

Interactive comment on “Sources and oxidative potential of water-soluble humic-like substances (HULIS_{WS}) in fine particulate matter (PM_{2.5}) in Beijing” by Yiqiu Ma et al.

Yiqiu Ma et al.

xhqi@pku.edu.cn

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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.

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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 HULISWS (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 HULISWS in summer. As we discussed in detail in the revised manuscript, line 258-270: "In addition to the four combustion-related sources, one secondary source was apportioned by PMF, contributing 30.1% of HULISWS throughout the year. MLR analysis was conducted to evaluate the effects of O₃, NO_x, SO₄²⁻,

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Hp+, and LWCP on the secondary formation of HULISWS (HULISWS_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 HULISWS 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 $1 \mu\text{g m}^{-3} \text{O}_3$ led to an increase of $0.028 \mu\text{g m}^{-3} \text{HULISWS_SEC}$. 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 HULISWS 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 HULISWS_SEC was produced in the non-heating season ($2.01 \mu\text{g m}^{-3}$) than in the heating season ($1.41 \mu\text{g m}^{-3}$).

We have also had more discussion on the contribution of secondary formation to DTT activity of HULISWS in the revised manuscript, line 295-312: "Secondary formation was the most important source for the extrinsic DTT activity of HULISWS in the non-heating season (44.1%, $0.015 \text{ nmol min}^{-1} \text{ m}^{-3}$) and the second largest contributor throughout the year (25.3%, $0.013 \text{ nmol min}^{-1} \text{ m}^{-3}$). 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 $30 \text{ pmol min}^{-1} \text{ per } \mu\text{g SOA}$ (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 HULISWS_SEC measured in this study is $7.45 \text{ pmol min}^{-1} \text{ per } \mu\text{g HULISWS_SEC}$,

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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 HULISWS_SEC (Table S2), suggesting that HULISWS 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 HULISWS_SEC. However, since secondary formation predominated in HULISWS 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 HULISWS-associated redox activity in Beijing. It should be noted that the contributions of secondary formation processes to both HULISWS and DTT activity of HULISWS could even have been underestimated in this study, because HULISWS 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 HULISWS. However, even after HLB separation, there are still a small amount of metal retained in the HULISWS 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

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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 HULISWS redox activity measurement, we adopt the same method in order to be consistent and make comparison with other HULISWS studies (Dou et al., 2015; Lin and Yu, 2011; Wang et al., 2017). In the revised version, we mentioned the DTT activity of HULISWS 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 HULISWS measured here may be underestimated and is not directly comparable to those using DTT assay conducted 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 HULISWS 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

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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 HULISWS. In the results and discussion part, we meant to report the good correlation between HULISWS and DTT activity to further clarify that our measurement of DTT activity of HULISWS 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 HULISWS is linear when DTT consumption is less than 90% (Lin and Yu, 2011). We have also examined the HULISWS-catalysed DTT consumption as a function of time and obtained a similar result as Lin and Yu (2011). In our study, the HULISWS-catalysed DTT consumption of all 66 samples are between 3.6% and 77.0%, and the measured DTT activity is linearly proportional to HULISWS 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 HULISWS 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 HULISWS secondarily formed from the aging process, and we've discussed them in the manuscript. As in the figure, we prefer to keep it unchanged.

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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 HULISWS, 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.

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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 HULISWS 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 HULISWS in the atmosphere and make comparisons to the redox activity value of HULISWS reported by previous studies. Since HULISWS 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.

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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:

Charrier, J. G., Richards-Henderson, N. K., Bein, K. J., McFall, A. S., Wexler, A. S. and Anastasio, C.: Oxidant production from source-oriented particulate matter - Part 1: Oxidative potential using the dithiothreitol (DTT) assay, *Atmos. Chem. Phys.*, 15(5), 2327–2340, 2015. Cho, A. K., Sioutas, C., Miguel, A. H., Kumagai, Y., Schmitz, D. A., Singh, M., Eiguren-Fernandez, A. and Froines, J. R.: Redox activity of airborne particulate matter at different sites in the Los Angeles Basin, *Environ. Res.*, 99(1), 40–47, 2005. Dou, J., Lin, P., Kuang, B. and Yu, J. Z.: Reactive oxygen species production mediated by humic-like substances in atmospheric aerosols: Enhancement effects by pyridine, imidazole, and their derivatives, *Environ. Sci. Technol.*, 49(11), 6457–6465, 2015. Janssen, N. A. H., Yang, A., Strak, M., Steenhof, M., Hellack, B., Gerlofs-Nijland, M. E., Kuhlbusch, T., Kelly, F., Harrison, R., Brunekreef, B., Hoek, G. and Cassee, F.: Oxidative potential of particulate matter collected at sites with different source characteristics, *Sci. Total Environ.*, 472, 572–581, 2014. Kramer, A. J., Rattanavaraha, W., Zhang, Z., Gold, A., Surratt, J. D. and Lin, Y. H.: Assessing the oxidative potential of isoprene-derived epoxides and secondary organic aerosol, *Atmos. Environ.*, 130, 211–218, 2016. Kreel, A., Leniak, W., Jeowska-Bojczuk, M., Mlynarz, P., Brasu, J.,

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Kozłowski, H. and Bal, W.: Coordination of heavy metals by dithiothreitol, a commonly used thiol group protectant, *J. Inorg. Biochem.*, 84(1–2), 77–88, 2001. Li, Q., Wyatt, A. and Kamens, R. M.: Oxidant generation and toxicity enhancement of aged-diesel exhaust, *Atmos. Environ.*, 43(5), 1037–1042, 2009. Lin, P. and Yu, J. Z.: Generation of reactive oxygen species mediated by humic-like substances in atmospheric aerosols, *Environ. Sci. Technol.*, 45(24), 10362–10368, 2011. Rattanavaraha, W., Rosen, E., Zhang, H., Li, Q., Pantong, K. and Kamens, R. M.: The reactive oxidant potential of different types of aged atmospheric particles: An outdoor chamber study, *Atmos. Environ.*, 45(23), 3848–3855, 2011. Song, Y., Zhang, Y., Xie, S., Zeng, L., Zheng, M., Salmon, L. G., Shao, M. and Slanina, S.: Source apportionment of PM_{2.5} in Beijing by positive matrix factorization, *Atmos. Environ.*, 40(8), 1526–1537, 2006. Tuet, W. Y., Chen, Y., Xu, L., Fok, S., Gao, D., Weber, R. J. and Ng, N. L.: Chemical oxidative potential of secondary organic aerosol (SOA) generated from the photooxidation of biogenic and anthropogenic volatile organic compounds, *Atmos. Chem. Phys.*, 17(2), 839–853, 2017. Wang, Y., Hu, M., Lin, P., Guo, Q., Wu, Z., Li, M., Zeng, L., Song, Y., Zeng, L., Wu, Y., Guo, S., Huang, X. and He, L.: Molecular characterization of nitrogen-containing organic compounds in humic-like substances emitted from straw residue burning, *Environ. Sci. Technol.*, 51(11), 5951–5961, 2017. Xiong, Q., Yu, H., Wang, R., Wei, J. and Verma, V.: Rethinking dithiothreitol-based particulate matter oxidative potential: Measuring dithiothreitol consumption versus reactive oxygen species generation, *Environ. Sci. Technol.*, 51(11), 6507–6514, 2017. Yu, L., Wang, G., Zhang, R., Zhang, L., Song, Y., Wu, B., Li, X., An, K. and Chu, J.: Characterization and source apportionment of PM_{2.5} in an urban environment in Beijing, *Aerosol Air Qual. Res.*, 13(2), 574–583, 2013. Zhang, R., Jing, J., Tao, J., Hsu, S. C., Wang, G., Cao, J., Lee, C. S. L., Zhu, L., Chen, Z., Zhao, Y. and Shen, Z.: Chemical characterization and source apportionment of PM_{2.5} in Beijing: Seasonal perspective, *Atmos. Chem. Phys.*, 13(14), 7053–7074, 2013.

Interactive comment on *Atmos. Chem. Phys. Discuss.*, <https://doi.org/10.5194/acp-2017-740>,

2017.

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