Response to the comments of Anonymous Referee #1

In this work the authors report OH radical observations in aqueous solutions of secondary organic aerosol in the absence of radiation. They postulate that organic hydroperoxides (ROOH) can decompose in water and form OH radicals. The formation rate of OH was enhanced in the presence of Fe^{2+}, following a Fenton-like mechanism to catalyze radical production. The manuscript is well written, and the experiments were carefully performed. I have a few minor comments, and recommend publication in ACP after these concerns are addressed.

Response:

We thank the referee for reviewing this manuscript and for providing positive comments. We respond to each comment in detail below.

Major comments:

How is the concentration of OH quantified? Since the major finding of this work is OH radical formation, it seems that the quantitation method should be clearly described and justified. It seems to me that the OH is estimated by fitting the EPR data (Supplement Figure S1). What is the sensitivity of the fitting to quantification? What are the detection limits, limit of detection, limit of quantification etc.? Are there standards for quantification? It is acceptable if no standards are available (since OH is very difficult to measure), but perhaps there are other methods (e.g. tracer method used by the Abbatt group in Toronto) for comparison? Given that OH is so difficult to measure, the authors should provide more evidence that their quantitation method is sound.

Response: We have described the method for radical quantification in section '2.2 CW-EPR spectroscopy' and in lines 10-22 of pg. 30022. We will add a paragraph giving details of the quantification method and the detection limit for clarification in the supplement:

"Briefly, peaks and a baseline of spectra were selected, followed by double integration of the peak intensity. Spin concentrations were calculated through the following equation (Eaton et al., 2010):

$$DI = c \cdot [G_R \cdot C_t \cdot n] \cdot \left[\frac{\sqrt{P} \cdot B_m \cdot Q \cdot n_B \cdot S \cdot (S+1) \cdot n_S}{f(B_1, B_m)} \right]$$

where c = constant determined by a standard sample with known number of spins, G_R = Receiver gain, C_t = Conversion time, n = Number of scans, P = Microwave power (W), B_m =

Modulation amplitude (Gauss), Q = Quality factor of resonator, n_B = Boltzmann factor for temperature dependence, S = Total electron spin, n_s = Number of spins, $f(B_1, B_m)$ = Spatial distribution of the microwave field and the modulation field, experienced by the sample. We calibrated this method using the stable radical TEMPOL and obtained a difference < 5% between the calculated and measured concentrations, confirming the reliability of the spin counting method. The absolute detection limit of number of spins in an EPR cavity (~20 μL) is estimated to be ~10^{12} spins, which translates to a detection limit of spin concentration of ~100 nM under our experimental conditions."

It was noted in the manuscript that the pH of SOA solution was in the range of of 4.8 – 6.4. In Fenton reaction, Fe^{2+} reacts with hydrogen peroxide to yield OH radical:

$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^{\cdot} + OH$
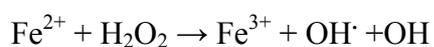
Can OH radical or OH ion generation be quenched under acidic condition? e.g.

$2Fe^{2+} + H_2O_2 + 2H^+ \rightarrow 2Fe^{3+} + 2\,H_2O$

What would be the pH effect for OH production from SOA? Will OH production be underestimated or overestimated in this paper, especially when the particle is inhaled into the lung where pH is around 7? (Richard and Francis, J Clin Invest. 1969)

Response: The referee is correct. Indeed the OH radical production can be influenced by the pH of solvent. We found that the formation of OH radicals was increased by ~20% at a pH of 7.4 using a phosphate-buffered saline solution. We have clarified this point and the potential role of pH in the revised manuscript. We intend to investigate pH effects on OH formation in more detail in follow-up studies.

The observation that ROOH (not HOOH or ROOR) decomposition leads to OH formation is interesting. Any speculations as to why ROOH preferentially decomposes? Also, the R group seems to be also important, since b-pinene forms more OH than a-pinene (and they are very similar). Also, why was isoprene SOA not studied? Isoprene SOA is known to contain a large amount of ROOH (Surratt et al., 2006) and is likely more important than terpene SOA.

Response: We speculate that an electron-donating R group within ROOH can promote the homolytic cleavage, as suggested in a previous study (Nam et al., 2000). We will clarify this point in the revised manuscript.

Isoprene SOA was more difficult to generate in our flow tube setup in relatively short reaction time with ozonolysis due to the low yield (Surratt et al., 2006). Recently, we have deployed a potential aerosol mass (PAM) chamber in collaboration with Prof. William Brune

(Penn State Univ.; added as a co-author) and formed isoprene SOA from OH photooxidation in the PAM chamber. We found that isoprene SOA can also form OH radicals under dark conditions with a similar yield as terpene SOA. The spectra of isoprene SOA will be added to Fig. 2 and the OH concentrations formed by isoprene SOA will be added to Fig. 4a. First results of ongoing experiments indicate a significant increase of OH yield with Fe^{2+} concentration, in line with the results on previously investigated precursors. The EPR spectra of the isoprene SOA show a dependence on the oxidant concentration level in the PAM chamber. The more complex behaviour of the isoprene SOA from OH photoxidation is under investigation and will be presented in a follow-up study.

The addition of Fe^{2+} leads to elevated OH concentrations, but the concentration of Fe^{2+} seems high relative to SOA for ambient particles. The mass ratios in aerosols are more likely to be around 0.01 to 0.1 (if we assume 10 ng/m3 of Fe and 1 ug/m^3 of SOA). Perhaps in cloud droplets, the ratios would be higher due to higher water content and therefore more soluble iron? I suggest adding some reference of ratio of organic to Fe in cloud droplets to clarify.

Response: Typical dissolved iron concentrations in cloud droplets are 0.1 – 2.5 μM (Deguillaume et al., 2005). The secondary organic compounds in cloud water also varies depending on the pollution levels and can be up to 1-2 mg L^{-1}, which equals to 5-10 μM by using 200 g mol^{-1} as the SOA molar weight. Hence the typical molar ratio between iron ions and secondary organic compounds in cloud water can be 0.01- 0.5, and the concentration ratios used in current study is in the reasonable range of real atmospheric situations.

Pg. 30027 line 7-11: The authors should be careful about making the hypothesis that the OH formation revealed in this study is analogous to autoxidation reactions.

From the cited studies, autoxidation reactions occur as a result of intramolecular reaction in the gas phase. These are favourable in the gas phase because the lifetimes of radicals are longer. The same type of mechanism is unlikely to happen in the condensed phase since the lifetimes of radicals are much shorter due to extensive quenching by other radicals. On the other hand, propagation of radicals is likely promoted by the higher concentrations. The authors should clarify that the hypothesized mechanisms are not similar.

Response: The referee is correct and raises an important point. Indeed, lifetime of radicals in the condensed phase may be shorter compared to the gas phase. However, recent studies have shown that some radicals are long-lived (Shiraiwa et al., 2011; Gehling and Dellinger, 2013) and they can be stabilized in the condensed phase by interacting with transition metals

(Truong et al., 2010). It is also well-know that autoxidation can occur in the condensed phase (i.e., an apple turns brown). We will clarify these points in the revised manuscript.

- The link to oxidative stress in the lung lining fluid is very interesting. What is the formation rate of OH compared to clearance rate by the mucus in the airway?

Response: Due to the scavenging effect of antioxidants, the OH radical would have a chemical lifetime on the order of nanoseconds. It is not totally clear whether this lifetime is sufficiently long to cause oxidative damage to cells, but it is well-established that OH radicals play a critical role in oxidative stress and physiological processes despite of very short lifetime (e.g., Winterbourn, 2008).

Minor/Technical comments: Pg. 30026 line 20: "illustrated"

Response: Correction will be made.

Fig. 4: why is there an abrupt change in OH concentration when Fe^{2+}/SOA reaches a certain ratio for a-pinene and b-pinene, but not for limonene?

Response: The decrease of OH radical production with increasing Fe^{2+} concentration is supposedly induced by reaction of the BMPO-OH adduct with Fe^{2+} (Yamazaki and Piette, 1990). Destruction of BMPO-OH can be viewed as iron-catalysed reactions, as Fe^{2+} is constantly recovered in the presence of peroxides. Hence, at high $[Fe^{2+}]$/[SOA], destruction dominates over production. Such behaviour is more prominent for α–pinene and β–pinene SOA, due to higher concentrations of organic hydroperoxides. For limonene SOA, the OH production increased rather gradually with lower abundance of organic hydroperoxides, leading in return to a less prominent destruction of the BMPO-OH adducts by Fe^{2+}. We will clarify this point in the revised manuscript and supplement.

Pg. 30020 line 5: RH for naphthalene experiments is 30%. What about the other experiments?

Response: The other experiments were conducted under dry conditions. This will be clarified in the revised manuscript.

Pg. 30020 line 9: the typical size is 50-400 nm. Is that by number? What is the volume mode or median diameter?

Response: The typical size of the SOA ranged from 50 to 400 nm in the number size distribution. The median diameters of the mass size distribution were 100 – 200 nm. We will clarify it in the revised manuscript.

Pg. 30020 line 15: I assume 0-20 ppb of ozone is what was measured after the ozone denuders. A clarification is needed. Acknowledgements usually include funding information.
Response: A clarification for the '0-20 ppb' ozone is added as follows: Typically 0-20 ppb of ozone was measured after ozone denuders.
The funding information is added.

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