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Interactive comment on "Identification of Organic Hydroperoxides and Peroxy Acids Using Atmospheric Pressure Chemical Ionization – Tandem Mass Spectrometry (APCI-MS/MS): Application to Secondary Organic Aerosol" *by* Shouming Zhou et al.

Anonymous Referee #1

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General Comments

In this manuscript the authors describe a new method for detecting hydroperoxides and peroxy acids in organic aerosol collected in filter samples. The method involves analysis of the extract following addition of ammonium acetate (when necessary) by atmospheric pressure ionization tandem mass spectrometry. The ammonium adducts $(M + NH_4)^+$ of the hydroperoxides and peroxy acids are observed in the mass spec-

trum and characteristically show loss of mass 51 due to $H_2O_2 + NH_3$. The method has been evaluated for a large suite of compounds relevant to the atmosphere, showing similar behavior for all, and it has also been shown that the compounds without hydroperoxide or peroxy acid groups do not show the mass 51 loss. The methods were employed to analyze SOA formed from the reaction of a-pinene with O_3, and only monomer hydroperoxides and peroxy acids were identified (no dimers or larger oligomers). The method is an important advance for atmospheric chemistry, since organic peroxides are a class of compounds whose importance is growing rapidly because of decreases in NOx and the recognition of the importance of atmospheric autoxidation. The manuscript is clear and concisely written, and I highly recommend it be published after the following minor comments are addressed.

Specific Comments

1. I wonder if the absence of detected peroxide dimers or other oligomers in the SOA could be due to decomposition that occurred prior to analysis. Krapf et al., Chem., 2016 measured a lifetime for organic peroxides in SOA formed from a-pinene ozonolysis of a few hours. And the organic chemistry literature indicates that peroxide decomposition pathways generally involve Baeyer-Villager reactions in which hydroperoxides or peroxyacids react with aldehydes or ketones to first form peroxyhemiacetals or acylperoxyhemiacetals (these would be observed as dimers), which then decompose to acids, esters, and alcohols. So it may be that once a dimer forms, it decomposes too soon to be observed here. This would be exacerbated by the long SOA sampling time of 72 hours. Perhaps some would be detected if the sampling time was shortened.

2. I am not sure of the necessity to speculate about mechanisms for formation of peroxides in Figure SI8. There is still very little known about these pathways and there are many proposed steps to getting to products, so to me it would be perfectly appropriate (and the authors would be on more solid ground) to just speculate on the structures of the products based on the observed mass spectrometry results. As a few examples of this issue, I believe it is well established now from structure activity calculations

(Vereecken & Peeters, PCCP, 2009, 2010) that radicals with RC(O)O structures imme-diately lose CO2. It is also not clear how an internal CO is lost in one of the steps shown, and I am not sure that the 184 compound is stable. I think it is just an excited intermediate that immediately loses OH. If the authors prefer to keep all this, then it would probably be useful to provide some references (perhaps Orlando and Tyndall, Chem. Soc. Rev. 2012 and elsewhere) to support the various proposed pathways.

Technical Comments

None.