General Comments: Tong et al. report the field measurement and laboratory experimental investigation on the production of reactive species (RS) including several radicals and hydroperoxides (ROOH) from fine PM dissolved in aqueous solutions. They explored the RS yields of fine PM from remote forest (Hyytiälä, Finland) and polluted urban air (Mainz, Germany and Beijing, China) and related these yields to different chemical constituents and reaction mechanism. They utilized ultrahigh-resolution mass spectrometry for the characterization of organic aerosol composition, electron paramagnetic resonance (EPR) spectroscopy with a spin-trapping technique for the determination of the concentrations $O_2{\cdot}^-$, HO_2, OH, carbon- or oxygen-centered organic radicals, and a fluorometric assay for the quantification of H_2O_2 concentration. They found that the mass-specific yields of radicals were lower for sampling sites with higher concentration of ambient PM2.5 (particles with a diameter < 2.5 μm), whereas the H_2O_2 yields exhibited no clear trend. They also found that the relative fractions of different types of radicals formed by ambient PM2.5 were comparable to the surrogate mixtures comprising transition metals, organic hydroperoxide, H_2O_2, and humic or fulvic acids. The experiments were carefully performed, and the analyses were precise. This paper is well-written and the subject showed here are within the scope of ACP. Therefore, I would be happy to accept the manuscript once they address following issues.

Specific Comments:

- In the title, abstract and throughout the text, the authors use the words "interaction of water with fine PM". What does this "interaction" really mean? Water itself only contains H_2O, OH^- and H^+. Although the authors wrote in page 12 "The presence of OH is related to multiple formation pathways, such as Fenton-like reactions, thermal or hydrolytic decomposition of peroxide-containing HOMs, and redox chemistry of environmentally persistent free radicals or aromatic compounds-containing humic-like substances", it is unclear how the observed radicals are actually formed. The key issue is: they already exist and persist in PM? or they are formed just after reactions in water, e.g., Fe^{2+} + ROOH, or an electron-transfer reaction from OH^- to some components in PM? It is fruitful to clarify the meaning of "interaction" and add more discussion on the possible mechanisms of radical formation.

- The authors infer that OH comes from HOMs containing peroxide-groups. However, it has been reported that the Fe^{2+} + ROOH (R=CH_3, C_2H_5) reaction in water produces RO + OH^-, rather than RO^- + OH [Chevallier et al., Atmos. Environ. 2004, 38, 921]. RO would produce HO_2. Then, what is a major source of OH-radicals in the present system?

- A PAM chamber experiment would produce atmospherically irrelevant RS species [Peng and

Jimenez, Chem. Soc. Rev., 2020, 49, 2570]. A major RS of PM in ambient air would be a species possessing multiple -OOH formed via autoxidation process involving intramolecular H-abstractions (i.e., HOM). Thus, the high vs. low O_3/OH condition critically influence the product identities and the distributions. Does this concentration gap influence the current conclusion? The authors should comment on the issue.

- Can the authors estimate how much O_2 is dissolved in solutions? The presence of O_2 in solutions could induce autooxidation reactions that give OH-radical signals of EPR [Floyd and Wiseman, Biochim. Biophys. Acta, 1979, 586, 196]. O_2 in solutions could also influence the Fenton-like chemistry and HOx cycles in the system [Chevallier et al., Atmos. Environ. 2004, 38, 921]. If the authors perform degassing of solutions (e.g., by Argon) before measurement, are the same results obtained? It would be better to perform such a test to understand the mechanism in more detail.

- C-centered radicals are expected to rapidly react with O_2 or recombine in condensed phases. Why were they so abundant (Figures 2 and 4)? What types of C-centered radicals can be assumed? The authors should comment on the issue.

- BMPO-OOH must decompose into other products in solutions (it decreases as a function time in Fig. S6). What are the decomposition products? Do the products influence the RS yields? The authors should comment on the issue.

- Fig. 3 shows H_2O_2 is the dominant RS in PM2.5, while radical species contribute just as minor components. What is the main source of the observed high H_2O_2? Furthermore, from the viewpoint of adverse health effects of PM inhalation, if $[H_2O_2] >> [\text{radicals}]$ in lung epithelium lining fluid, how important are these radicals? It would be better to add some discussion on these issues.

Minor Comment:

- Line 858, “participated”