Point-by-point Response to Review Comments on

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

Reviewer #2:

It’s well known that the toxicity of PM$_{2.5}$ is greatly related to its chemical composition and pollution sources. This work analyzed PM$_{2.5}$ samples collected in Beijing during a one-year period, and the levels and oxidative potential (indicated by DTT) of a major water-soluble PM$_{2.5}$ component, i.e. water-soluble humic-like substances (HULIS$_{WS}$), were reported. With the aid of various characteristic source tracers, PMF was applied to apportion the major sources of both HULIS$_{WS}$ and its associated DTT activity. There are some new and interesting findings. The major sources of both HULIS$_{WS}$ and DTT activity were coal combustion, biomass burning, traffic exhaust, waste incineration, and secondary formation. Waste incineration was probably identified as a contributor to HULIS$_{WS}$ for the first time. Moreover, HULIS$_{WS}$ from vehicle emissions was found 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. This paper is well-written. The study is clear, informative, and novel in general, and the major data and their interpretation are scientifically sound. I suggest it to be considered by ACP for publication if the following concerns could be addressed.

Author Response: Thanks for the comments.

1. Line 22: Is it necessary to define the waste as “plastic waste”, as terephthalic acid is a marker of plastics?

Author Response: Since terephthalic acid is an important industrial material for making PET (polyethylene terephthalate) plastics, they have been found to be abundant in plastic burning smokes. In developing countries, plastic materials are dumped as domestic waste, which makes the waste plastic-enriched. In this case, terephthalic acid serves as a marker of plastic burning and plastic-enriched domestic waste burning. Therefore, we will keep the name of this factor as “waste incineration”.

2. Line 39-40: Add “an” before electron and “a” before continuous.

Author Response: This revision has been done.

In the revised manuscript, line 40-41 (in the manuscript file of "BJ HULIS_clear"; the same below): "The reversible redox sites in $HULIS_{WS}$ fraction could serve as an electron transfer intermediate and lead to continuous production of ROS (Lin and Yu, 2011)."

3. Line 71: If the samples were taken every 6 days for a one-year period, there should be 60 samples. Why there were 66 samples as listed in line 123?

Author Response: In winter time, we collected several additional samples during severe polluted periods.

In the revised manuscript, line 70-71, we've added "…with several additional samples collected during severe polluted periods".

4. Line 100: How many individual hopanes have been identified? I guess the input species "hopane" in PMF must be the sum of all identified hopanes, right? What are the concentrations of hopanes? What are the water-soluble ions identified? The author may need to include a table in the supplementary information that provide levels of hopanes, water-soluble ions, EC and OC in the batch of $PM_{2.5}$ samples analyzed.

Author Response: Five individual hopanes were identified, and these 5 hopanes were lumped together and put into PMF analysis. The concentrations of the measured hopanes, ions, EC and OC were listed in Table S1 in the revised supplementary material.

In the revised manuscript, line 103-104, we've added: "Concentrations of hopanes, levoglucosan, water-soluble ions, EC and OC were listed in Table S1 in the Supplementary Material."

5. Line 108: DTPA was spiked to chelate transition metals. Could it also affect or even remove some $HULIS_{WS}$ components?

Author Response: In the previous work by Lin and Yu (2011), they assessed the DTT consumption by 1) $HULIS_{WS}$ sample without DTPA; 2) $HULIS_{WS}$ samples with DTPA; and 3) standard mixture solution of metals with concentrations similar to those measured in $HULIS_{WS}$ fraction. They found that the DTT consumption by residue metals in the absence of DTPA is similar to the difference between DTT consumption by equivalent amount of $HULIS_{WS}$ in the absence and presence of DTPA. Their result suggested that the DTPA spiked to chelate transition metals could barely affect the $HULIS_{WS}$ components. Although Dou et al. (2015) found that DTPA could suppress the DTT response of quinone by about 20%, considering this method is widely accepted in $HULIS_{WS}$ redox activity measurement, we adopt the same method in order to be consistent and make comparison with other $HULIS_{WS}$ studies (Dou et al., 2015; Lin and Yu, 2011). In the revised version, we mentioned the DTT activity of $HULIS_{WS}$ measured was underestimated and could not be directly comparable with that does not use DTPA as metal chelators.

In the revised manuscript, line 126-128, we've added: "Since DTPA was added to suppress DTT consumption by metals ions throughout the incubation process and may affect the DTT response of quinones (Dou et al., 2015), the DTT activity of $HULIS_{WS}$ measured here may be underestimated and is not directly comparable to those studies conducting DTT assay experiments without DTPA."

6. Lines 130 to 131: Were all the reference data observed during a one-year period and comparable to present study?

Author Response: Data reported for Guangzhou and Nansha sites were the average concentration of samples collected during a one-year period (2009 January – 2009 December). For data measured in Lanzhou, they were the average concentration of samples collected during two representative periods (June-July in summer and December in winter during 2012-2013).

Reference:

Dou, J., Lin, P., Kuang, B., Yu, J.Z., 2015. Reactive oxygen species production mediated by humic-like substances in atmospheric aerosols: Enhancement effects by pyridine, imidazole, and their derivatives. Environ. Sci. Technol. 49, 6457–6465.

Lin, P., Yu, J.Z., 2011. Generation of reactive oxygen species mediated by Humic-like substances in atmospheric aerosols. Environ. Sci. Technol. 45, 10362–10368.

Reviewer #3:

1. This paper is of general interest. It provides insights on sources of DTT activity associated with organic species in Beijing.

Author Response: Thanks for the valuable comments.

2. There are, however, some major issues to address. First, the grammar is an issue; the paper needs editing.

Author Response: The paper has been carefully revised and the grammar issue has been addressed.

3. Secondly, unfortunately the authors apparently quantified DTT activities using a non-standard method, ie that of Li et al., 2009, which differs from the original DTT protocol described by Cho et al. (2005). The Cho method is widely utilized and is the basis for most DTT activities reported in the published literature. This means that the DTT activities reported here cannot necessarily be directly compared to generally published results, unless some type of conversion factor is given. This should be noted in the paper, discussed in detail (ie, difference in protocols explained), and optimally, a conversion factor given based on further experimental work by the authors.

Author Response: The major difference between the DTT protocol used by Cho et al. (2005) and Li et al. (2009) is that in Cho's method, at the designed incubation time, trichloroacetic acid was added to quench the reaction. However, Li et al. (2009) found the reaction between DTNB and DTT was very fast, so the absorption reached its maximum value immediately and were very stable for more than 2 hours. Thus, Li et al. (2009) modified Cho's method by eliminating the quenching step. Actually, many recent papers have adopted the modified DTT procedure developed by Li et al. (2009), such as Rattanavaraha et al. (2011), Janssen et al. (2014), Kramer et al. (2016), and Xiong et al. (2017). A few studies have examined the DTT activity of HULIS_{WS} (Dou et al., 2015; Lin and Yu, 2011), and they also used a DTT protocol based on Li et al.'s method (2009). Therefore, to let our results be directly comparable to those reported in previous studies, we followed the same protocol of DTT assay as described in Dou et al. (2015) and Lin and Yu (2011).

4. Finally, despite a large contribution, there really is no explanation or in depth discussion of why the secondary PMF factor contributes most to DTT activity in summer.

Author Response: This is mainly due to leading contribution (50.1%) of secondary aerosol formation to $HULIS_{WS}$ in summer. As we discussed in detail in the revised manuscript, line 257-269 (in the manuscript file of "BJ HULIS_clear"; the same below): "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}). "

We have also had more discussion on the contribution of secondary formation to DTT activity of $HULIS_{WS}$ in the revised manuscript, line 294-311: "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, β-pinene, and α-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."

Specific Comments:

5. Discuss possibility that DTPA not only reduces contributions of metals to DTT activity, but also additional species, such as quinones. Could this result in significant under-measurement of DTT activity in this work? What was the justification for wishing to remove metals contribution to DTT? Are they not part of HULIS, ie possibly as a part of a metal-OM complex?

Author Response: In this paper, we meant to measure the DTT activity of organic $HULIS_{WS}$. However, even after HLB separation, there are still a small amount of metal retained in the $HULIS_{WS}$ fraction (e.g. Cu: 17%, Fe: 10%, Zn: <5%; Lin and Yu, 2011). Based on previous studies, some metals (e.g. Cu) could cause considerable DTT consumption yet contribute negligibly to ROS generation, some (e.g. Fe) are inactive in DTT oxidation (Xiong et al., 2017), and some could form complex with DTT and cause false positive DTT activity (Kreel et al., 2001). So in the assessment of oxidative potential of organic compounds, many papers added EDTA as the metal chelator in the incubation solution at the beginning of DTT experiment to eliminate the influence of metals (Kramer et al., 2016; Rattanavaraha et al., 2011). However, Charrier et al. (2015) found EDTA could not only chelate metal but also significantly suppress the DTT response of quinone by ~80%, and this could lead to a large system error in DTT experiment. Besides EDTA, DTPA is another common metal chelator. Although DTPA could also suppress the DTT response of quinone by about 20% (Dou et al., 2015), in order to eliminate the influence of metals and decrease the system error in DTT assay, Lin and Yu, (2011) chose DTPA instead of EDTA as metal chelator. Moreover, considering this method is widely accepted in $HULIS_{WS}$ redox activity measurement, we adopt the same method in order to be consistent and make comparison with other $HULIS_{WS}$ studies (Dou et al., 2015; Lin and Yu, 2011; Wang et al., 2017). In the revised version, we mentioned the DTT activity of HULIS_{WS} measured was underestimated and could not be directly comparable with that does not use DTPA as metal chelators.

In the revised manuscript, line 126-128, we've added: "Since DTPA was added to suppress DTT consumption by metals ions throughout the incubation process and may affect the DTT response of quinones (Dou et al., 2015), the DTT activity of HULIS_{WS} measured here may be underestimated and is not directly comparable to those studies conducting DTT assay experiments without DTPA."

6. Lines 116 to 120. This paragraph is not clear. Why should DTT activity be proportional to HULISws concentration with this method. This was a finding reported in the results, but it appears from this paragraph that it simply results from the method used. Clarification is needed.

Author Response: Thanks for this comments. Yes, the result that DTT activity is proportional to HULIS_{WS} concentration is derived from the method we used. In our paper, the incubation time (90 min) of DTT assay fell into the linear time-dependent range. In another word, the catalytic reaction rate is constant, that is, the reaction is zero-order with respect to DTT (Lin and Yu, 2011). Thus, the catalytic DTT oxidation rate is proportional to the concentration of catalyst, that is, the abundance of DTT active moieties in HULIS_{WS}. In the results and discussion part, we meant to report the good correlation between HULIS_{WS} and DTT activity to further clarify that our measurement of DTT activity of HULIS_{WS} fell into the linear range. In order to eliminate misleading, we now modified our expression in the revised version.

In the revised manuscript, line 116-119, we also added: "Previous study observed that the time-dependent consumption of DTT catalysed by HULIS_{WS} was linear when DTT consumption was less than 90% (Lin and Yu, 2011). We have also examined the HULIS_{WS}-catalysed DTT consumption as a function of time and obtained a similar result as Lin and Yu (2011). In our study, the HULIS_{WS}-catalysed DTT consumption of all 66 samples were between 3.6% and 77.0%, and the measured DTT activity was linearly proportional to HULIS_{WS} mass concentration."

7. Somewhere explicitly define the difference between total HULIS, HULIS and HULIS- associated DTT. I assume HULIS-associated DTT is just the DTT activity of the HULIS sample? Sometimes, just the term HULIS is used, which adds to the confusion. Is this total HULIS? Consistency throughout the paper is needed. Suggest call it HULISws mass concentration and DTT activity of HULISws to distinguish the two.

Author Response: This is a nice suggestion. Total HULIS_{WS} and HULIS-associated DTT have been revised to HULISws mass concentration and DTT activity of HULISws in the revised version accordingly.

8. The PMF factors need clarification. Vehicle emissions apparently include POA (primary) and SOA from vehicle emissions, maybe this should be noted in the figs?

Author Response: It is true that both vehicle emissions and biomass burning factors contain $HULIS_{WS}$ secondarily formed from the aging process, and we've discussed them in the manuscript. As in the figure, we prefer to keep it unchanged.

9. Is secondary aerosol mainly biogenic SOA, or are there anthropogenic species contributing to it? If both, can they be separated?

Author Response: In Figure 3, we could see that some anthropogenic SOA markers (e.g. 1,2,3-benzenetricarboxylic acid and 1,2,4-benzenetricarboxylic acid) were also resolved in this secondary factor. So this factor is a mixed source of both biogenic and anthropogenic SOA. But we think it is probably dominated by biogenic SOA, and it is difficult to differentiate the biogenic SOA and anthropogenic SOA in this study due to the lack of appropriate anthropogenic SOA markers. Moreover, as we discussed in detail in the manuscript, some anthropogenic SOA in $HULIS_{WS}$, which were formed from the aging of biomass burning and vehicle emissions, were resolved in the biomass burning and vehicle factors instead of this secondary factor, and could not be accurately quantified again due to the lack of appropriate anthropogenic SOA markers.

10. Why is there little sulfate in coal combustion?

Author Response: Since most sulfate (~70%) was assigned to the secondary PMF factor, there is only little sulfate in coal combustion factor. Results from previous PMF analysis of Beijing $PM_{2.5}$ samples showed that secondary sulfate factor was always well separated from the coal combustion factor (e.g. Song et al. (2006); Yu et al. (2013); Zhang et al. (2013)), and our result is consistent with those from previous source apportionment studies.

11. Are there secondary species in biomass burning?

Author Response: Yes, small fractions of 4M5NC and 3M6NC were resolved in the biomass burning factor, which indicated that SOA from aging of biomass burning might also be resolved in this factor.

12. The discussion of possible reasons why DTT activities of the secondary factor are so high in summer needs more attention. Are the authors saying that biogenic SOA is the cause? There are papers that make this dubious claim (Kramer, A., W. Rattanavaraha, Z. Zhang, A. Gold, J. D. Surratt, and Y.-H. Lin (2016), Assessing the oxidative potential of isoprene-derived epoxides and secondary organic aerosol, Atmos. Env., 130, 211- 218.).

Author Response: Please refer to the above response to comment 4.

13. Given that most sulfate is in this factor (and surprisingly in contrast to the coal combustion factor), it seems that the factor is really all about oxidation processes (as the name for the factor implies). One explanation is that this factor really has contributions from all source, such as coal, vehicles, and even biomass burning, given the loss of levoglucosan through oxidation (although this source is lower in summer). Verma et al, 2015a noted the strong dependence of aging on enhanced quinone DTT activity. This factor may just represent this process. Despite significant discussion of the other factors, this factor is not considered sufficiently give the large role it plays in summer DTT activities, a major finding of the paper.

Author Response: Please refer to our response to comment 4.

14. Lines 271 and on. DTT per HULIS mass is reported. This is interesting, but also interesting would be DTT activities per OM. One could also expand the comparisons of these types of numbers from this study to the large list reported in a recent paper (Shiraiwa et al., 2017), Aerosol health effects from molecular to global scales, Envir. Sci Technol. , 51, 13545-13567). Make sure to note differences in DTT analytical methods when doing the comparison (eg, no metals in this work).

Author Response: In this paper, we only measured the DTT activity to HULIS$_{WS}$ fraction instead of the whole organic matter (OM). So it does not make much sense to normalize the DTT activity obtained in this study by the mass of OM. Our major objective is to explore the oxidative potential of HULIS$_{WS}$ in the atmosphere and make comparisons to the redox activity value of HULIS$_{WS}$ reported by previous studies. Since HULIS$_{WS}$ is just a fraction of OM, results obtained in this study are not comparable to those obtained on the OM or total PM$_{2.5}$ extract.

15. Regarding trash burning and DTT activities, also see: Vreeland, H., J. J. Schauer, A. G. Russell, J. D. Marshall, A. Fushimi, G. Jain, K. Sethuraman, S. N. Tripathi, and M. H. Bergin (2016), Chemical

characterization and toxicity of particulate matter emissions from roadside trash combustion in urban India, Atmos. Env., 147, 22-30.

Author Response: Thanks for this suggestion and we have read the paper carefully. The paper above did not mention the detailed DTT protocol they used. Considering they mentioned Cho's method, we assume they did not add metal chelators during the incubation process. However, when using water to extract $PM_{2.5}$ collected on quartz filters, not only WSOM but also water-soluble metals could be extracted. Therefore, the DTT activity reported by them was induced by both WSOM and metals. This makes it incomparable to our result.

Reference:

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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, ~~total~~ $HULIS_{WS}$ mass concentration, various $HULIS_{WS}$ species, and ~~$HULIS_{WS}$ associated~~ 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

~~Air pollution caused by ambient f~~Fine particulate matter ($PM_{2.5}$) pollution has caused both~~is a significant~~ environmental and public health problems worldwide. $PM_{2.5}$ can travel deep~~that carries various pollutants may be transported~~ into the human lung ~~respiratory~~ and ~~thus~~ lead to ~~myriad~~ various ~~health~~ respiratory diseases, such as respiratory tract infections, chronic cough, and asthma ~~effects~~ (Becker et al., 2005; Nel, 2005). Given the various sources and complex chemical composition of $PM_{2.5}$, the underlying m~~M~~echanisms of $PM_{2.5}$ exposure-induced adverse ~~these~~ health effects are ~~is~~not fully understood ~~up to date~~yet. H~~h~~owever, it has been postulated that~~perturbing the redox equilibrium through the generation of excessive reactive oxygen species (ROS) is considered as a fundamental way, which has been proposed to be related with the high redox-active components in $PM_{2.5}$.~~, the ~~high~~ redox-active components on $PM_{2.5}$, such as t~~T~~ransition 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. ~~are two such components with high oxidative potential (Charrier and Anastasio, 2012; Chung et al., 2006). More recently, another abundant water-soluble organic component, i.e. humic-like~~

~~substances (HULIS$_{\text{WS}}$), have also been recognized to be highly redox-active (Dou et al., 2015; Lin and Yu, 2011; Verma et al., 2015a).~~

Humic-like substances (HULIS$_{\text{WS}}$) are a mixture of compounds~~ that~~ containing polycyclic ring structures with aliphatic side chains and multiple polar functional groups. They account for~~, and~~ 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$_{\text{WS}}$ have~~ also~~ recently been recognized to be highly redox-active and they play a significant role in driving PM-associated ROS formation (Dou et al., 2015; Lin and Yu, 2011; Verma et al., 2015a). The reversible redox sites in HULIS$_{\text{WS}}$ fraction could serve as an electron transfer intermediate~~ry~~ and lead to continuous production of ROS (Lin and Yu, 2011).~~ Actually, many recent studies have reported the significant role of HULIS$_{\text{WS}}$ in driving PM-associated ROS formation (Dou et al., 2015; Lin and Yu, 2011; Verma et al., 2015a).~~ Dithiothreitol (DTT) assay have been widely used~~is frequently applied~~ to evaluate the oxidative ~~potential ~~capacity of HULIS$_{\text{WS}}$ and PM$_{2.5}$~~ components~~.~~, especially for organic compounds (Xiong et al., 2017). By adopting this method,~~ Verma et al. (2015b) found that HULIS$_{\text{WS}}$ contributed~~aused~~ approximately 45% of DTT activity of the water extracts from PM$_{2.5}$ samples collected~~d~~ in Atlanta, USA,~~. Th~~ which~~is~~ was 5% higher than that induced by water-soluble metals~~ (Verma et al., 2015b)~~. Lin and Yu (2011) also ~~Furthermore,~~found that~~e DTT activity of~~ HULIS$_{\text{WS}}$ accounted for~~is~~ ~~about ~~79%±12% of DTT activity caused by~~the whole~~ WSOM fraction in PM$_{2.5}$ sampled~~s~~ in Pearl River Delta (PRD) region, China~~ (Lin and Yu, 2011)~~. G~~, suggesting a substantial health threat induced by HULIS$_{\text{WS}}$. Thus, g~~iven the considerable amount of HULIS$_{\text{WS}}$ in PM$_{2.5}$ and their ~~high ~~ROS generation ability, both field measurements and smog chamber experiments have been conducted to determine their formation ~~mechanisms~~ pathways and ~~atmospheric ~~origins in the atmosphere (Kautzman et al., 2010; Lin et al., 2010b; Sato et al., 2012). Biomass burning and secondary formation have been suggested to be the major sources of atmospheric HULIS$_{\text{WS}}$ (Kautzman et al., 2010; Lin et al., 2010b). However, ~~until now, ~~studies on the quantitative source apportionment of HULIS$_{\text{WS}}$ ~~remain relatively rare~~are still limited (Kuang et al., 2015), and information on the source-specific contribution to their redox activity is lacking.

Beijing, the capital of China located in the North China Plain, is a political and cultural center with an extremely dense~~ly~~ population. 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 m^{-3} in 2013 (Li et al., 2017). Therefore, it presents an ideal location to study the chemical characteristics of HULIS$_{\text{WS}}$ as well as their sources and potential redox activity.

In this study, our major objective is to investigate the ROS-forming ability of HULIS$_{\text{WS}}$ in relation to different sources and meteorological conditions. Thus, a total of 66 PM$_{2.5}$ samples collected in Beijing during a 1-year period were analyzed. Concentrations of total HULIS$_{\text{WS}}$ were quantified, together with some characteristic individual HULIS$_{\text{WS}}$ species and the major aerosol components. ~~HULIS$_{\text{WS}}$-associated~~The redox activity of HULIS$_{\text{WS}}$ was~~ also~~ determined using a DTT assay. Positive matrix factorization (PMF) analysis was ~~applied ~~conducted to determine the sources of both HULIS$_{\text{WS}}$ and their associated redox activity. Such a comprehensive source apportionment study of HULIS$_{\text{WS}}$-related ROS-generation potential has not been previously reported. Results from this study could provide not only quantitative information regarding the sources and toxicity of HULIS$_{\text{WS}}$, but also a deeper understanding of the source-specific oxidative potential of Chinese urban organic aerosols in general. This may be useful for the future development of source-targeted air pollution control policies in Beijing and may provide public-health benefits.

2 Material and methods

2.1 Sample collection

PM$_{2.5}$ samples were collected at the Peking University Atmosphere Environment Monitoring Station (PKUERS) on the campus of Peking University (39°59'21"N, 116°18'25'E, approximately 30 m above the ground), Beijing, China. A high-volume air sampler coupled with a ≤2.5 μm inlet (HIVOL-CABLD, ThermoFisher Scientific, Waltham, MA, USA) was used to conduct sampling at 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, 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 was operated synchronously (16.7 L min^{-1}, TH-16A, Wuhan Tianhong Instruments Co. Ltd, China) to collect PM$_{2.5}$ onto three 47-mm Teflon filters and one quartz fiber filter for the determination of PM$_{2.5}$ mass, elemental carbon (EC) and organic carbon (OC), and inorganic ionic species.

2.2 Chemical analysis

HULIS$_{\text{WS}}$ 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 ~~individual~~ HULIS$_{\text{WS}}$ species identification and 3 cm^2 for ~~total~~ HULIS$_{\text{WS}}$ 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$_{\text{WS}}$. 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$_{\text{WS}}$ 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 ~~spectroscopy~~ spectrometry (GC-MS; 5975-7890A, Agilent, Santa Clara, CA, USA) analysis. Detailed information on this analysis is provided in the Supplementary Material.

For the ~~analysis~~ quantification of ~~total~~ HULIS$_{\text{WS}}$ mass concentration, 6.0 mL of pure methanol was used to elute HULIS$_{\text{WS}}$ from HLB cartridge instead of 1.5 mL of basic methanol (2% ammonia, w/w). This ~~was~~ is ~~replaced by 6.0 mL of pure methanol in SPE step~~ to avoid possible influence of ammonia in the following DTT experiments (Lin and Yu, 2011), and ~~. The~~ larger ~~amount~~ volume of ~~solvent~~ methanol was used to maintain the elution efficiency (Lin and Yu, 2011). ~~Detailed information for the GC-MS quantification~~Comparison on the GC-MS peak intensities~~y~~ of individual HULS$_{\text{WS}}$ 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$_{\text{WS}}$ instead of HULIS$_{\text{WS}}$_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 t~~T~~he procedure of ~~the DTT assay follows that used by~~ Li et al. (2009) and Lin and Yu (2011) for DTT experiments. 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. Finally, the absorbances of the reacted sample solutions were measured at 412 nm within 30 min using an ultraviolet-visible (UV-Vis) spectrophotometer (8453, Hewlett Pakard, Palo Alto, CA, USA). Considering that some transition metals may still remain~~ed~~ in the $HULIS_{WS}$ fraction even after HLB purification, sufficient amount of DTPA was added in the procedure to chelate all the remaining transition metals, such as Cu, Mn, and Fe, to eliminate the ~~redox-activity~~DTT consumption ~~induced~~ by these metals (Lin and Yu, 2011). For the control samples, blank filters were used instead of real samples.

~~Based on p~~Previous study observed that~~experiments,~~ the time-dependent consumption of DTT catalysed by $HULIS_{WS}$ wa~~i~~s linear when DTT consumption wa~~i~~s less than 90% (Lin and Yu, 2011). We have also examined the $HULIS_{WS}$-catalysed DTT consumption as a function of time and obtained~~In this study, verification experiments were also performed with~~ a similar result as Lin and Yu (2011). In our study, ~~Give that~~ the $HULIS_{WS}$-catalysed DTT consumption ~~rates for~~ of all ~~the~~ 66 samples ~~in this study were~~ were between 3.6% and 77.0%, and the measured DTT activity was~~is~~ linearly proportional~~ly related~~ to $HULIS_{WS}$ mass concentration.

The $HULIS_{WS}$-catalysed DTT consumption of each sample was normalized by the volume of air sampled (DTT_V, defined as 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 and expressed in units of mol min^{-1} per μg $HULIS_{WS}$) (Dou et al., 2015; Verma et al., 2014), respectively. The mathematical expressions of DTT_V and DTT_m are shown below.

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

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

Since DTPA was added to suppress DTT consumption by metals ions throughout the incubation process and may affect the DTT response of quinones (Dou et al., 2015), the DTT activity of $HULIS_{WS}$ measured here may be underestimated and is not directly comparable to those studies conducting DTT assay experiments without DTPA.

2.4 Source apportionment

In this study, the United States Environmental Protection Agency PMF 5.0 was applied to identify ~~and apportion~~ the sources of ~~both~~ $HULIS_{WS}$ and apportion their contributions to both $HULIS_{WS}$ and ~~$HULIS_{WS}$-associated~~ the extrinsic ~~redox~~ DTT activity of $HULIS_{WS}$. As suggested by Henry et al. (1984), 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 and 13 species were included in PMF analysis, which was an adequate sample size to obtain a statistically reliable PMF result. Details of PMF parameter settings are provided in the Supplementary Material.

3 Results and discussion

3.1 ~~Total~~ HULIS$_{WS}$ mass concentration and ~~HULIS$_{WS}$-associated~~the DTT activity of HULIS$_{WS}$

In this study, the ~~concentrations of total~~ HULIS$_{WS}$ mass concentration and ~~HULIS$_{WS}$-associated~~ DTT activity of HULIS$_{WS}$ in 66 PM$_{2.5}$ samples were quantified. The annual 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 m^{-3}). This was approximately 20% higher than those measured in three other Chinese cities: 4.83 μg m^{-3} in Guangzhou (Kuang et 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 of ~~total~~ HULIS$_{WS}$ mass concentration was observed (Figures 1, 2), with significantly higher levels ($p < 0.05$, Mann–Whitney test) in the heating season (November through March; average 7.93, median 6.15 μg m^{-3}) than in the non-heating season (April through October; average 3.72, median 2.86 μg m^{-3}). This could be mostly attributed to the intensive coal and biomass burning activities performed for residential heating during the heating season. In addition, the lower temperatures and mixing height~~s~~ during the heating season could also ~~favor~~favour the formation of particle-bound HULIS$_{WS}$ species. However, the contributions of total HULIS$_{WS}$ to organic matter (OM, calculated by ~~OC~~ multiplying OC with ~~the ratio of~~ 1.98 and 1.50 for the heating and non-heating seasons, respectively, 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 (27.4% ± 12.0%, Figure 1), indicating higher levels of ~~other~~ combustion-generated organic compounds other than HULIS$_{WS}$ were emitted in the heating seasons ~~other than HULIS$_{WS}$~~as well.

~~For HULIS$_{WS}$-associated~~ The extrinsic DTT activity of HULIS$_{WS}$~~, they~~ exhibited similar temporal variation as HULIS$_{WS}$ (Figure 2), with significantly higher 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 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 the HULIS$_{WS}$ effluent were chelated by DTPA, the DTT activity measured here could be attributed entirely to the DTT active moieties in HULIS$_{WS}$. T~~o further investigate the~~ intrinsic ~~ROS-generation ability~~DTT activity of HULIS$_{WS}$~~, the DTT consumption rate was normalized~~ describes the intrinsic ROS-generation ability of HULIS$_{WS}$, ~~for HULIS$_{WS}$ mass (DTT$_m$, expressed in units of pmol min^{-1} per μg HULIS$_{WS}$ (Verma et al. 2014). T~~and the 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 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~~of~~ six PM$_{2.5}$ samples collected during winter in Guangdong, China (Dou et al., 2015). This difference might be attributed to the different chemical components and sources of HULIS$_{WS}$ in these two regions.

~~In fact, a strong correlation between total HULIS$_{WS}$ and HULIS$_{WS}$-associated DTT activity was observed (R^2 = 0.78).~~

3.2 Individual species of HULIS$_{WS}$

Because the main objective of this study was to identify the sources of HULIS$_{WS}$ and quantify the source-specific contributions to both HULIS$_{WS}$ and their associated redox activity, we mainly focused on the identification of organic markers in the chemical analysis. A total of 25 species were identified and quantified in the HULIS$_{WS}$ fraction of PM$_{2.5}$ ~~through~~ using GC-MS, including 12 aromatic acids, five nitrophenol analogues, three aliphatic acids, and five biogenic secondary organic aerosol (SOA) tracers (Table S2~~1~~ in the Supplementary Material, Hu et al., 2008)

All 12 aromatic acids, including three hydroxyl benzoic acids, three benzenedicarboxylic acids, three benzenetricarboxylic acids, 2-hydroxy-5-nitrobenzoic acid, vanillic acid, and syringic acid, exhibited higher levels during the heating season than during the non-heating season (Figure S2 in the Supplementary Material). Among these acids, terephthalic acid (TPha) was the most abundant (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 ~~total~~ HULIS$_{WS}$ mass concentration. Compared with other Chinese cities, the concentration of TPha in Beijing was substantially higher 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 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 polyethyleneterephthalate (PET) plastics, which are widely used for bottles and containers; therefore, it has been suggested as a tracer for the pyrolysis of domestic waste (Kawamura and Pavuluri, 2010; Simoneit et al., 2005). ~~Meanwhile,~~ ~~b~~Benzenetricarboxylic acids were considered to be secondarily formed from the photodegradation of organic precursors, such as polycyclic aromatic hydrocarbons (PAHs) (Kautzman et al., 2010). Therefore, 1,2,3-benzenetricarboxylic acid (123Ben) and 1,2,4-benzenetricarboxylic acid (124Ben) were also included in the PMF analysis.

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

Five biogenic SOA tracers including 3-hydroxyglutaric acid, 3-hydroxy-4,4-dimethylglutaric acid, 3-methyl-1,2,3-butanetricarboxylic acid, 3-isopropylglutaric acid, and 3-acetylglutaric acid were identified and quantified. Because they were all formed from the atmospheric oxidation of monoterpenes and had similar temporal variations, they were grouped as SOA markers of monoterpenes (MonoT) in the PMF analysis (Hu et al., 2010). Briefly, MonoT showed higher concentrations during the non-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 opposite to~~ that of total~~ HULIS$_{WS}$ mass concentration. Because of the higher biogenic volatile organic compounds (VOCs) emissions, more intense solar radiation, and higher temperature and humidity in the non-heating season, more active secondary formation could lead to higher concentrations of biogenic SOA (Guo et al., 2012).

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

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

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 attributed to coal combustion (Tan et al., 2016; Tao et al., 2016; Zhang et al., 2013). Factor B had a high loading of levoglucosan and was determined as biomass burning (Hu et al., 2010; Tao et al., 2016). Factor C was considered to be waste incineration, due to the high level of TPha. Factor D was dominated by hopanes, tracers for fuel combustion, suggesting traffic related activities (Hu et al., 2010). In particular, the two anthropogenic SOA markers, 4M5NC and 3M6NC, were mostly assigned to this factor (4M5NC 46%, and 3M6NC 33%) instead of factor C (4M5NC 14%, and 3M6NC 25%). These two species were mainly formed through the photo-oxidation of cresols, which were directly emitted through wood combustion or produced from toluene through its reaction with OH radicals in the presence of NO_X (Iinuma et al., 2010). Traffic emissions were a significant source of~~for~~ single-ring aromatics, especially toluene, in Chinese megacities (Huang et al., 2015). In this study, the sampling site was located in an urban area influenced by considerable vehicular emissions of NO_X and toluene, which may have led to subsequent secondary formation of 4M5NC and 3M6NC. Therefore, the fourth factor was considered as a mixed source including both primary emission and the aging process of traffic exhaust. The fifth factor was characterized by a predominant loading of MonoT, SO_4^{2-}, and NH_4^+; thus, it was considered as a secondary aerosol formation source.

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

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

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~~ total~~ 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~~ of~~ 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~~ and other HULIS$_{WS}$ compounds~~ 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 ~~polycyclic aromatic compounds~~PAHs were ~~favorably~~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 ~~total ~~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 ~~favors~~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 ~~the ~~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 ($p < 0.0$~~0~~1; Table S3~~2~~ 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$_{WS\text{-}SEC}$). Sulfate was found to be the most significant factor with a regression coefficient of 0.066 (Table S4~~3~~ 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 ~~HULIS$_{WS}$-associated~~extrinsic DTT activity of HULIS$_{WS}$ were assessed using PMF~~ result~~. 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, ~~Similar to the source apportionment results of HULIS$_{WS}$, biomass burning was identified as the major contributor to HULIS$_{WS}$-associated DTT activity in the heating season, and secondary formation was the most important source in the non-heating season (Figure 4B).~~ the four combustion-related sources accounted for 75% of ~~HULIS$_{WS}$-associated~~the extrinsic DTT~~redox~~ 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. ~~Furthermore, t~~The intrinsic DTT activities of the HULIS$_{WS}$ from the five identified sources were ~~derived~~calculated (E.q.(2)). HULIS$_{WS}$ from vehicle emissions ~~constituted~~ was found to be the most DTT~~ROS~~-active ~~HULIS$_{WS}$, with a maximum activity of~~ (12.0 pmol min^{-1} per μg HULIS$_{WS\_VE}$), followed by waste incineration (9.25 pmol min^{-1} per μg

HULIS$_{\mathrm{WS\_WI}}$), biomass burning (9.10 pmol min^{-1} per μg HULIS$_{\mathrm{WS\_BB}}$), secondary formation (7.45 pmol min^{-1} per μg HULIS$_{\mathrm{WS\_SEC}}$), and coal combustion (6.22 pmol min^{-1} per μg HULIS$_{\mathrm{WS\_CC}}$).

Similar to the source apportionment results of HULIS$_{\mathrm{WS}}$, biomass burning was identified as the ~~major~~ leading contributor to extrinsic ~~HULIS$_{\mathrm{WS}}$-associated~~ DTT activity of HULIS$_{\mathrm{WS}}$ in the heating season (39.4%, 0.015 nmol min^{-1} m^{-3}), and throughout the year~~secondary formation was the most important source in the non-heating season~~ (33.6%, 0.017 nmol min^{-1} m^{-3}~~Figure 4B~~). 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)~~. Those compounds, such as quinones and hydroxyquinones,~~, which could be extracted into the HULIS$_{\mathrm{WS}}$ fraction and lead to DTT consumption (Chung et al., 2006; Verma et al., 2015a). ~~Additionally~~Moreover, Wang et al. (2017) found large amounts of nitrogen-containing organic compounds (NOCs) including nitroaromatics and nitrogen-containing bases in HULIS$_{\mathrm{WS}}$ 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 ~~as reported by Dou et al. (2015) the~~ nitrogen-containing ~~alkaloids~~ bases emitted from biomass burning could also enhance the ROS-generation ability of HULIS$_{\mathrm{WS\_BB}}$ (Dou et al., 2015), which may explain the observed intrinsic DTT activity of HULIS$_{\mathrm{WS\_BB}}$.

Secondary formation was the most important source for the extrinsic DTT activity of HULIS$_{\mathrm{WS}}$ 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$_{\mathrm{WS\_SEC}}$ measured in this study is 7.45 pmol min^{-1} per μg HULIS$_{\mathrm{WS\_SEC}}$, 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$_{\mathrm{WS\_SEC}}$ (Table S4), suggesting that HULIS$_{\mathrm{WS}}$ 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$_{\mathrm{WS\_SEC}}$. However, since secondary formation predominated in HULIS$_{\mathrm{WS}}$ 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$_{\mathrm{WS}}$-associated redox activity in Beijing. It should be noted that the contributions of secondary formation processes to both HULIS$_{\mathrm{WS}}$ and DTT activity of HULIS$_{\mathrm{WS}}$ could even have been underestimated in this study, because HULIS$_{\mathrm{WS}}$ 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$_{\mathrm{WS}}$ throughout the year (18.5%, 0.009 nmol min^{-1} m^{-3}), HULIS$_{\mathrm{WS\_VE}}$ has the highest intrinsic DTT activity among all sources (12.0 pmol min^{-1} per μg HULIS$_{\mathrm{WS\_VE}}$). ~~To further investigate the intrinsic ROS-generation ability of HULIS$_{\mathrm{WS}}$, the DTT consumption rate was normalized for HULIS$_{\mathrm{WS}}$ mass (DTT$_{\mathrm{m}}$, expressed in units of pmol min^{-1} per μg HULIS$_{\mathrm{WS}}$ (Verma et al. 2014). The average intrinsic DTT activity of HULIS$_{\mathrm{WS}}$ in Beijing was 9.91 pmol min^{-1} per μg HULIS$_{\mathrm{WS}}$ (median 9.02, range 2.74–25.8 pmol min^{-1} per μg HULIS$_{\mathrm{WS}}$), which was higher than the reported average DTT$_{\mathrm{m}}$ activity (6.4 ± 1.2 pmol min^{-1} per μg HULIS$_{\mathrm{WS}}$) of six PM$_{2.5}$ samples collected~~

~~during winter in Guangdong, China (Dou et al., 2015). This difference might be attributed to the different chemical components and sources of HULIS$_{WS}$ in these two regions.~~

~~Furthermore, the intrinsic DTT activities of the HULIS$_{WS}$ from the five sources were derived. HULIS$_{WS}$ from vehicle emissions constituted the most ROS-active HULIS$_{WS}$, with a maximum activity of 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$_{WS\_CC}$).~~ Similarly, Bates et al. (2015) revealed that the water-soluble PM$_{2.5}$ ~~(WS-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). ~~In the present study, vehicle emission was found to be the highest redox-active source for HULIS$_{WS}$, a large fraction of WS-PM$_{2.5}$. However, because the remaining water-soluble metals in HULIS$_{WS}$ were chelated through DPTA, the high intrinsic ROS activity of HULIS$_{WS\_VE}$ is believed to be mostly due to the highly oxygenated OC content in HULIS$_{WS\_VE}$.~~

Waste incineration was also an~~other~~ important primary source of the extrinsic ~~HULIS$_{WS}$-related~~ 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 ~~even~~ 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.

~~Although HULIS$_{WS\_SEC}$ was less DTT-active than HULIS$_{WS\_VE}$, HULIS$_{WS\_WI}$, or HULIS$_{WS\_BB}$, secondary aerosol formation served as the second largest contributor (25.3%) to HULIS$_{WS}$-associated redox activity throughout the year. Higher levels of DTT activity mediated by HULIS$_{WS\_SEC}$ were observed in the non-heating season (0.015 nmol min^{-1} m^{-3}) than in the heating season (0.011 nmol min^{-1} m^{-3}), accounting for 44.1% and 14.5% of HULIS$_{WS}$ DTT activity in each season, respectively. The relatively low intrinsic DTT activity of HULIS$_{WS\_SEC}$ may be mostly attributed to its abundance of biogenic SOA components such as organosulfates and organonitrates (Chen et al., 2011), which were found to have negligible ROS-generating ability (Kramer et al., 2016). 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$_{WS\_SEC}$.~~

In summary, four combustion-related sources and one secondary formation source of PM$_{2.5}$-bound HULIS$_{WS}$ and their associated ROS ~~potential~~ activity were identified by PMF ~~in this study~~. 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$_{\mathrm{WS}}$ from vehicle emissions was identified as the most ROS-active, and HULIS$_{\mathrm{WS}}$ 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$_{\mathrm{WS}}$ from different sources will be relevant for future inquiries into more detailed chemical speciation of HULIS$_{\mathrm{WS}}$, 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~~3~~ and Figure S1-S7 are provided.

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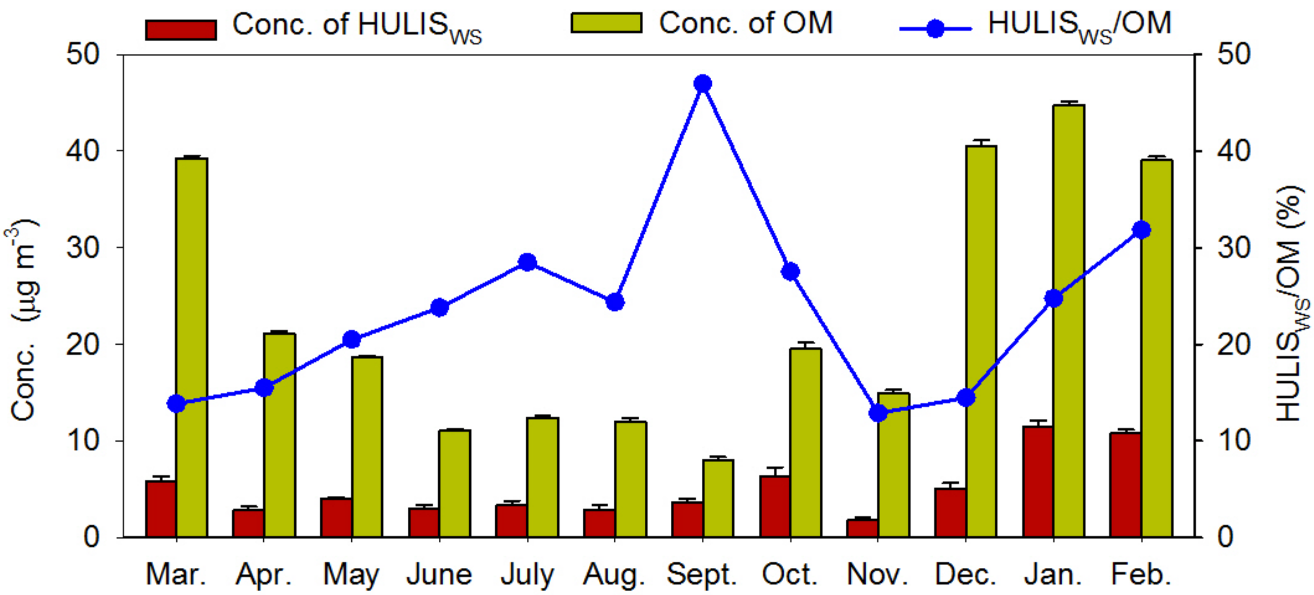
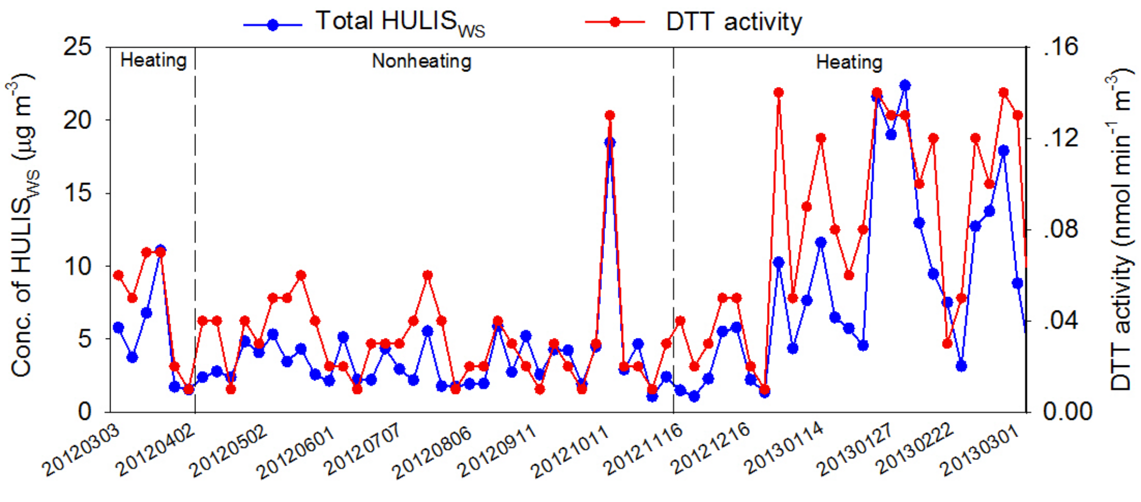


Figure 1: Monthly average concentrations (average ± standard error) of ~~total~~ $HULIS_{WS}$ mass concentration and organic matter (OM) in $PM_{2.5}$ collected in Beijing. The monthly percentage contributions of $HULIS_{WS}$ to OM are shown in the blue line.



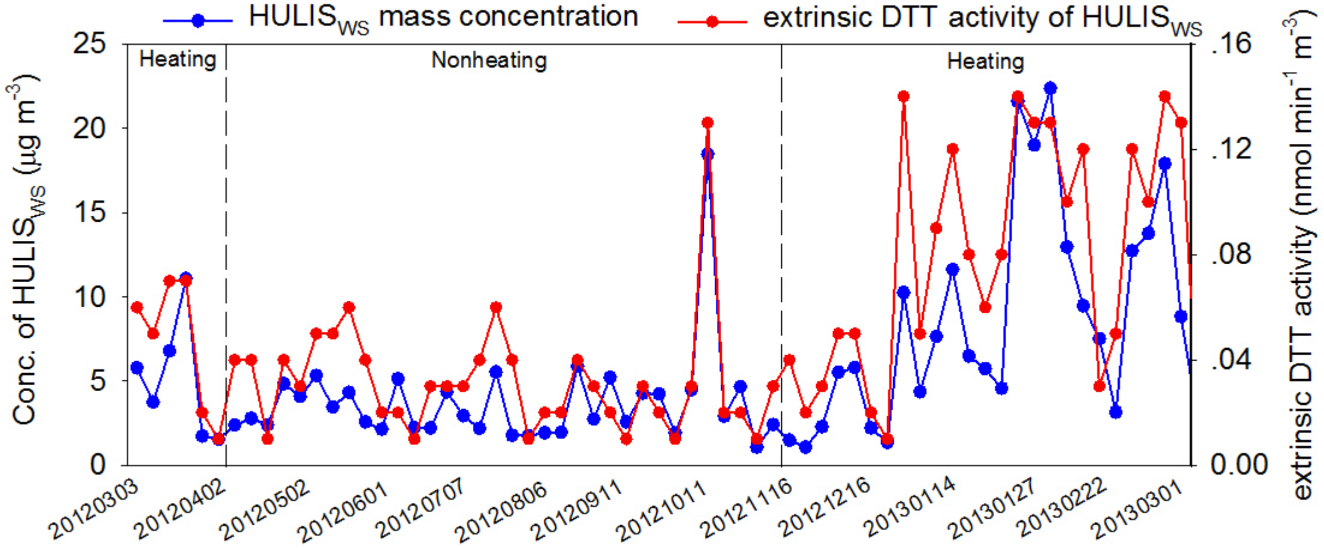
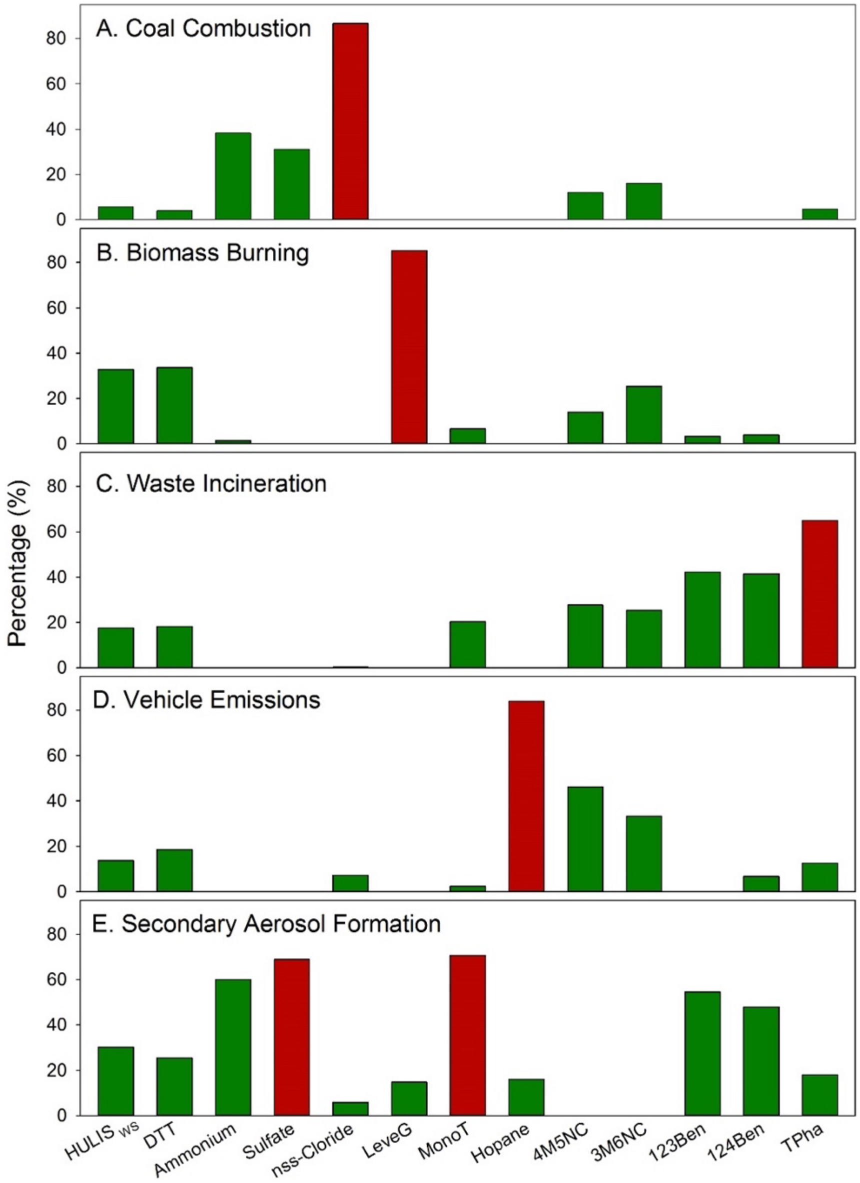


Figure 2: Temporal variation of ~~total~~ HULIS$_{WS}$ mass concentration and ~~associated~~ extrinsic DTT activity of HULIS$_{WS}$ in Beijing.



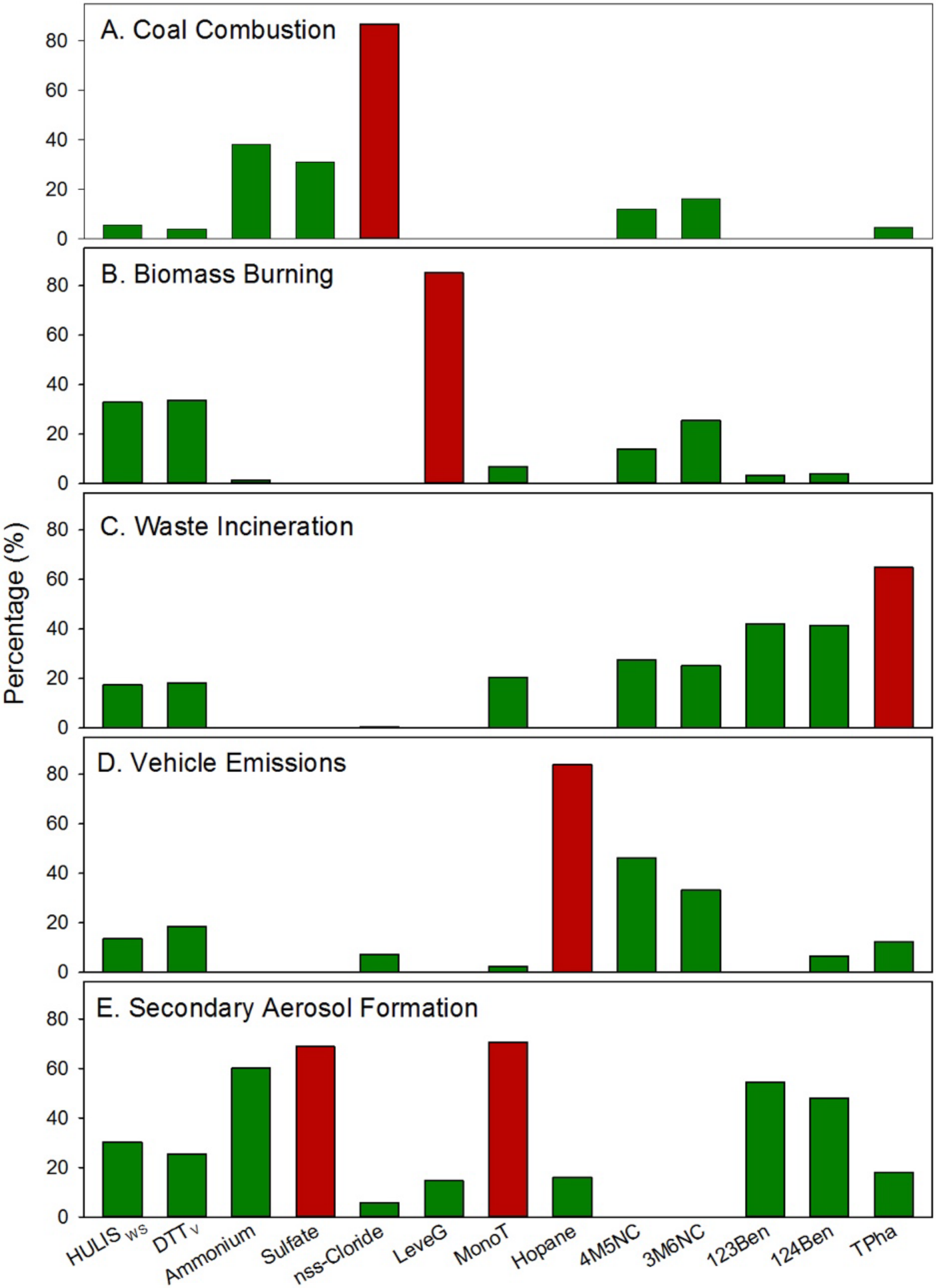
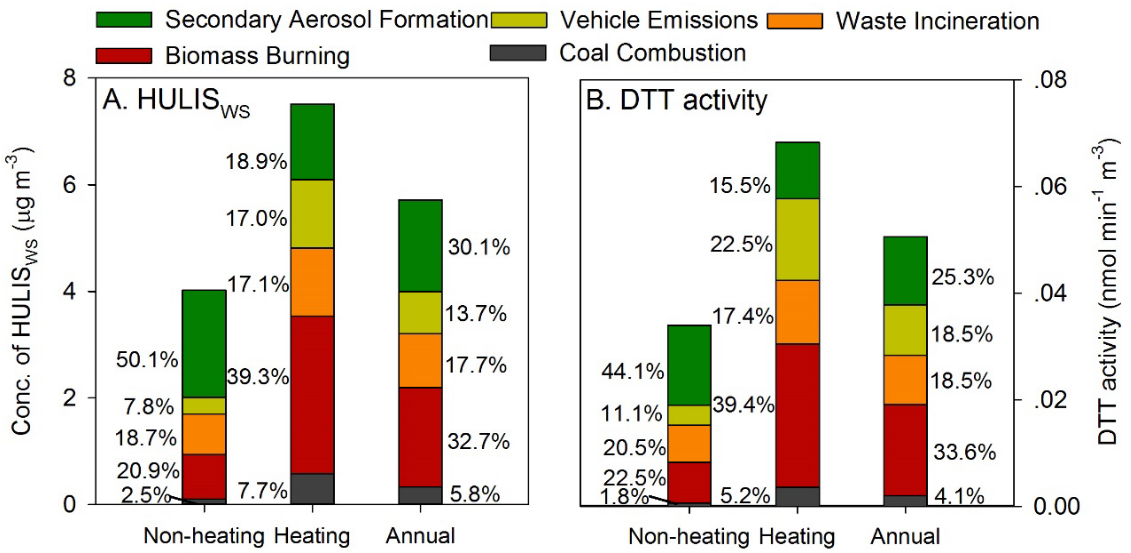


Figure 3: Distribution of HULIS$_{WS}$, HULIS$_{WS}$-associated DTT activity and other measured species in the five sources resolved by PMF. Columns in dark red indicate characteristic tracers of each source.



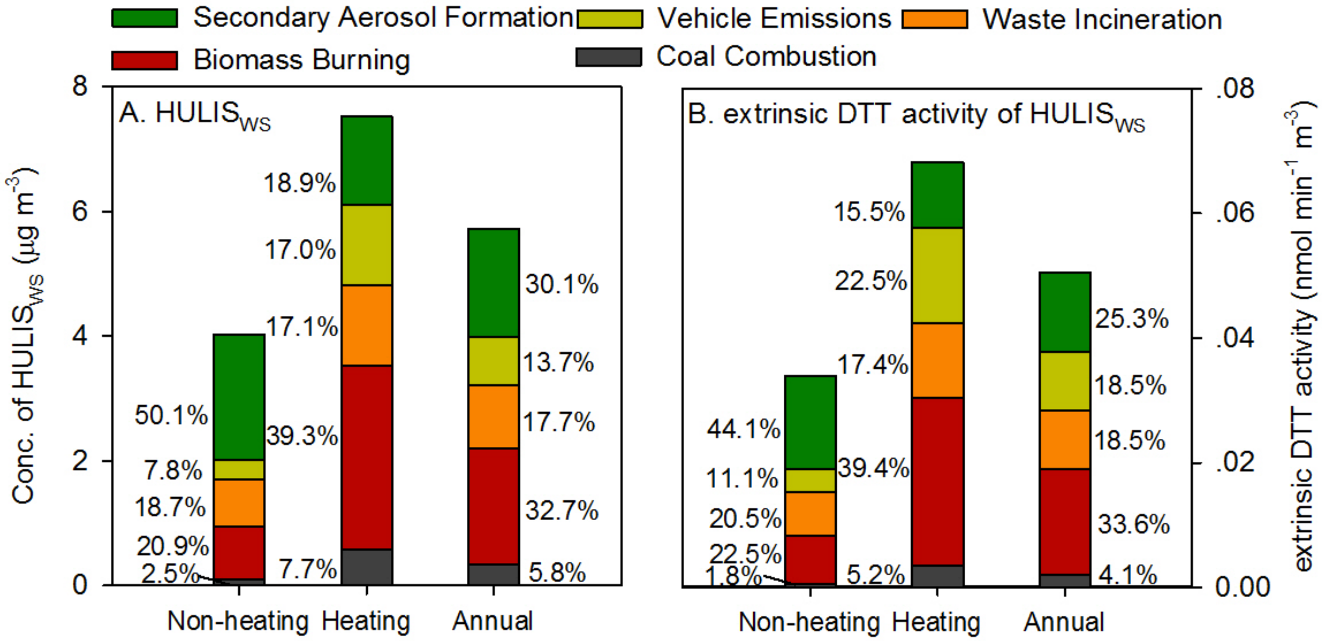


Figure 4: Source-specific contributions to ~~total~~ HULIS$_{WS}$ mass concentration (panel A) and ~~HULISWS-associated~~extrinsic DTT activity of HULIS$_{WS}$ (panel B).