"Development of a sensitive long pathlength absorbance photometer to quantify peroxides in aerosol particles (Peroxide-LOPAP)"

We thank all Referees for their helpful and thoughtful comments. Our response to each specific point made by the Referees follows (referee comments in italic, our answers in normal font).

Responses to referee #1:

There are a number of existing approaches available for peroxide analysis. The authors argue that some of the drawbacks for these justify the need for a different approach, but I am not sure that I am convinced by these. For example, the horseradish peroxidase catalyzed technique has the same sensitivity for all peroxides that undergo the reaction, and dialkyl peroxides can be analyzed by hydrolyzing these compounds prior to analysis. The approach taken in this work is not particularly sensitive, and there are potential problems that may make the technique less useful than existing approaches. Unlike chromatographic techniques, the method does not provide information on the chemical identity of the peroxides present. Also, because the iodide oxidation reaction is not selective, there is the potential for interference from other redox-active species present in the sample. Such potential interferences would make the use of this instrument in the field challenging given the wide variety of chemical species present in these samples, and the use of this approach may be limited to lab studies. However, this may also be an issue in chamber work where redox-active organic components may also be present.

We primarily aimed at quantifying the total amount of peroxides in chamber generated organic aerosols, which would not be possible with chromatographic methods. The horseradish peroxidase catalyzed technique is indeed very sensitive but has two major drawbacks: on the one hand, as reported by Wang and Glaze (1998), different peroxides react at different rates and hence would exhibit different sensitivities. On the other hand we aimed for a quantitative extraction of the overall peroxides content from the aerosol filter sample and therefore use a 1:1 mixture of an aqueous and an organic solvent to favor the extraction of peroxides with limited water solubility, which we expect to be present in the aerosol systems investigated here. Using the horseradish peroxidase catalyzed technique requires an aqueous solvent to sustain the catalytic function of the enzyme. Furthermore, organic solvents cause a quenching effect on the fluorescence yield of the enzymatically produced dimer. E.g., a 1:1 mixture of water and methanol reduces the peak height by a factor of about 10 (Wang and Glaze, 1998). In our system we could demonstrate nearly quantitative extraction from a spiked filter even of peroxides with large aliphatic moieties. Redox-cycling from redox-active substances is minimized by the strongly reduced oxygen content (1 ppb).

Specific comments:

1) Page 1434 line 25: Hydroperoxides are known to decompose in the presence of metals. Were any tests performed to investigate peroxide degradation during sample collection?"

Response: In our smog chamber experiments we generated secondary organic aerosol from α-pinene and therefore did not expect to have metals in the aerosol. Hence we did not test for losses of hydroperoxides catalyzed by metals. This has to be considered for measurements in ambient aerosol samples but is clearly beyond the scope of this publication.

2) Some more details in the results section would be useful. Aerosol masses are given for the OH + pinene experiments, but I didn't see this information given for the ozone experiments in the text (although it is in Figure 6). Seed aerosol was used for the second HONO/pinene experiment, but no information on the characteristics (e.g., size distribution) of the seed are given. Seed aerosol is not described for the other experiments. It would be helpful to state that no seed aerosol were used if this is the case. If no seed aerosol was used in these other experiments, it would be helpful to explain why the experimental designs were different.

Response: A seed was only used for one experiment. We mention that now explicitly. We also added the information in the text as the reviewer suggests.

3) In the low NOx experiments, there is probably a substantial amount of H2O2 present from HO2 self-reaction. Is this likely to contribute significantly to the peroxide signal?

Response:
Since our instrument cannot distinguish between different kinds of peroxides we can not quantify the specific amount of H_2O_2 in the aerosol. In the experiments at 50% relative humidity the partitioning of H_2O_2 into the aerosol is most probably small as the water content of the aerosol particles is very small. As we are interested in the total amount of peroxides we do not distinguish between H_2O_2 and organic peroxides.

4) Page 1443 lines 10-13. Presumably the peroxide yields for aged aerosols are corrected for wall loss of particles?

Response: We report the peroxide content of the suspended particles. A correction would be highly speculative. We do not know the composition of the particles lost to the walls. If they are processed similar to the suspended ones the result would be the same. not the particle-borne peroxide yield. We clarified this in the text which now reads: "The resulting time series of the peroxide content in the aerosol particles is given in Fig. 6. The peroxide mass fractions in the suspended particles ranged between 34% and 12 %..."

5) Page 1445 lines 10-11. I think this is the critical issue that perhaps merits more discussion. There are likely other reaction products that interfere with the analysis as well. How can these be distinguished from the peroxide products?

Response: Besides the PANs (peroxyacyl nitrates), there are quinones which might interfere in the test reaction as well. PANs are also peroxides. Quinones are not expected in α-pinene SOA experiments. However, they may be present in aerosols from other precursors, mainly from aromatic compounds, and might influence the signal. We mention this possibility in the manuscript now.
A possibility to distinguish the effect of interfering species from the peroxide signal might be to use a two-channel-system: two filter halves (from an aerosol particle filter sample) have to be analyzed in parallel, one as described in the manuscript, while in the second channel all peroxides must be removed. This can be done by the catalytic decomposition at a metal surface, e.g. by adding platinum to the analyte in the second channel. The difference of the signal from these channels would then be the peroxide signal.

6) The authors show that t-butyl hydroperoxide reacts with iodide on a slower timescale than the other peroxides tested. In the chamber experiments, is it possible to exploit these different reaction timescales to extract some crude information about the identity of the peroxides generated? (For example could the analysis be run for 60 and 300 min and the change in signal used to infer the yield of tertiary peroxides?)

Response: Yes, this is possible. If we were to compare our signal after 60 minutes of test reaction to the signal after 300 or even more minutes, an increase would directly result from unreactive, sterically or electronically stabilized organic peroxides. However, we would need to extract the sample in at least twice the present amount of solvent. This would reduce the detection limit accordingly.

Response to referee #2:

1) The authors might note at the end of the Introduction or perhaps in the Conclusions that long-path methods cannot always be used to improve spectrophotometric method detection limits. An important requirement is that the solvents and reagents used in the method do not absorb significantly. Otherwise, the reagent blank absorbance can be so high in a long-path instrument that the absorbance is essentially saturated, in which case one cannot distinguish the absorbance of the sample from that of the blank.

Response: That is a good comment and we mention this now in the text. We would like to point out that in Figure 2 a blank spectrum is presented (violet line) showing the low absorbance resulting from the solvents and the test reagent potassium iodide (KI).

2) Page 1441: Is any evidence observed for decomposition of peroxides using an HCl solution for extraction? It is known that strong acid catalyzes the decomposition of hydroperoxides to carbonyls + H2O.

Response: The sensitivities of different peroxides show only small differences likely caused by different reactivities of the peroxides as shown in Figure 4. If catalytic decomposition takes place during the analysis, all tested peroxides (H2O2, R-OOH and R-OO-R) would show very similar decomposition rate constants.
To estimate the effect of acid catalyzed decomposition, we give here an estimation based on two examples from literature data:
(a) Miner and Hagan (1972) determined the decomposition rate constant of H_2O_2 in a 1.7 M aqueous solution of nitric acid and a temperature between 93 and 99 °C (boiling point of solution) to be 0.144 ($\pm$ 0.012) x 10^{-4} s^{-1}. Using this value, 5% of the initial amount of H_2O_2 would decompose within 60 min, assuming a first-order reaction.
(b) Seubold and Vaughan (1953) determined the decomposition rate constant for cumene hydroperoxide in 50% (by weight) aqueous acetic acid containing 0.1 M of p-toluenesulfonic acid at 40 °C to be 0.326 ($\pm$ 0.07) x 10^{-4} s^{-1}. With this rate constant 12% of the cumene hydroperoxide would decompose within 60 min, assuming a first-order reaction.
Taking into account the peroxide degradation by the reaction with iodide in our analysis, the decomposition of the reactive peroxides by hydronium ions would be below 5% within 60 min. This is now discussed in the text.

3) Page 1443: Has the efficiency of the 3 μm pore size filters been tested for collection of these size particles?

Response: From our experience a 3 μm pore size filter (filter area = 2.27 cm^2) is close to 100% efficient for collection even of particles in the submicrometer range at the sample flow rate of 14-15 l min^{-1}.

4) Page 1445, line 3: Please provide a justification for the concentration assumed for HO2 radicals in these experiments. Was this obtained by modeling or just guessed at? How uncertain is this value and what is the effect on the estimated HO2 vs NO reaction with RO2 radicals? Are the authors certain that the conditions are such that RO2 + RO2 reactions are negligible?

Response: The HO_2 radical concentration was guessed in the ACPD version. We now replace this section with a discussion of Master Chemical Mechanism (MCM) model simulations for the high and low NOx case. We compared the simulated formation of the first generation peroxide product hydroperoxy-pinanol and the second generation product perpinonic acid for the two experimental cases. These two compounds were considered surrogates of peroxides that can partition into the particle phase. Both, hydroperoxy-pinanol and perpinonic acid concentrations were roughly a factor of three higher in the low NOx case after 3 hours of simulation. This is in fairly good agreement

with the three times higher peroxide content in the low NOx experiment compared to the high NOx experiment.
The section was rewritten according to these model results.

5) Page 1445, line 15: I suggest changing "atmospherically relevant" to "typical atmospheric". Although this phrase is commonly used, the word "relevant" implies that experiments conducted at higher concentrations are irrelevant (otherwise why use this word?), which is clearly not the case since most of what is known about the kinetics and products of VOC reactions has been obtained at high concentrations. Smog chamber experiments fail to mimic the atmosphere in many ways (radical composition, VOC and oxidant composition, particle composition, light spectrum and intensity, walls, etc.), which the authors do not mention, so it is misleading to suggest that because the VOC or aerosol concentration is typical of the atmosphere that the results are relevant.
Results must be interpreted with caution and with an understanding of atmospheric chemistry regardless of experimental conditions.

Response: This is a good point and we will change this according to the recommendation.

References:

Miner, F. J., and Hagan, P. G.: Rate of hydrogen-peroxide decomposition in nitric-acid solutions, Ind. Eng. Chem. Process Des. Develop., 11, 547-549, doi:10.1021/i260044a017, 1972.

Seubold, F. H., and Vaughan, W. E.: Acid-catalyzed decomposition of cumene hydroperoxide, J. Am. Chem. Soc., 75, 3790-3792, doi:10.1021/ja01111a055, 1953.

Wang, K. X., and Glaze, W. H.: High-performance liquid chromatography with postcolumn derivatization for simultaneous determination of organic peroxides and hydrogen peroxide, J. Chromatogr. A, 822, 207-213, doi:10.1016/s0021-9673(98)00598-6, 1998.