Response to Anonymous Referee #1

Thank you very much for your time and constructive comments. Here are our responses to your comments.

Major revisions:

1. Table 1 shows mass, concentration, and effective surface area of $PM_{2.5}$ particles, with no chemical analysis done. Instead, the authors cite other papers from previous years on the chemical characteristics of these particles. It is emphasized in the manuscript that chemical processes are the major contributors to the observed trends. The lack of chemical analysis of the $PM_{2.5}$ particles used in this study would add more weight to the credibility of analysis.

A: Thanks for your constructive suggestion. We have done this. 23 elements, 6 soluble inorganic ions and 4 organic acids of $PM_{2.5}$ particles were detected. We have added a table (Table 5) and related discussions into the revised manuscript.

2. Since the same filter was used for experiments at different humidities, how long did each experiment take? Why not each humidity was done on a separate 'unexposed' filter? This means that the particles from the first experiment are different than the second, third, etc. Emphasize that the 'uptake' coefficient measured in these experiments is 'average' uptake on aged particles.

A: The uptake experiment at a certain RH took 2 h for PAA and 1 h for H_2O_2; including the time for the balance of peroxide on blank filter and particles-loaded filter. The balance concentrations of PAA/H_2O_2 have been detected at least for three times. Because we only got 4 identical $PM_{2.5}$ samples at a time, we don't have enough filters to change for every RH. But this would not influence the experimental results for the following reasons. First, although the experiments were carried out on the same filter, our results can be repeated well. The repeat experiments were carried with increasing RH and decreasing RH (see Fig. 3 and Fig. 5 in the revised manuscript). This suggests that $PM_{2.5}$ particles can retain the reactivity toward PAA and H_2O_2 on the experimental time scale. Second, we have added an experiment to compare the uptake coefficients of PAA on the exposed $PM_{2.5}$ filter and the unexposed $PM_{2.5}$ filter at 60% RH, and no obvious difference was observed between this two uptake coefficients (see Table 1 in the revised manuscript). Therefore, we think the reuse of the filter for experiments at different RH has no significant effect on the results.

Because the reuse of the filter has no significant on the results, we suggest there is no obvious difference between the initiate uptake and the average uptake. Therefore, we do not emphasis whether the uptake is "average uptake".

3. Page 5723, line 20-24: where is the data that show the trends in these lines?

A: The positive trends of γ_{PAA} and γ_{H2O2} with RH were given in Figures 3 and 5 in the revised manuscript, respectively. We have added $R_{\gamma H2O2}$ to Figure 6 in the revised manuscript.

4. Page 5724, line 10: this line discusses data on the effect of decreasing relative humidity on the uptake, but the reader is referred to Figs. 3 and 5, which were recorded with increasing RH, and contain no data on decreasing RH?!

A: The uptake with decreasing relative humidity is a part of the repeat experiments. In the revised manuscript, we have used different symbols in Figures 3 and 5 (in the revised manuscript) for the γ values measured with increasing and decreasing RH.

5. Page 5728: the literature summary in section 3.3 is useful to understand the heterogeneous chemistry of H_2O_2. However, it is used to extrapolate on the behavior of PAA under the same conditions. Since the authors have the experimental setup optimized for measuring uptake of PAA on different samples, why not run few more experiments to show data relevant to PAA to support the extrapolations?

A: Thank you for your constructive suggestion. We have analyzed the compositions of $PM_{2.5}$, ADS and ATD particles. The results shows that inorganic soluble ions such as SO_4^{2-}, NO_3^- and NH_4^+ comprise a large fraction of $PM_{2.5}$ particles and that the concentration of these ions in ADS is much higher than in ATD. These data are in line with the potential role of the aqueous phase chemistry, as the presence of soluble ions can lead to the formation of aqueous particle droplets or aqueous layers on the particle surface at high RH. As PAA and H_2O_2 are both soluble peroxides, they are expected to have some similarities with respect to the heterogeneous chemistry on aqueous particles. As we show here, the γ values of PAA and H_2O_2 on $PM_{2.5}$ are both positively correlated with RH. Therefore, we suggest the behavior of H_2O_2 can be extrapolated to PAA.

6. Page 5729: the authors refer to 'pristine' particles, but their experiments were not conducted on this type of particles. Need fixing.

A: We have revised it.

7. Figure 4: the line shown is connecting the data points. Why not use Eq.12 to show best fit from this empirical equation?

A: We have revised it (see Fig. 4 in the revised manuscript).

8. Figure 7: same comment as for Figure 4, where Eq. 14 and 15 could be used to show best fits?

A: We have revised it (see Fig. 7 in the revised manuscript).

Minor revisions:

1. Abstract, page 5714, line 11: state enhancement magnitude quantitatively

A: γ_{PAA} at 90% RH is 5.4±1.9 times of that at 3% RH and γ_{H2O2} at 90% RH is 2.4±0.5 times of that at 3% RH. We have stated it in the revised manuscript.

2. Introduction, page 5715, lines 8-15: sentence too long, consider splitting into two

A: We have split the previous long sentence into short ones, i.e., "Recent studies have combined field and model data to ascertain the importance of heterogeneous pathway. For example, de Reus et al. (2005) have demonstrated that in the subtropical island, the concentration of gaseous H_2O_2 was largely overestimated by a standard gas-phase chemical mechanism. Whereas when the heterogeneous uptake of H_2O_2 and/or HO_2 on the surface of aerosols was accounted for in the model, the observed and modeled values were in better agreement".

3. Introduction, line 21: start new paragraph starting with "To the best of our knowledge...".

A: We have started a new paragraph beginning with "To the best of our knowledge".

4. In this same paragraph, add details about known sources and sinks

A: Thank you for your constructive suggestion. The peroxide compounds are mainly produced by the bimolecular reaction of HO_2 and RO_2 radicals (e.g. R1 and R2), and their minor sources include the ozonolysis of alkenes and biomass burning.

$HO_2 + HO_2 (+ H_2O) \rightarrow H_2O_2 + O_2$ （R1）

$HO_2 + CH_3C(O)OO \rightarrow CH_3C(O)OOH$ （R2）

Their traditional removal pathways include reacting with OH radicals, photolysis and deposition. We have added these details into the revised manuscript.

5. Introduction, page 5716, line 3: rewrite this sentence, how is it related to the one

following it.

A: We have rewritten this sentence to make it more related to the following one, i.e., therefore, we undertake PAA as representative organic peroxide to investigate its kinetics and discuss its mechanisms of the heterogeneous reactions on ambient $PM_{2.5}$ as well as mineral dust particles over a wide range of relative humidities (3–90%). We also estimate the contribution of heterogeneous reactions to PAA budget in the atmosphere. As a comparison, we investigate the kinetics of H_2O_2 uptake on $PM_{2.5}$.

6. Introduction, page 5716, line 10: add 'uptake' after 'H_2O_2'

A: We have revised it.

7. Section 2.1, page 5716: reformat by adding name of chemicals first, and then chemical formula inside brackets for consistency. Add the word 'gas' after N_2 and O_2. Add details about the mineral dust samples used

A: We have revised them.

8. Section 2.2.1, page 5717: describe briefly how the concentration of PAA and H_2O_2 was determined in the gas mixture

A: A H_3PO_4 solution (5×10^{-3} M) was used to scrub gaseous peroxide in a glass scrubbing coil. The collection efficiency was 85% for PAA and 100% for H_2O_2 at 277 K (Hua et al., 2008; Liang et al., 2013). The peroxide-containing scrubbing solution was analyzed immediately by an online high-performance liquid chromatography (HPLC, Agilent 1200). We have added these into the revised manuscript.

9. Section 2.2.2, page 5718: Were $PM_{2.5}$ particles collected on the filter subjected to any washing prior to installing in reactor?

A: No, there is no any washing prior to installing the filter.

10. Section 2.2.3, page 5718: replace 'Fig. 1' with 'Figure 1'. Comment on the reactivity of stainless valves towards the gases used relative to PFA valves. Add details about the type of tubing used for gas flow. What is residence time of the gas inside the reactor?

A: We have replaced "Fig.1" with "Figure 1", added the comment of stainless valves' reactivity, and added details about the tubing system. The residence time of the gas inside the reactor is about 2.8 s, and we have added it into the revised manuscript.

11. Section 2.2.3, page 5719, line 8: {C} is better defined as the number of molecules of gaseous peroxide for consistency with its unit.

A: We have redefined the expression as "the concentration of the molecule number of gaseous peroxide".

12. Section 2.3, page 5720: how long does it take to collect a chromatogram? What are the retention times of PAA and H_2O_2 under these HPLC conditions?

A: The time of collecting a chromatogram was 10 min for PAA and 5.0 min for H_2O_2. The retention times of PAA and H_2O_2 were 8.9 min and 4.0 min, respectively. We have added this information into the revised manuscript.

13. Section 2.4, page 5720, line 21: replace 'dispersive' with 'dispersed'

A: We have revised it.

14. Page 5724, line 15-20: rewrite for a better transition to section 3.2

A: We have rewritten this part as "For PAA, however, no data regarding its kinetics on mineral dust has been available in the literature. Therefore, we investigated the heterogeneous reaction of PAA on mineral dust as a comparison of that on $PM_{2.5}$".

15. Page 5726, line 1-3: remove the questions or convert them to introductory sentences where appropriate in the discussion below.

A: We have removed the questions.

16. Page 5727, line 8: replace 'are' with 'is'

A: We have revised it.

17. Page 5728, line 14: replace 'cation' with 'mineral'

A: We have revised it.

18. Table 1: add units in the column headings

A: We have revised it.

19. Figure 2: spell out 'SD'

A: We have replaced "SD" to "standard deviation". We have revised it.

20. Figure 5: start the y-axis at '0' same as Figure 4 for consistency

A: We have revised it.