

Review for “Relationship between Chemical Composition and Oxidative Potential of Secondary Organic Aerosol from Polycyclic Aromatic Hydrocarbons” by Shunyao Wang et al.

**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  $O_2^-$ . However, Dellinger et al. (*Chem. Res. Toxicol.*, 14, 1371-1377, 2001.) suggested that semiquinone is responsible for reducing  $O_2$  to  $O_2^-$ , but hydroquinone is responsible for transforming  $O_2^-$  to  $H_2O_2$ . Is there any conflict of Figure 1 with literature?
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  $45\pm 3$  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.

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.).
4. In line 173-174, the authors said 'The SOA extracts were first evaporated to complete dryness in a 5.0 L min<sup>-1</sup> of N<sub>2</sub> 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<sub>t</sub> compared to the N<sub>2</sub> 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?
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<sub>t</sub>) 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<sub>m</sub>). 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<sub>m</sub> 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.
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.
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.

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 found 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.
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'.