Response to comments from referee #2

We appreciate the valuable and thoughtful comments provided by the referee.

Our response and corresponding modifications are listed below.

General comments:

The authors of current manuscript investigated the correlation of chemical composition of laboratory generated naphthalene and phenanthrene SOA (NSOA and PSOA) with their oxidative potentials (OP) using dithiothreitol (DTT) assay in combination with LC-MS and NMR techniques. They found the oligomer-rich fractions but not the peroxides dominate the OP activity of NSOA and PSOA. Furthermore, they found the ozonolysis of NSOA particles can elevate their OP prominently. Later on, they found the DTT activities of the mixtures of copper ions with redox-active organics or SOA are not additive. Based on NMR measurement, the authors assigned this phenomenon to the formation of complexes. Overall the presented results are interesting and the scientific is sound. The manuscript was written well. Therefore I would like to recommend this manuscript to be published in Atmos. Chem. Phys. if my following concerns can be fully addressed.

Specific comments:

1. In Figure 1, the authors illustrated that both of hydroquinone and semiquinone can reduce O_2 to $O_2^{\cdot-}$. However, Dellinger et al. (Chem. Res. Toxicol., 14, 1371-1377, 2001.) suggested that semiquinone is responsible for reducing O_2 to $O_2^{\bullet -}$, but hydroquinone is responsible for transforming $O_2^{\bullet -}$ to H_2O_2. Is there any conflict of Figure 1 with literature?

Response: Thank you very much for this comment. Redox-active quinones act as electron transfer agent that can constantly transfer electrons from reductants to oxidants (e.g. from NADPH to O_2). The redox-chemistry for quinones inside human body is relative complicated through both enzymatic and nonenzymatic redox cyclings accompanied by the generation of ROS while Fig.1 presented in our manuscript is highly simplified. Base on the previous studies, quinones at a reduced state (semiquinone and hydroquinone) are able to be oxidized by monooxygenase or peroxidase enzymes, molecular oxygen (autoxidation) and metal ions (Roginsky et al., 1999;Monks et al., 1992;Bolton et al., 2000). Transfering electrons from $O_2^{\bullet -}$ to H_2O_2 has been proved to be an alternative pathway for hydroquinone to evolve into semiquinone/quinone.

2. In lines of 161 to 163, the authors said “Within 3 days of collection, the filters were extracted in methanol (HPLC grade, 99.9%, Sigma Aldrich, St. Louis, MO, USA), by ultrasonication at room temperature for more than 3 minutes.” Respect to this experiment procedure, I have two questions. Firstly, Krapf et al. (Chem, 1, 603-616, 2016.) demonstrated that ‘OOH-containing molecules are labile and decay with a half-life of only 45±3 min’. So the aging of SOA in freezer for 3 days may significantly decrease the final OP of them? Secondly, the authors extracted SOA into methanol and then measured their OP with DTT assay. Considering organic solvent has different effect from water to influence the OP of ambient particulate matters (Yang et al., Atmos. Environ. 2014), I am wondering how significant the methanol and ultra-sonication operation will influence the OP of SOA here.

Response: Krapf et al. (2016) showed OOH-containing molecules are labile and decay with a half-life of only 45±3 min. This SOA peroxide thermal-decomposition fate was investigated under room temperature. In this work, the SOA samples were stored under -20 ℃ after being collected and wrapped in prebaked aluminum foil. In the study of Jiang et al. (2017), they have tested the DTT response against the stability of peroxide. They stored organic peroxide and hydrogen peroxide under room temperature and 4 ℃. The DTT responses were maintained above 90% within 3 days under both temperatures. Moreover, peroxide stored under 4 ℃ exhibited a higher DTT response than that of room temperature, indicating lower storage temperature could prevent the thermal decomposition of organic peroxide. Admittedly, the peroxide content in SOA is labile, but the stability of SOA peroxide under the storage condition of our study (-20 ℃) seems unlikely to make a significant difference in the DTT results.

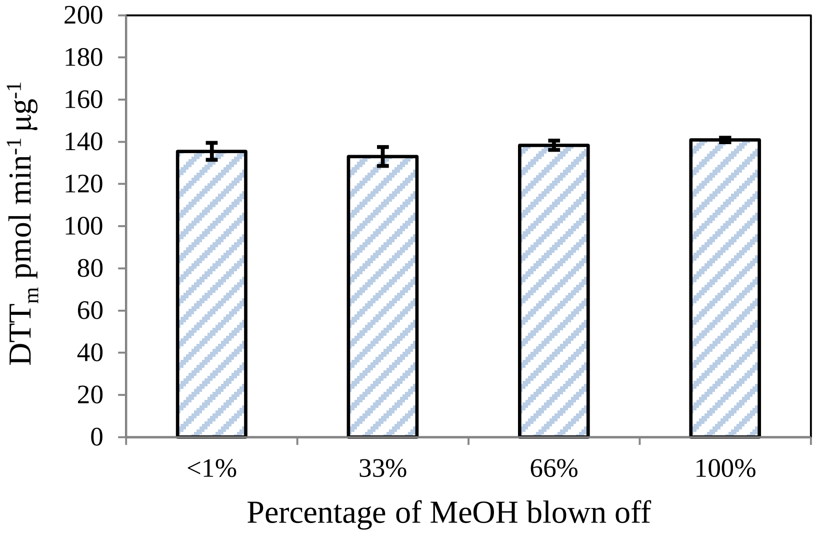
Based on previous studies (McWhinney et al., 2011), quinones are the major OP contributors in PAH derived SOA and their solubility in methanol are generally higher than in MQ water. Also Yang et al. (2014) suggested that quartz filter absorbs water during extraction which might bring about the loss of SOA. As a result, we consider using methanol as our SOA extraction solvent and then reconstitute with phosphate buffer for DTT analysis. The effects on SOA composition coming from ultra-sonication has been discussed by Mutzel et al. (2013), which found ultra-sonication might elevate the peroxide content (thermal-lability) inside SOA. Despite the higher measured peroxide content, there is no associated change in the OP of SOA. We therefore conclude that we find no evidence of association between peroxide content and OP in NSOA.

3. In line 171: the author said “….DTT, an antioxidant that…”. This is a wrong description. DTT is normally used as a surrogate of biological reductant (NADPH etc.), but itself is not antioxidant (Charrier and Anastasio. Atmos. Chem. Phys., 12, 9321-9333, 2012. Shiraiwa et al., Environ. Sci. Technol., 2017, 51 (23), pp 13545-13567.).

Response: This sentence has been revised as “……DTT, an antioxidant surrogate that……” in line 171.

4. In line 173-174, the authors said “The SOA extracts were first evaporated to complete dryness in a 5.0 L min^{-1} of N_2 using a blow off system (N-EVAP, Organomation, USA).” Then in lines of 468-470, the authors indicated that “The overall increased volatility may lead to evaporation of smaller redox-active molecules and decrease the DTT_t compared to the N_2 exposure group.” So whether the loss of small molecular redox active compounds have also happened during the evaporation of SOA, and how significant this process will influence the DTT of SOA especially the monomer rich fraction?

Response: Thank you for pointing this out. The N_2 blow-off procedure is for SOA methanol extracts while the later conclusion of “carbon loss due to volatility” was based on the EC/OC results after heterogeneous ozonolysis of SOA filter. The duration for heterogeneous oxidation ranges from 1 hour to 24 hours in our study while the N_2 blow off procedure for SOA methanol extracts only lasts for 30-40 minutes. Also the evaporation rate may be lower in a dilute methanol solution. However, there may still be potential volatile losses of low molecular weight high volatility SOA compounds during the N_2 blow off procedure. To assess the potential impacts on the DTT activity, we evaporated SOA methanol extracts under the N_2 blow-off system to various extents, with which 100%, 66%, 33%, <1% of methanol were remained. All the solutions were then reconstituted the same experimental concentration by adding methanol and phosphate buffer. There was no significant difference among each experimental group. Thus, we conclude the evaporation of high volatile SOA compounds during N_2 blow-off procedure is not likely to cause a significant underestimation of the OP studied here.



5. In Fig 5 c and d, the sub-captain is “contribution to NSOA DTT activity”, but the pie charts actually showed the relative total DTT decay rate (DTT_t) of different N/PSOA fractions. The misleading word “contribution” here is different from the one used in line 336 of the manuscript, which is based on 1, 2- and 1, 4-naphthoquinone particulate concentrations exactly (McWhinney et al. 2013, which is DTT_m). Considering the current study cannot quantify the recovery of monomer-rich and oligomer-rich compounds from N/PSOA (as stated by the authors in lines 410 to 412), the authors should not be able to use mass normalized DTT value to predict the contribution of monomer-rich and oligomer-rich fractions to DTT_m of N/PSOA. The caption and relevant illustration for Figure 5 c and d should be improved and clarified clearly, especially to compare with the work by McWhinney et al.

Response: We apologize for not clarifying this.

Line 10 in Abstract has been modified as “…dominates DTT activity in both SOA systems…”

Text in section 3.3 has been revised to “… in Fig. 5, both the monomer-rich and oligomer-rich fractions are reactive towards DTT. Compared to the DTT_t of NSOA before LC separation, the relative DTT_t of monomer-rich fraction and oligomer-rich fraction were 16±3% and 56±10%, respectively (Fig. 5c). For PSOA, relative DTT_t from monomer-rich fraction and oligomer-rich fraction were 40±8% and 50±5%, respectively (Fig. 5d).”

The sub-caption for Fig. 5c and d has been revised to “Relative DTT_t from monomer-rich fraction and oligomer-rich fraction in NSOA (c) and PSOA (d) systems.”

6. Respect to the results discussed in section 3.5 especially that showed in the Figure 8, whether the Cu initiated Fenton like reactions or relevant redox chemistry also play significant role? The authors are encouraged to discuss this aspect in the manuscript

Response: Thanks for this suggestion. First, we observed that the OP reduction of quinones in our study has a structural dependence. It was with 1,2-NQN and 2,3-DHN that we witnessed a significant OP depletion but not with 1,4-NQN and 1,3-DHN. Similar OP depletion trend should be observed with the four quinones after Cu was added to the system if Cu initiated Fenton like reactions or other relevant redox chemistry also played significant roles in the OP depletion.

While the Fenton reaction is faster under acidic conditions (Zepp et al., 1992;Kang and Hwang, 2000), we would expect the additional OH ·or HOO ·produced through the Fenton reaction under controlled pH conditions to elevate the OP level while this is inconsistent with what we observed with 1,2-NQN, 2,3-DHN and PAH derived SOA. Combining the NMR organic molecular structural information, we propose that the OP depletion in our study is more likely due to the binding between organics and Cu.

7. It will be useful to add the averaged carbon oxidation state values of monomer and oligomer rich fractions of N/PSOA into Figure 6.

Response: Thanks for this advice. Since most of the m/z peaks in ESI-MS spectra (negative mode) are polar compounds due to the electron spray ionization. The ESI-MS signal weighed $\overline{OS}$c of both monomer and oligomer would not be comprehensive and representative enough for the total SOA system we studied here. Also, the calculation of $\overline{OS}$c relies on the molecular formula of each compound while the accuracy of peak fitting for higher m/z range (oligomer) might be lower than that of the lower m/z range (monomer). So far, we are currently unable to add accurate $\overline{OS}$c values for monomer and oligomer rich fractions of N/PSOA.

8. The section of ‘References’ should be improved carefully, e.g. the references of Mentel et al., 2015 (in line 347) and Tong et al., 2016 (in line 383) could not be find in reference list. In addition, in line 740: ‘2009’ should be ‘2010’. In line 680, the reference of ‘Di Lorenzo et al., Geophys. Res. Lett., 43, 458-465, 2016’ should be separated with the previous one.

Response: References of this manuscript has been checked and corrected.

9. Typos should be corrected for the whole manuscript, e.g. blank space should be used between number and unit: ‘160W’ should be ‘160 W’

Response: Typos of this manuscript has been checked and corrected.

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