon (OC) were analyzed by a thermal/optical transmittance  
89 aerosol carbon analyzer, which is thoroughly described in our previous study (Hu et al. 2008). Cations and  
90 anions were quantified using an ion chromatography (IC) system (DX500, Dionex, Sunnyvale, CA, USA).  
91 Other major elements were analyzed using X-ray fluorescence (XRF) by Desert Research Institute (Reno,  
92 Nevada, USA). Hopanes and steranes were determined using in-injection thermal desorption GC-MS.  
93 Levoglucosan and monoterpene SOA tracers were quantified by GC-MS, and the detailed procedure was  
94 described in Hu et al (Hu et al. 2008). All the above mentioned analysis were done in 2006 and 2007. The  
95 quantification of HULIS mass and speciation of carboxylic and hydroxylic components in HULIS extracts  
96 were conducted in 2012. We adopted the approach developed by Varga et al. (2001) for HULIS isolation.

97 Briefly, a portion of filters (9-18 cm<sup>2</sup> for quantification of HULIS mass; 1 × 12 cm<sup>2</sup> for characterization of  
98 HULIS species) was cut into small pieces and extracted with 9 mL of distilled de-ionized (DDI) water in an  
99 ice ultrasonic bath. The extracts were filtered with 0.45 μm PTFE filters (Grace, USA) and acidified to pH of  
100 2 by 2.4 M of HCl. Since HULIS is considered as a relatively more hydrophobic fraction of water soluble  
101 PM<sub>2.5</sub>, a solid phase extraction cartridge (Oasis HLB, 30 μm, 60mg/cartridge, Waters, USA) was used to  
102 isolate HULIS from the DDI water extracts. The HLB cartridge was rinsed by 1.0 mL of methanol solution,  
103 followed by 1.0 mL of 0.01 M HCl. After sample loading, the cartridge was flushed with 1.0 mL of DDI  
104 water for two times, and eluted with three portions of 0.5 mL of methanol containing 2% ammonia (w/w).  
105 The basic methanol eluate was then dried with a gentle flow of ultrapure nitrogen at 40 °C. The dried samples  
106 were re-dissolved in 1.0 mL of DDI water for the quantification of HULIS mass concentration. An aliquot of  
107 20 μL of the aqueous solution was injected into a high performance liquid chromatography system coupled  
108 with an evaporative light scattering (ELSD3000) detector. Detailed procedure on the analysis of HULIS were  
109 described by Lin et al. (2010a).

110 The individual carboxylic and hydroxylic species in HULIS fraction were identified and quantified  
111 using GC-MS with prior chemical derivatization (7890-5975C, Agilent, USA). The dried samples were  
112 derivatized with 100 μL of BSTFA and 50 μL of pyridine at 70 °C for two hours. After cooling down, 30 μL  
113 of tetracosane-d<sub>50</sub> (50 μg mL<sup>-1</sup> in n-hexane) was added as internal standard. Separation of compounds was  
114 carried out on a HP-5MS column (5% Phenyl Methyl Siloxane, Capillary 30.0m×250 μm×0.25 μm, HP). The  
115 temperature of oven initially started from 80 °C, held for 5 min, then ramped at 3 °C/min to 200 °C, held for  
116 2 min, and finally reached 300 °C at 15 °C/min, and held for 15 min. Authentic standards were used to

117 establish the calibration curves for most identified compounds; while for those without authentic standards,  
118 their isomers or surrogates with similar structures were used for calibration.

119 The recovery tests were carried out using spiked pre-baked blank following the same procedures. For  
120 aromatic acids and nitrophenols, authentic standards were used for most of them, including 3-hydroxybenzoic  
121 acid, 4-hydroxybenzoic acid, phthalic acid, isophthalic acid, 1,3,5-benzenetricarboxylic acid, 4-nitrophenol,  
122 4-nitrocatechol, vanillic acid, and syringic acid. For those without authentic standards, surrogate isomers  
123 were used, i.e. 3-hydroxybenzoic acid for 2- and 4-hydroxybenzoic acids, 1,3,5-benzenetricarboxylic acid  
124 for 1,2,3- and 1,2,4-benzenetricarboxylic acids, and phthalic acid for terephthalic acid. The recoveries of  
125 aromatic acids and nitrophenols ranged in 72-97%. For pimelic acid and azelaic acid, their recoveries were  
126 in the range of 83%-106%, while recovery for adipic acid was 52%.

127

### 128 **3. Results and Discussions**

#### 129 **3.1. Meteorology Condition**

130 As we described in Hu et al. (2008), based on backward trajectories of air masses and spatial pollution  
131 pattern of SO<sub>2</sub> in Hong Kong, the sampling days were classified into two categories, namely regional days  
132 (July 14<sup>th</sup>, 24<sup>th</sup>, 26<sup>th</sup>, and August 1<sup>st</sup>, 2016) and local days (July 8<sup>th</sup>, 10<sup>th</sup>, 12<sup>th</sup>, 16<sup>th</sup>, 20<sup>th</sup>, 22<sup>th</sup>, 28<sup>th</sup>, 30<sup>th</sup>, August  
133 3<sup>rd</sup>). Briefly, on regional days, air mass blowing across the whole PRD region greatly influenced the  
134 concentration levels of air pollutants in Hong Kong. On local days, air masses came from the ocean, and  
135 pollutants were mainly emitted from local sources, such as vehicle exhaust and marine vessels emissions.

#### 136 **3.2 HULIS mass concentration and carboxylic and hydroxylic species in HULIS**



137 The ambient concentrations of PM<sub>2.5</sub> mass, EC and OC were reported in our previously study (Hu et al.  
138 2008). On regional days, concentrations of both PM<sub>2.5</sub> mass (average: 39.92±18.80 µg m<sup>-3</sup>, range: 15.80 –  
139 77.40 µg m<sup>-3</sup>) and OC (8.60±3.34 µgC m<sup>-3</sup>, 2.22 – 14.22 µgC m<sup>-3</sup>) were considerably higher than those on  
140 local days (12.42±4.90 µg m<sup>-3</sup>, 2.72 – 22.50 µg m<sup>-3</sup> for PM<sub>2.5</sub> mass; 2.47±1.13 µgC m<sup>-3</sup>, 0.61 – 4.77 µgC m<sup>-3</sup>  
141 for OC), indicating the strong influence of regional transport on PM<sub>2.5</sub> pollution in Hong Kong. Similarly,  
142 ambient levels of HULIS mass were obviously higher on regional days (4.11±1.76 µg m<sup>-3</sup>, 0.84-7.25 µg m<sup>-3</sup>)  
143 than on local days (0.56±0.30 µg m<sup>-3</sup>, 0.16-1.25 µg m<sup>-3</sup>). Same trend was reported in Ma et al. (2019), in  
144 which HULIS also showed high average concentrations under regional pollution (3.64±1.68 µg m<sup>-3</sup>) than  
145 under local emissions (1.32±0.67 µg m<sup>-3</sup>). However, during this summer sampling campaign, heavy  
146 rainstorms were encountered on several local sampling days (Hu et al. 2008). As a result, really low PM<sub>2.5</sub>,  
147 OC, and HULIS mass concentrations were obtained on those days and the average local day HULIS levels  
148 reported here was lower than that in Ma et al. (2019). Nevertheless, the mean HULIS concentration on  
149 regional days in this study was comparable to that in Ma et al. (2019) and those observed in other cities in  
150 PRD region, such as TW (4.9 µg m<sup>-3</sup>), GZ (4.83 µg m<sup>-3</sup>) and NS (4.71 µg m<sup>-3</sup>) (Lin et al. 2010a; Kuang et al.  
151 2015).

152 Sixteen carboxylic and hydroxylic compounds were identified and quantified, which included eleven  
153 aromatic acids, two nitro-phenols, and three aliphatic acids. Concentrations of individual species in HULIS  
154 were presented in Table 1. We've also identified several monoterpenes SOA tracers in the HULIS extracts,  
155 such as 3-isopropylglutaric acid, 3-hydroxyglutaric acid, 3-acetylglutaric acid, 3-hydroxy-4,4-  
156 dimethylglutaric acid, 3-methyl-1,2,3-butanetricarboxylic acid, and β-caryophyllinic acid. However,

157 concentrations of these compounds in HULIS were significantly lower than those in the methanol extracts of  
158 the same batch of PM<sub>2.5</sub> samples (Hu et al. 2008). This is probably due to the lack of aromatic moiety and  
159 presence of multiple carboxylic and/or hydroxylic groups in their structures, thus they are too hydrophilic to  
160 be well retained on the HLB cartridge. Moreover, they are actually not strictly defined as HULIS according  
161 to the HULIS definition given by Graber and Rudich (2006). Therefore, they were not included in Table 1.

162 The eleven aromatic acids were classified into benzenedicarboxylic acids (BDAs), benzenetricarboxylic  
163 acids (BTAs), hydroxyl benzoic acids (HBAs) and others. Of these acids, BDAs and BTAs were most  
164 abundant at all four sites. The three identified BDAs were phthalic acid (PhA), isophthalic acid (IPhA) and  
165 terephthalic acid (TPhA). Both PhA and TPhA showed higher levels on regional days than on local days,  
166 indicating their regional pollution sources. PhA is ubiquitous in atmospheric particles and were detected in  
167 PM<sub>2.5</sub> samples collected in various cities, such as GZ and Xi'an (Ho et al. 2011; Wang et al. 2012; Zhao et  
168 al. 2014). Although PhA could be emitted from primary sources such as biomass burning, chamber studies  
169 have observed the secondary formation of PhA as the photo-oxidation product of naphthalene and its methyl-  
170 analogs in the atmosphere (Kautzman et al. 2010; Kleindienst et al. 2012). Therefore, it was also used as the  
171 indicators for SOA formation from PAHs in some studies (Ho et al. 2006; He et al. 2018). The summer-time  
172 mean concentration of PhA measured in this study was 7.0 – 43.1 ng m<sup>-3</sup>, falling within the range of that  
173 measured in other PRD region (0.0 – 73.2 ng m<sup>-3</sup>) (He et al. 2018). Higher levels of PhA were observed on  
174 regional days (9.45 ± 3.92 ng m<sup>-3</sup>, 2.61 – 16.19 ng m<sup>-3</sup>) than that on local days (2.70 ± 0.31 ng m<sup>-3</sup>, 2.18 –  
175 3.21 ng m<sup>-3</sup>). On regional days, air masses coming from the northern PRD region brought extra amounts of  
176 primary PhA emitted from biomass burning into Hong Kong. Moreover, our previous study found that the

177 concentrations of aerosol phase PAHs on regional days were about three times of those on local days (Ma et  
178 al. 2016). During regional transport, aging of these PAHs precursors may also lead to further production of  
179 PhA.

180 Previous studies have measured TPhA from the combustion of plastics, and a strong correlation between  
181 TPhA and 1,3,5-triphenylbenzene, tracer for the open-burning of plastic products, was observed (Simoneit  
182 et al. 2005; Kawamura and Pavuluri 2010; Zhao et al. 2014). Therefore, incineration of plastics is considered  
183 as an important source of atmospheric TPhA in urban areas. In this study, the average concentration of TPhA  
184 was 4.54 ng m<sup>-3</sup> during summer, which is only one-twentieth of that reported in Beijing (98.1 ng m<sup>-3</sup> in  
185 nonheating seasons) (Ma et al. 2018). This is because the major approach to manage municipal solid waste  
186 (MSW) in Hong Kong is to dispose them to landfills. However, in Beijing, both incineration plants and  
187 landfills are commonly used to treat MSW, and same for the PRD region. This may explain the higher levels  
188 of TPhA in HULIS observed under regional pollutions than under local emissions. Moreover, an expected  
189 higher level of TPhA was measured at YL than the other three sites on regional days (Table 1), given YL is  
190 the site closest to Shenzhen and most vulnerable to polluted air mass transported from the PRD region.

191 Three BTAs species, i.e. 1,2,3-benzenetricarboxylic acid (1,2,3-Ben), 1,2,4-benzenetricarboxylic acid  
192 (1,2,4-Ben) and 1,3,5-benzenetricarboxylic acid (1,3,5-Ben), were identified. Among the aromatic acids,  
193 1,2,3-Ben and 1,2,4-Ben were most abundant. Both of them showed higher levels on regional days than local  
194 days, especially for 1,2,3-Ben, the difference was up to 12 times. Fraser et al. (1998) found these three BTAs  
195 could be directly emitted from motor vehicles, but recent field measurements suggested that they could also  
196 be secondarily formed through the photo-oxidation of PAHs (Sheesley et al. 2010). Both of them were then

197 input into PMF analysis, and some valuable information on their sources in Hong Kong was obtained from  
198 PMF result.

199 Two nitro-phenolic compounds, namely 4-nitrocatechol (4NC) and 4-nitrophenol (4NP), were  
200 quantified in HULIS on regional days, with concentrations ranging from 0.45 to 5.23 ng m<sup>-3</sup> and 0.46 to 3.42  
201 ng m<sup>-3</sup> for 4NC and 4NP, respectively. However, neither of them was detected on local days. Some studies  
202 showed that these nitro-phenolic compounds may come from both primary emissions and aging of  
203 automobile exhaust and biomass burning (Harrison et al. 2005; Claeys et al. 2012; Kitanovski et al. 2012;  
204 Kahnt et al. 2013). A strong correlation ( $R^2=0.95$ ,  $p<0.01$ ) between 4NP and 4NC (Figure 1) was observed  
205 in this study, indicating the same origins of these two compounds.

### 206 3.3. Source contributions to ambient HULIS

207 In this study, the US EPA PMF 5.0 was adopted to apportion the source contributions to ambient HULIS.  
208 Thirteen species were input into PMF, including HULIS mass, EC, OC, lumped hopanes and steranes (H+S),  
209 levoglucosan, lumped monoterpene SOA tracers (MonoT), nickel (Ni), vanadium (V), SO<sub>4</sub><sup>2-</sup>, oxalate, 1,2,3-  
210 Ben, 1,2,4-Ben, and the lumped 4NP and 4NC (NP+NC). To obtain statistically reliable results from PMF,  
211 the minimum number of sample required is  $30+(V+3)/2$ , where V is the number of input species (Henry et  
212 al. 1984). Thirty-eight samples were used for PMF analysis here, which satisfied the sample size requirement.

213 The criteria of setting the uncertainties for each species was illustrated in detail in our previous study  
214 (Hu et al. 2010). Briefly, the uncertainties are 0.4 of their respective mean values for OC, V, Ni, sulfate, and  
215 oxalate, and 0.2 of the mean values for EC and HULIS. The uncertainties of organic tracers were set as 0.4  
216 of the minimum values for H+S and levoglucosan, and 0.4 of the mean values for 1,2,3-Ben, 1,2,4-Ben,

217 MonoT and NP+NC. In the final result, 10% extra modeling uncertainty were applied to improve the  
218 interpretability of resolved factors.

219 We did preliminary PMF analysis with 4 to 7 factors, and adopted Q values, explained variation (EV),  
220 and the rationality of resolved source profiles as the criteria to evaluate PMF solutions. In PMF solution with  
221 7 factors,  $\text{Na}^+$ ,  $\text{Mg}^{2+}$  and  $\text{Cl}^-$  were included as markers for sea salt, and Al and Si were included as tracers of  
222 dust. However, both sea salt and dust sources showed zero contributions to HULIS. Therefore, these two  
223 sources were not considered in the final solution and their corresponding tracers were removed from the input  
224 species in PMF. We then performed PMF analysis with 5 factors, but the markers of SOA and secondary  
225 inorganic aerosol (SIA) were mixed together and could not be separated distinctly into two factors. Therefore,  
226 the four-factor solution was selected as the final solution, which showed the most reasonable source profiles  
227 and a minimum Q value in all preliminary PMF runs.

228 One hundred base runs were performed to obtain the minimum Q value of the solution, and the ratio of  
229  $Q_{\text{Robust}}$  (222.9) to  $Q_{\text{True}}$  (222.3) was 1.003, indicating almost no impact of outliers. Strong correlations were  
230 observed between measured and predicted values of each species. Particularly, the  $R^2$  value between  
231 predicted HULIS and measured HULIS was up to 0.92. Scaled residuals were also examined, and they  
232 showed normal distribution between -2 and +2 for all species. In bootstrap model, 100 bootstrap runs were  
233 performed, and the result of the bootstrap model was consistent with the base run. Fpeak rotation values were  
234 adjusted from -1 to +1, and the result of non-rotation was the most explicable. Both bootstrap and Fpeak  
235 models indicated a stable solution of base run.

236 The distribution of species among the four factors was shown in Figure 2. Factor 1 had a high loading

237 of MonoT, sulfate and oxalate, indicating it was the secondary aerosol formation (SOA/SIA) source. Factor  
238 2 was identified as biomass burning, evidenced by the prominent loading of levoglucosan. Factor 3 was  
239 distinguished by high loadings of V and Ni, indicating it was the marine vessels source. Factor 4 was vehicle  
240 emissions source, as it was dominated by H+S and EC.

241 The PMF-apportioned source contributions to HULIS on both local and regional days and during the  
242 whole summer sampling campaign were shown in Figure 3a. Secondary aerosol formation, including SIA  
243 and SOA, had a predominant contribution to HULIS on both regional (53.9%) and local days (52.2%),  
244 accounting for about 52.7% of HULIS in summer. This is consistent with the previous finding by Kuang et  
245 al. (2015), where secondary formation process contributed  $70\pm 21\%$  of HULIS in GZ (an urban site) in  
246 summer. The PMF-apportioned mass contribution of secondary formation to HULIS showed a stark  
247 difference (~5 times) between regional and local days, indicating regional transport played a very important  
248 role on secondary formation of HULIS in the region. Consistently, higher levels of air pollutants transported  
249 from the PRD were observed on regional days during the sampling period (Hu et al. 2008), which led to more  
250 rapid oxidation and SOA formation from volatile organic compounds (VOC) precursors.

251 About 70% of MonoT was resolved into SOA/SIA factor. Laboratory experiments revealed that  
252 monoterpenes could undergo photo-oxidation, ozonolysis, and reactions with  $\cdot\text{NO}_3$  radical to form HULIS  
253 (Xu et al. 2015). Besides, recent studies proposed that PAHs, e.g. naphthalene, could undergo OH-initiated  
254 photo-oxidation with the presence of  $\text{NO}_x$  and generate products with single aromatic ring, which have  
255 characteristic functional groups of HULIS (Kautzman et al. 2010; Shakya and Griffin 2010). In addition,  
256 HULIS may also be formed through the acid-catalyzed heterogeneous reactions of isoprenoid or terpenoid

257 (Limbeck 2003; Yang et al. 2011; Huang et al. 2014b). The strong correlation between sulfate and oxalate  
258 ( $R^2=0.90$ ,  $p<0.01$ ) indicates that in-cloud processing may be an important SOA formation pathway in Hong  
259 Kong (Hu et al. 2010). HULIS well correlated with both of them ( $R^2=0.72$ ,  $p<0.01$  for sulfate, Figure 1;  
260  $R^2=0.79$ ,  $p<0.01$  for oxalate), suggesting that part of HULIS may be formed through cloud processing.  
261 Additionally, organosulfates are another important constituent of HULIS (Lin et al. 2012b), which are formed  
262 through the oxidization of biogenic VOCs under acidic conditions. Surratt et al. (2008) have conducted a  
263 series of chamber experiments and proposed several formation mechanisms of organosulfates, in which both  
264 daytime OH-initiated photo-oxidation and nighttime  $\text{NO}_3$ -initiated oxidation were proposed to lead the  
265 production of organosulfate from their monoterpene precursors.

266 Besides MonoT, more than 40% of NP+NC were resolved into the SOA/SIA source as well, indicating  
267 the secondary origins of these compounds in Hong Kong atmosphere. On the other hand, 1,2,4-Ben, was  
268 resolved into all four factors, indicating it has various sources in the region. Sheesley et al. (2010) proposed  
269 that 1,2,3-Ben may be secondarily formed from multi-step degradation of aromatic precursors emitted from  
270 motor vehicles. Our PMF results showed that more than 80% of 1,2,3-Ben was resolved in biomass burning  
271 and SIA/SOA factors, suggesting they are mainly from primary emission of biomass burning and aging of  
272 aromatic VOCs in this area. Both 4NP and 4NC were reported to be formed in the photo-oxidation of aromatic  
273 hydrocarbons, such as benzene, in smog chambers (Sato et al. 2012; Kahnt et al. 2013). Benzene is mainly  
274 emitted from vehicle exhaust and biomass burning, and it can undergo hydroxylation to form phenols and  
275 the following nitration to form NP (Harrison et al. 2005; Borrás and Tortajada-Genaro 2012; Kahnt et al.  
276 2013; Huang et al. 2014a). For 4NC, hydrogen atom of NP can be subtracted by oxygen to form catechol and

277 further formation of NC through reaction with NO<sub>2</sub> (Huang et al. 2014a). Although primary emissions from  
278 vehicles just showed a negligible contribution to HULIS in this study, the loadings of considerable amounts  
279 of 1,2,3-Ben and NP+NC in the SOA/SIA factor implied that some HULIS might be produced during the  
280 aging process of vehicle exhaust. More laboratory evidences are needed to support this statement.

281 Biomass burning is the second largest contributor to HULIS, which accounted for 27.9% (0.55 μg m<sup>-3</sup>)  
282 of HULIS in Hong Kong during summer. It was also identified as a major source of HULIS in GZ (11%) and  
283 NS (8%) during summer. The amount of HULIS apportioned to biomass burning was 1.22 μg m<sup>-3</sup> on regional  
284 days, which was about 5 times of that on local days (0.24 μg m<sup>-3</sup>). Similar pattern of its contribution to OC  
285 on both local and regional days were reported in our previous paper (Hu et al. 2010), given that more intensive  
286 BB activities took place in the northern PRD region than in Hong Kong. The HULIS/OC ratio calculated in  
287 factor 2 was 0.46 μg per μgC, higher than that (0.34±0.05) measured in aerosols from fresh rice straw burning.  
288 This suggests part of HULIS from biomass burning may have a secondary origin through the further oxidation  
289 of biomass burning VOCs. Levoglucosan and non-sea salt K<sup>+</sup> (nss-K<sup>+</sup> corrected with equation: [nss-  
290 K<sup>+</sup>]=[K<sup>+</sup>]-0.0554[Na<sup>+</sup>]) are commonly used as tracers of biomass burning (Zhang et al. 2010). In this study,  
291 HULIS well correlated with levoglucosan and nss-K<sup>+</sup> (R<sup>2</sup>=0.65, p>0.01 for levoglucosan; R<sup>2</sup>=0.77, p<0.01  
292 for nss-K<sup>+</sup>), which confirms the considerable contribution of BB to HULIS (Figure 1).

293 Similar to NS and GZ (Kuang et al. 2015), marine vessels were the second largest primary contributor  
294 to HULIS (0.20 μg m<sup>-3</sup>, 17.4% of HULIS) in Hong Kong during summer. This further confirmed the  
295 contribution of ship exhaust to HULIS in the PRD region. Hong Kong has one of the busiest container ports  
296 in the world. There are about 21 ports in the PRD region, and the Kwai Chung Port in Hong Kong is one of



297 the largest coastal ports in the region with marine vessels emitting considerable amount of PM<sub>2.5</sub>, SO<sub>2</sub> and  
298 other air pollutants (Hong Kong Environmental Protection Department 2014). The PMF-apportioned  
299 contributions of marine vessels to HULIS mass were 0.35 and 0.14 μg m<sup>-3</sup> on regional and local days, which  
300 accounted for 11.0% and 20.3% of HULIS mass under these two synoptic conditions, respectively.

301 Based on PMF results, we also calculated the source contributions to HULIS at the four sites in Hong  
302 Kong (Figure 3b). However, no significant difference was observed. Secondary formation was the leading  
303 source to HULIS at all four sites, followed by biomass burning and marine vessels. This finding is consistent  
304 with Kuang et al.(2015), which reported that the sources of HULIS in the PRD region were mainly regional,  
305 such as secondary formation and biomass burning. As such, small spatial variations of pollution sources  
306 contributing to HULIS within PRD was expected.

307

#### 308 **4. Conclusion**

309 HULIS in PM<sub>2.5</sub> samples collected at four different sites in Hong Kong during the summer of 2006  
310 were analyzed. It had a mean concentration of  $4.11 \pm 1.76 \mu\text{g m}^{-3}$  on the days under regional pollution ( $0.84$   
311  $- 7.25 \mu\text{g m}^{-3}$ ), which was about eight times higher than that on local days ( $0.56 \pm 0.30 \mu\text{g m}^{-3}$ ,  $0.16 - 1.25 \mu\text{g}$   
312  $\text{m}^{-3}$ ). Four sources of HULIS were resolved by PMF, which were secondary aerosol formation, marine vessels,  
313 biomass burning, and vehicle emissions. Simultaneous monitoring and analysis data from these four sampling  
314 sites showed that sources of HULIS in Hong Kong were mainly regional with no obvious spatial variation,  
315 which is similar to what was observed in the PRD region (Kuang et al. 2015). Secondary aerosol formation  
316 was the predominant contributor to HULIS (52.7%), followed by biomass burning (27.9%), marine vessels  
317 (17.4%), and vehicle emissions (2.1%). The high loadings of 1,2,3-Ben, 1,2,4-Ben, and NP+NC in biomass

318 burning factor implied that some HULIS might be produced during the aging process of biomass burning  
319 plume.

320

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442



**Table 1. Average concentrations of HULIS and individual species in HULIS fraction at four sites on regional and local days**

Average Concentration	Days Influenced by Regional Sources					Days Influenced by Local Sources				
	YL	TW	TC	HKUST	Four Sites (Min-Max)	YL	TW	TC	HKUST	Four Sites (Min-Max)
HULIS ( $\mu\text{g m}^{-3}$ )	4.76	3.32	4.89	3.75	4.11 (0.84 – 7.25)	0.67	0.67	0.38	0.49	0.56 (0.16 – 1.25)
HULIS_C/OC (%)	21.34	16.49	26.42	21.36	21.83 (11.84 – 35.72)	13.94	9.63	9.60	14.06	12.31 (5.61 – 27.69)
2-Hydroxybenzoic acid	1.20	1.16	1.34	1.13	1.21 (1.08 – 1.43)	1.08	1.09	1.30	1.08	1.13 (1.07 – 1.44)
3-Hydroxybenzoic acid	1.13	1.15	1.21	1.11	1.16 (1.06 – 1.25)	1.09	1.11	1.09	1.07	1.09 (1.06 – 1.15)
4-Hydroxybenzoic acid	1.08	1.21	1.39	1.10	1.22 (0.91 – 1.57)	0.97	1.04	0.96	0.94	0.97 (0.92 – 1.18)
Phthalic acid	9.44	7.84	11.92	8.20	9.45 (2.61 – 16.19)	2.74	2.87	2.79	2.50	2.70 (2.18 – 3.21)
Isophthalic acid	1.88	2.11	1.54	1.88	1.82 (0.69 – 2.48)	1.62	1.79	1.28	1.51	1.55 (0.21 – 1.87)
Terephthalic acid	11.09	6.51	8.83	9.19	8.56 (3.25 – 21.76)	3.26	3.33	1.61	2.38	2.69 (0.30 – 7.03)
1,2,3-Benzenetricarboxylic acid	12.45	13.02	12.84	10.96	12.23 (0.41 – 18.37)	1.18	1.57	0.53	0.43	0.90 (0.00 – 4.63)
1,2,4-Benzenetricarboxylic acid	12.98	12.49	12.06	11.88	12.18 (1.68 – 19.72)	6.07	9.04	1.29	1.89	4.44 (0.37 – 13.31)
1,3,5-Benzenetricarboxylic acid	2.49	2.42	2.41	2.53	2.46 (1.96 – 2.78)	2.38	2.40	2.34	2.34	2.36 (2.32 – 2.44)
Vanillic acid	0.43	0.50	0.52	0.59	0.53 (0.26 – 1.00)	0.32	0.33	0.28	0.15	0.26 (0.00 – 0.45)

Syringic acid	0.63	0.58	0.49	0.50	0.53 (0.00 – 1.07)	0.19	0.27	0.02	0.04	0.13 (0.00 – 0.69)
4-Nitrophenol	0.91	1.71	0.55	1.75	1.27 (0.46 – 3.42)	0.00	0.00	0.00	0.00	0.00 (0.00 – 0.00)
4-Nitrocatechol	0.87	3.20	0.78	2.79	2.05 (0.45 – 5.23)	0.00	0.00	0.00	0.00	0.00 (0.00 – 0.00)
Adipic acid	2.32	2.24	3.47	1.65	2.46 (1.31 – 4.11)	1.66	2.60	1.43	1.47	1.74 (1.26 – 3.89)
Pimelic acid	1.84	1.91	1.96	1.69	1.85 (1.54 – 2.06)	1.64	1.88	1.78	1.57	1.69 (1.54 – 2.07)
Azelaic acid	6.02	5.98	4.65	4.21	4.95 (2.70 – 7.27)	4.07	6.53	2.15	2.32	3.64 (0.00 – 11.86)

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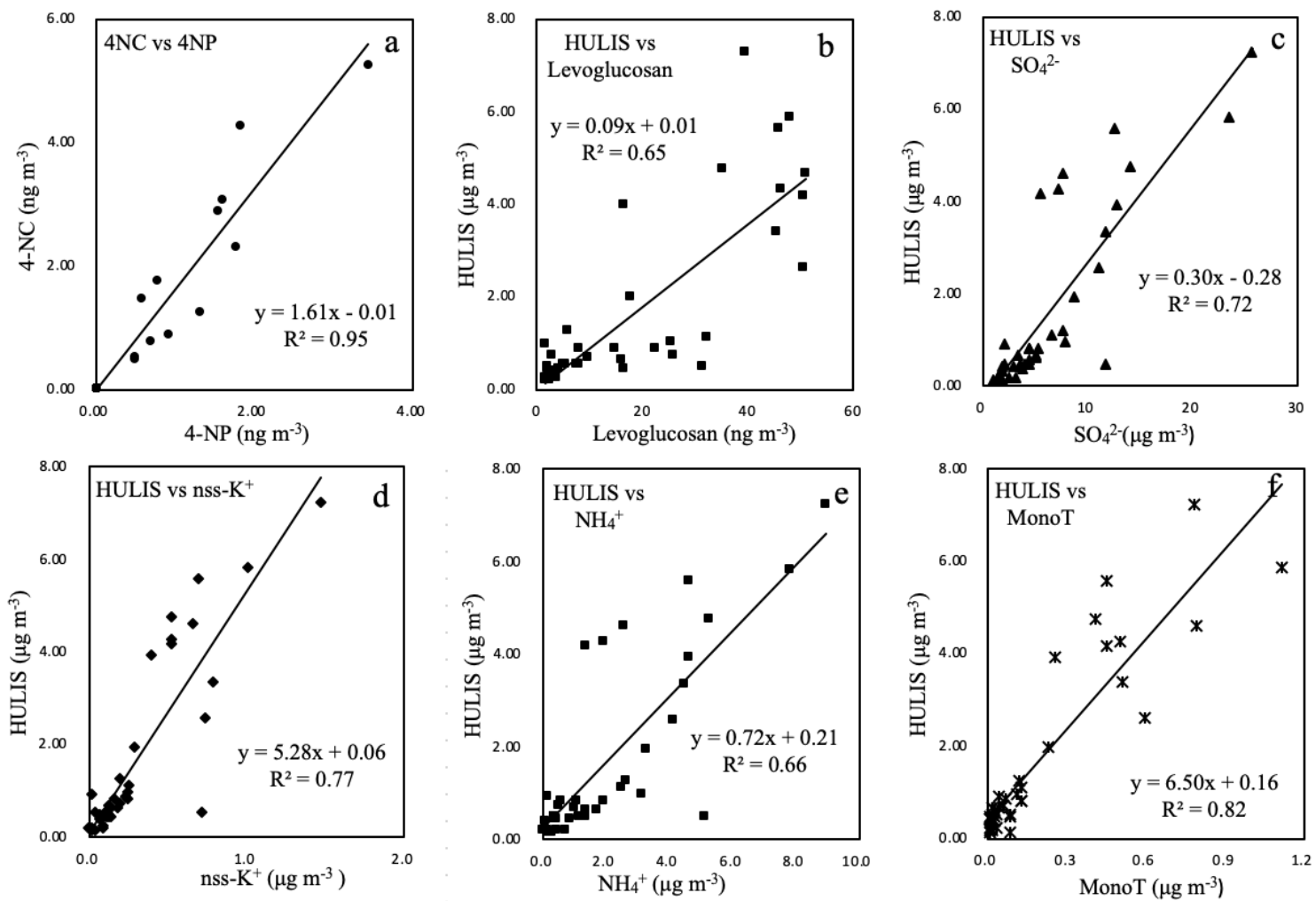


Figure 1. Correlations between species (a. 4NCvs 4NP; b. HULIS vs Levoglucosan; c. HULIS vs SO<sub>4</sub><sup>2-</sup>; d. HULIS vs nss-K<sup>+</sup>; e. HULIS vs NH<sub>4</sub><sup>+</sup>; f.

HULIS vs MonoT )

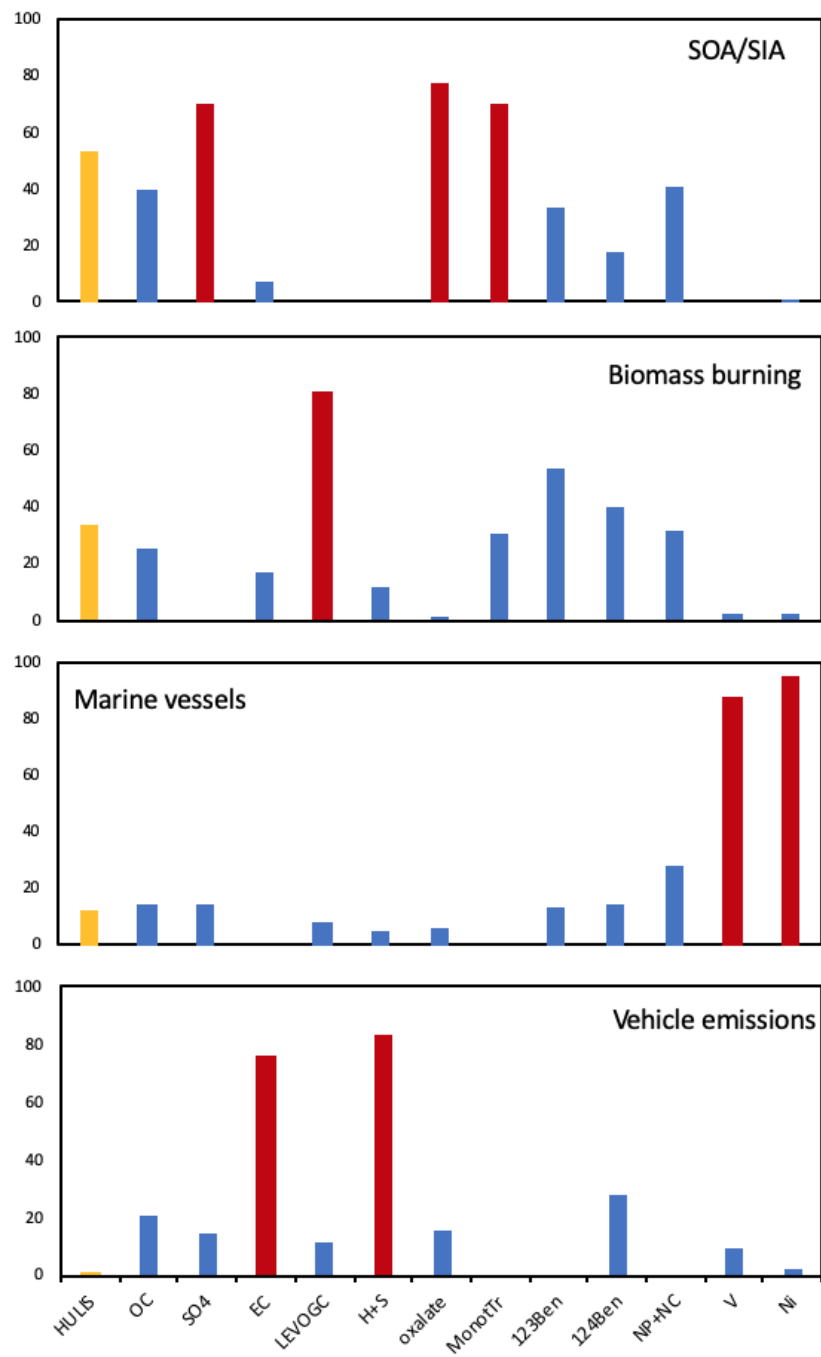
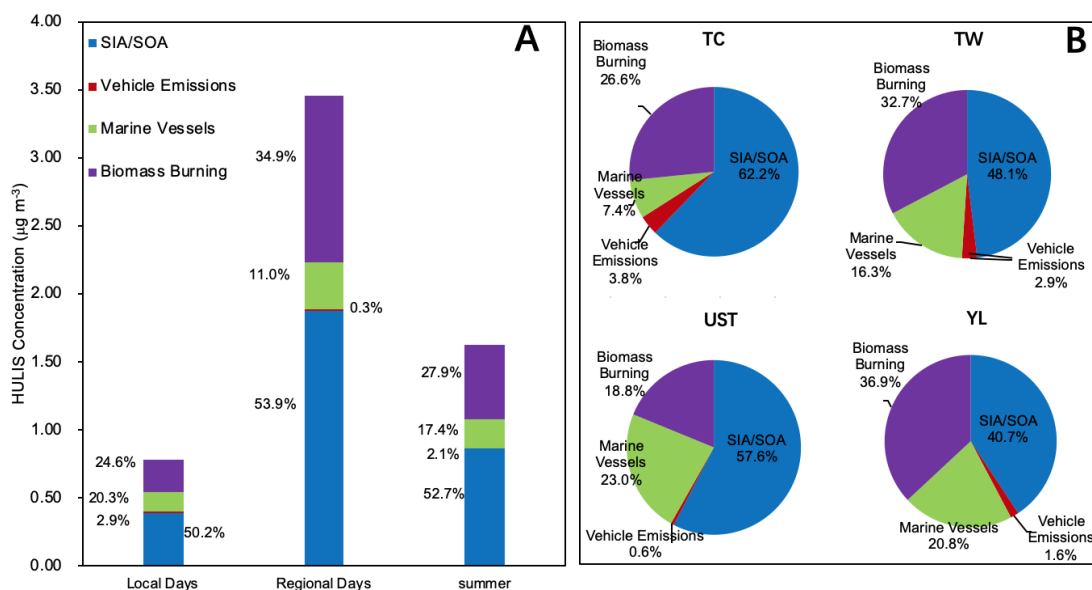


Figure 2. Distribution of species among the four factors resolved by PMF



**Figure 3. Source contributions to HULIS in Hong Kong during summer (a) on regional and local days, and (b) at four different sites.**