Response to the comments of Anonymous Referee #2

Tong et al. report systematic investigations on RS yields of ambient PM in clean and polluted environments using EPR spectroscopy. Furthermore, they found that using the surrogate mixtures can reproduce the relative fractions of different types of radicals formed by ambient PM, which would be useful for future laboratory studies. This ms is generally well written, highlighting the complicated mechanisms responsible for radical formation, but it lacks mechanistic insight into how different chemical compositions in PM generate different relative fractions of RS. I hope to see more detailed discussions about the mechanisms in the text, although it is understood that it may be beyond the scope of this study. Overall, I support this ms to be published in ACP after addressing the following points.

Response: We thank the referee #2 for reviewing and providing positive comments. The point-by point responses are given below. We have highlighted changes to the manuscript text in blue.

Major points

Can you elaborate why naphthalene and beta-pinene were used as representative SOA in Beijing and Hyytiälä, respectively? Anthropogenic and biogenic representatives?

Response: Thank you. First, monoterpenes have been found as major volatile organic compounds (VOC) associated with SOA formation in Hyytiälä, and the α- and β-pinene are isomers accounting for > 60% of the total VOC (Kourtchev et al., 2008;Hakola et al., 2012). Moreover, previous studies found that α- and β-pinene exhibit high SOA yield upon oxidation by O_3 (Lee et al., 2006;Zhang et al., 2015), and the β-pinene SOA exhibit higher potentials in generating radicals and H_2O_2 in water (Tong et al., 2016;Tong et al., 2017;Tong et al., 2018;Tong et al., 2019). Therefore, β-pinene was chosen as representative biogenic precursor for the SOA formation in Hyytiälä. In contrast, naphthalene has been found as key anthropogenic VOC in Beijing. Naphthalene has a high SOA yield from photooxidation and potentially contributes to SOA formation in Beijing (Chan et al., 2009;Huang et al., 2019). Recent studies also indicate that naphthalene SOA contains redox-active substances and may play an important role in the cytotoxicity of Beijing PM (Liu et al., 2020;Han et al., 2020). Thus, we choose naphthalene as representative anthropogenic precursor for the SOA formation in Beijing. We add the following section in the SI (lines 55-67) to elaborate why naphthalene and β-pinene were used as representative SOA precursors in Beijing and Hyytiälä, respectively:

Selection of SOA precursors

Monoterpenes have been found as major volatile organic compounds (VOC) in Hyytiälä, and α- and β-pinene are isomers accounting for > 60% of the total VOC (Kourtchev et al., 2008;Hakola et al., 2012). Previous studies found that both α- and β-pinene exhibit high SOA yield upon oxidation by O_3 *(Lee et al., 2006;Zhang et al., 2015), and β-pinene SOA exhibits a higher potential in generating RS in water (Tong et al., 2016;Tong et al., 2017;Tong et al., 2018;Tong et al., 2019). To shorten the collection time of SOA and minimize the influence of aerosol aging on the aqueous RS detection, β-pinene was chosen as representative biogenic precursor for the SOA formation in Hyytiälä. In contrast, naphthalene has been found as key anthropogenic VOC in Beijing, which has high SOA yield upon photooxiation and potentially important contribution to SOA formation in Beijing (Chan et al., 2009;Huang et al., 2019). Recently studies also indicate that naphthalene SOA are redox-active substances and may play an important role in cytotoxicity of Beijing PM (Liu et al., 2020;Han et al., 2020). Thus, we choose naphthalene as representative anthropogenic precursor for the SOA formation in Beijing.*

For the sample treatment procedure of HA or FA water suspensions, why was the procedure necessary? So, does it mean that a water-soluble fraction of HA or FA was extracted and only analyzed?

Response: Yes, we only analyzed the water-soluble fraction of HA or FA. There are reasons for filtering out the insoluble fraction of HA or FA as discussed in the following. According to previous studies, humic-like substances frequently account for a small mass fraction of ambient $PM_{2.5}$ (< 10%, see Table S3). The solubility and chemical reactivity of these substances are largely unknown. The used HA or FA standard compounds can only be partly dissolved in water through a slow kinetic process. Thus, it is difficult to make an equivalent concentration of HA or FA suspension that can represent the water-soluble and insoluble fractions of humic-like substances contained in one ambient $PM_{2.5}$ sample. Moreover, only by keeping the initial concentration of aqueous-phase HA or FA known, the chemical reaction mechanism of the surrogate compounds can be understood quantitatively. Finally, the co-existence of solid phase and aqueous-phase HA or FA in the surrogate solutions will complicate the chemistry upon inducing surface adsorption and chemistry. To clarify the necessity to use water-soluble fraction of HA and FA in this study, we add the following text in lines 29-37 of SI:

HA or FA are used in this study as standard surrogate compounds for humic-like substances and are known to only partly dissolve in water through a slow kinetic process (Baduel et al., 2009;Verma et al., 2015). Thus, it is difficult to generate an equivalent concentration of a HA or FA suspension that can represent the water-soluble and insoluble fractions of humic-like substances contained in one ambient $PM_{2.5}$ *sample. Only by keeping the initial concentration of aqueous-phase HA or FA known, the chemical reaction mechanism of the surrogate compounds can be understood quantitatively. Beyond this, the co-existence of solid phase and aqueous-phase HA or FA in the surrogate solutions will complicate the chemistry of the surrogate compounds upon potentially inducing surface adsorption and surface chemistry effects. Thus, for simplicity, we only analyzed the water-soluble fraction of HA or FA in this study.*

Relative fractions of different radicals, particularly organic and OH radicals, seem to be dependent on the origin of PM samples. What would be the most important factor determining such relative fractions?

Response: Thank you for pointing out this important question. To clarify the PM source-dependent formation mechanisms of radicals, we add the following discussions in the main text (lines 282-293):

We speculate that hydrolytic or thermal decomposition of ROOH may play a major role in the formation of RS by $PM_{2.5}$ *from remote forest locations like Hyytiälä, where large fractions of peroxide-containing HOM have been detected (Mutzel et al., 2015;Tröstl et al., 2016;Tong et al., 2019;Pye et al., 2019;Roldin et al., 2019;Bianchi et al., 2019). ROOH can generate* ${}^{\bullet}OH$ *and O-centered organic radicals through decomposition* ($ROOH \rightarrow RO^{\bullet} + {}^{\bullet}OH$) *and Fenton-like reactions* ($Fe^{2+} + ROOH \rightarrow Fe^{3+} + RO^{\bullet} + OH^{-}$; $Fe^{2+} + ROOH \rightarrow Fe^{3+} + RO^{-} + OH^{\bullet}$) *(Tong et al., 2016). Interconversion of* $RO^{\bullet}$, $R^{\bullet}$ *and* $ROO^{\bullet}$ *radicals can lead to the formation of* $O_2^{\bullet -}$ *and* H_2O_2 *(Chevallier et al., 2004;Tong et al., 2018), which can further react with* Fe^{2+} *to form* ${}^{\bullet}OH$ ($Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + {}^{\bullet}OH + OH^{-}$). *In* $PM_{2.5}$ *from urban areas, transition metal ions and HULIS are expected to play a major role in aqueous-phase formation and interconversion of* ${}^{\bullet}OH$, $O_2^{\bullet -}$ *and* H_2O_2 *(Lloyd et al., 1997;Valavanidis et al., 2000;Zheng et al., 2013;Hayyan et al., 2016;Lakey et al., 2016;Tan et al., 2016;Kuang et al., 2017;Ma et al., 2018;Li et al., 2019).*

In Figure 4, why were only transition metals shown in its absolute concentration, whereas the others were in the relative abundance (%)?

Response: The used ICP-MS method for quantification of water-soluble transition metals is well-established and accurate. Therefore, we can obtain reliable results on the abundances of target transition metals in Hyytiälä, Mainz, and Beijing PM as well as the absolute concentrations of metal ions in water extracts of these PM. However, it remains a challenge to use mass spectrometry in combination with HPLC techniques to differentiate and quantify aromatic or HOM mixtures in ambient $PM_{2.5}$, due to the various relationships of chromatographic area and concentrations of different aromatics or HOMs (Tong et al., 2019). Therefore, we cannot give the absolute concentration information of all aromatic compounds and HOMs. To clarify the different unit in Figure 4, we add the following text in lines 51-54 of SI:

Due to the technique limitation, we are not able to quantify different aromatic or HOM species. In contrast, the method for quantification of water-soluble transition metals is well-established. Therefore, we can obtain reliable results on the absolute concentrations of target transition metals in Hyytiälä, Mainz, and Beijing PM or their water extracts.

Lines 369-373: Why did naphthalene SOA have a lower radical yield than β-pinene SOA with the same mass concentration? This information should be important to generalize the findings of this study.

Response: To clarify the different mass-specific radical yields of naphthalene SOA and β-pinene SOA, we add the following text in lines 68-76 of SI:

The mass-specific radical yield of laboratory-generated SOA is strongly dependent on the abundance of peroxide-containing highly oxygenated organic molecules (Tong et al., 2019), which are involved in radical formation upon thermal-, hydrolytic-, and photolytic- decompositions as well as Fenton-like reactions in water (Chen et al., 2011;Badali et al., 2015;Tong et al., 2016). Previous studies found that the mass fraction of organic peroxides in β-pinene SOA (42%) can be two times higher than in Naphthalene SOA (19-28%) (Kautzman et al., 2010;Tong et al., 2018). Our recent findings showed a positive correlation of HOM abundance and radical yields by both ambient PM and laboratory-generated SOA (Tong et al., 2019). Therefore, we suggest that the low abundance of peroxide-containing HOMs in naphthalene SOA is the major reason for its lower radical yield than β-pinene SOA.

It seems that consistently the higher relative fraction of C-centered radicals is associated with the lower relative fraction of OH radicals. Does it suggest that OH radicals are consumed by something to generate C-centered radicals? This point deserves detailed discussions in the text.

Response: Thank you. We agree with that aqueous OH radicals may react with water-soluble organic compounds to form O-centered organic radicals, the rearrangement of which can form C-centered organic radicals (Chevallier et al., 2004). We noted this point by adding the following text in lines 270-271 of the main text:

Moreover, rearrangement reactions in water can convert RO$^\bullet$ into R$^\bullet$ (Chevallier et al., 2004), which may warrant further investigation.

When HA was replaced by FA, the dominant radical species becomes O_2^- from C-centered radical. Do you any explanation on the different radical distribution?

Response: The major formation of $O_2^{\bullet-}$ in aqueous mixtures of CHP+Fe^{2+}+FA but C-centered radicals in CHP+Fe^{2+}+HA may reflect the different reactivities of FA from HA in Fenton-like reactions. To clarify this point, we add the following text in lines 408-412:

Different reactivities of HA and FA are also reflected by the different RF values of $O_2^{\bullet-}$ and C-centered radicals observed at high concentrations of FA and HA (Figure 6h vs. Figure 6f) as well as in reactions mixtures with copper instead of iron ions (Figure S6). Further investigations will be required to resolve the underlying reaction mechanisms and kinetics.

Lines 496-498: It is said that “the higher relative amount of detected radicals and H_2O_2 formed by urban $PM_{2.5}$ can see as a measure of higher potential oxidative damage”, but the totally formed radical amount decreases with PM mass. The statement seems contradicting and needs clarification.

Response: Thank you. We replaced this sentence with the following text (lines 431-433):

Overall, our findings show how the composition of $PM_{2.5}$ can influence the amount and nature of aqueous-phase RS, which may explain differences in the chemical reactivity and health effects of particulate matter in clean and polluted air.

Minor points:

Line 236: The -> the

Response: We corrected this typo.

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