June 1, 2015

Dear Dr. Prof. Nizkorodov,

Enclosed please find our revised manuscript entitled “Heterogeneous reaction of peroxyacetic acid and hydrogen peroxide on ambient aerosol particles under dry and humid conditions: kinetics, mechanism and implications” (MS. No. acp-2015-70), and reply to you. We have finished the responses to reviewers’ comments and revised our manuscript. The changes relative to the preceding manuscript version are specified as follows:

(1) We have made a detailed description of the experiments, such as the difference of γ_{PAA} on exposed and unexposed $PM_{2.5}$ particles (add Table 1), the experiment time at a certain RH, the retention time of peroxide compounds, the collection of ADS particles, the resuspension apparatus and so on.

(2) We have estimated the lower limit of γ_{PAA} on $PM_{2.5}$, ADS and ATD particles according to the reviewer’s suggestion and added these in Table 3.

(3) We have added Table 4 to list a summary of the RH dependence of γ_{H2O2} on mineral dust in literature.

(4) We have measured the soluble species and elements of $PM_{2.5}$ particles and added Table 5 to show the results.

(5) As per the reviewers’ suggestions, we have used different symbols for γ_{PAA} and γ_{H2O2} values obtained with ascending and descending RHs in Fig. 3 and Fig. 5, respectively.

(6) As per the reviewers’ suggestions, we have used empirical equation to show the best fit instead of connecting the data points in Fig. 4 and Fig. 7, respectively.

(7) As per the reviewers’ suggestions, we have added the ratio of γ_{H2O2} at 90% RH to γ_{H2O2} at 3% RH ($R_{\gamma H2O2}$) on $PM_{2.5}$ particles in Fig. 6.

(8) Technical points and usage errors that the three reviewers pointed out and we found have been corrected in the revised manuscript.

Thanks for your time.

Sincerely yours,

Zhongming Chen and co-authors

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.

Response to Dr. Chen (Referee)

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

This work reported the heterogeneous reaction of peroxyacetic acid (PAA) and hydrogen peroxide (H_2O_2) on ambient fine particles at different relative humidities and found that this heterogeneous reaction could be an important but yet unconsidered loss pathway of gaseous PAA. The work is of interest to atmospheric chemistry community and the results can help to better understand the atmospheric budget of peroxides and their impacts on atmospheric chemistry. In this regard, I would recommend publication of this paper in ACP after the authors fully address the points as follows.

Major revisions:

1. Page 5718 line 25-26: Give a more detailed description of the uptake experiments, e.g., the reaction time for each RH, any treatment of the samples before moving to next RH.

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. The RH was then changed to a different value with no any treatment for the filter samples. The resolution of PAA and H_2O_2 concentration measurements corresponds to the HPLC retention time of PAA and H_2O_2, which is 8.9 min and 4.0 min, respectively. There is no any treatment before moving to the next RH. We have added a detailed description into the revised manuscript.

2. Page 5724 line 4-6: How did the authors conclude that "the larger value of H_2O_2 than that of PAA in low humidity indicated a physical process is important for the uptake of H_2O_2 onto $PM_{2.5}$ when humidity is low"?

A: Thank you for pointing out this. In this study, we suggest that chemical process dominate the uptake of peroxide rather than physical process and $R_{y,PAA}$ is larger than $R_{y,H2O2}$. However, γ_{H2O2} at low RH is larger than γ_{PAA}, we once considered this might suggest the importance of physical process in low humidity. Now, we find this statement is not appropriate and we have deleted it in the revised manuscript.

3. Page 5724 line 9-10: It cannot be seen from Figures 3 and 5 that the measurements

of PAA and H_2O_2 are performed with both increasing and decreasing RH.

A: In the revised manuscript, we have used different symbols for γ values obtained with ascending and descending RHs (see Fig. 3 and Fig. 5).

4. Page 5728 line 24-26: Give the data to support that ADS particles are coated with salts but ATD not.

A: We used ultrasonic method to extract the sulfate ion of ADS and ATD particles. The concentration of SO_4^{2-} in ADS and ATD particles was 20.3 µg mg^{-1} and 0.2 µg mg^{-1}, respectively. The concentration of NO_3^- in ADS and ATD particles was 0.97 µg mg^{-1} and 0.21 µg mg^{-1}, respectively. The concentration of NH_4^+ in ADS and ATD particles was 0.98 µg mg^{-1} and 0.52 µg mg^{-1}, respectively. The concentration of Na^+ in ADS and ATD particles was 5.13 µg mg^{-1} and 0.52 µg mg^{-1}, respectively. We have added these data into the revised manuscript.

5. Page 5729 line 5-7: The conclusion "chemical processes rather than physical processes dominate the heterogeneous reaction of peroxide compounds on $PM_{2.5}$ and aged mineral dust particles" is contrary to that "physical process is important for the uptake of H_2O_2 onto $PM_{2.5}$ when humidity is low" (Page 5724 line 4-6).

A: Thank you for pointing out this. This is the same with Question 2. Due to the previous statement is not so appropriate, we have deleted the latter one.

Minor revisions:

1. Page 5723 line 3 and 8, and Page 5725 line 14: The definition of H_2O is already given on page 5722 line 22.

A: We have deleted the extra definitions.

2. Page 5727 line 17-19: The literature result is not helpful to explain the positive RH dependence of the uptake coefficient of H_2O_2 on $PM_{2.5}$.

A: We have deleted the discussion based on this literature result.

3. English usage needs to be significantly improved (here are just some examples) Page 5715 line 18: delete "on" Page 5716 line 3: "undertook" should be "undertake" Page 5720, line 21: "dispersive" should be "dispersed" Page 5727, line 25: delete "consider".

A: We have corrected the errors in English usage the reviewer pointed out and we found and believe that the English is significantly improved in the revised manuscript.

Response to Anonymous Referee #3

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

1. Concerns regarding estimation of effective particle surface area (A_{es})

Estimation of available surface area (A_{es}, in this manuscript) for heterogeneous reactions is an ongoing challenge in the field. However, I have two broad issues related to the method (described in Section 2.4) used to estimate A_{es}.

The first is related to the use of the filter geometric surface area to approximate A_{es} at high particle loadings (P5721L10–13). From what I understand, the assumption here is that, in the "plateau regime", where Lf no longer changes with particle mass, the affective surface area can be approximated by the geometric surface area. However, in the Bedjanian et al. (ACP 2013) paper that's cited, it is explicitly acknowledged that the geometric surface area is a lower limit for the available surface area, and that uptake coefficients calculated using this value are thus upper limits. I don't think that it's reasonable to simply assume that, in cases where $Lf > Lf_c$, $A_{gs} = A_{es}$.

The second issue concerns differences between the experiments reported here and those reported in the Bedjanian paper (and in other papers looking at gas-dust interactions using flow tube techniques, Knudsen cell, etc.), and the appropriateness of applying the conceptual framework from these latter papers in this study.

In these other types of experiments, a linear increase in γ implies that the addition of more substrate results in a proportional increase in surface area available for uptake (whether the "entire" surface area is available for uptake is another issue entirely: see the Interactive Comment from Anonymous Referee #2 for the Bedjanian *et al.* paper), and a levelling off of γ at high sample masses implies that the gas-phase species can't access all of the sample over the timescale of the uptake experiment (i.e. that uptake is limited by diffusion into the lower layers of the "thick" sample).

In the present work, however, PAA and H_2O_2 are passing directly through the filters and thus theoretically should be passing through, or "accessing", all of the sample, even if it is "thick". So, the plateau regime in these experiments means something else entirely: to me, it implies an issue with particle agglomeration, which is becoming more prominent as more $PM_{2.5}$ is collected on the filter, i.e. that

PAA/H_2O_2 aren't accessing the "interior" of the agglomerations. In my mind, this agglomeration should also be an issue, albeit a lesser one, at lower particle masses.

In short, I think that the "low-mass regime = linear", "high-mass regime = plateau" is too simplistic a conceptual framework to employ here. Indeed, the linear fit to the left-most data points in Figure 2 is questionable at best.

On a more specific note, it isn't clear to me how Equations 10 and 11 (P6722L56) were derived, since Lf wasn't measured for ADS and ATD as a function of particles mass (from what I understand; only two masses were used). This requires explanation, especially if these A_{es} values were used to calculate for these samples.

In summary, I think that the paper would be greatly strengthened by a reevaluation of the approach used to estimate A_{es}. It might be useful to provide estimates of higher and lower bounds for this quantity, and then to calculate the range of associated γ values. In the end, all γ values should be accompanies by a description of the surface area used in their calculation.

A: As you point out, how to accurately estimate the effective surface area (A_{es}) for heterogeneous reactions is a challenge. Brunauer-Emmett-Teller (BET) surface area (A_{BET}) and geometric surface area (A_{gs}) are usually considered to be the upper limit and the lower limit for A_{es} respectively. The uptake coefficient (γ) estimated by the A_{gs} is several orders of magnitude higher than that by A_{BET} (Shen et al., 2013). In the field observations in Beijing, the lifetime of PAA is about 4.1−5.8 h in summer (Zhang et al., 2010; Liang et al., 2013). Taking OH radical reaction, photolysis and deposition into account, the lifetime of PAA is 44.2 h on haze days and 17.6 h on non-haze days, which is much longer than the observed results. Therefore, the heterogeneous reaction is potentially important to the removal of PAA. If we use the total surface area of $PM_{2.5}$ particles by size distribution (A_{ps}) to calculate γ, the corresponding average value of γ_{PAA} is $(1.10\pm0.56)\times10^{-5}$, and the estimated lifetime of PAA is 28.3 h on haze days and 16.6 h on non-haze days. Apparently, this estimated lifetime is 3−7 times of the observations. When using the method in this study to estimate A_{es}, the corresponding average value of γ_{PAA} is $(2.70\pm0.59)\times10^{-4}$, and the estimated lifetime of PAA is 3.0 h on haze days and 7.1 h on non-haze days, which fits well with the observed results. Therefore, although the estimated A_{es} in this study is a lower limit, it is consistent with the actual situation.

Besides, due to the loss of surface area during stacking, A_{ps} are not appropriate to estimate A_{es}. Assume there is no any other process (e.g. agglomeration and deliquesce) occurring during stacking, then we can use a simple cubic packing model to estimate the loss during stacking (Keyser et al., 1993):

$$A'_{ps} = \rho_b S_g (h_e + h_i) \tag{1}$$

$$S_g = \frac{6}{\rho_t d} \tag{2}$$

$$\rho_b = \frac{\pi}{6}\rho_t \tag{3}$$

$$h_e = \frac{d}{2} \tag{4}$$

$$h_i = d(N_L - \frac{1}{2}) \tag{5}$$

$$\mathrm{L} = \frac{A_{ps} - A'_{ps} A_{gs}}{A_{ps}} \times 100\% \tag{6}$$

where A'_{ps} is the total surface area of stacked $PM_{2.5}$ particles per unit geometric area, $cm^2\ cm^{-2}$; ρ_b is the bulk density, $g\ cm^{-3}$; S_g is the specific surface area, $cm^2\ g^{-1}$; h_e is the external thickness of $PM_{2.5}$ particles, cm; h_i is the internal thickness of $PM_{2.5}$ particles, cm; ρ_t is the true density of $PM_{2.5}$ particles, 1.42 $g\ cm^{-3}$ on haze days and 1.96 $g\ cm^{-3}$ on non-haze days; N_L is the number of $PM_{2.5}$ particle layers; L is the loss percentage.

The calculated L is about 22%. Besides, $PM_{2.5}$ particles in Beijing summer contains large portion of soluble inorganic components which are hygroscopic. (see Table 5 in the revised manuscript) shows the components of $PM_{2.5}$ particles in our study. It turns out that the concentration of SO_4^{2-}, NO_3^- and NH_4^+ ions take up 66.6% on haze days and 48.1% on non-haze days. The deliquescence relative humidity (DRH) is suggested to be 79% for $(NH_4)_2SO_4$, 39% for NH_4HSO_4 and 62% for NH_4NO_3 at 298K (Cziczo et al., 1997; Lightstone et al., 2000), and the DRH of $PM_{2.5}$ is even lower than that of the individual salt particles (Seinfeld and Pandis, 2006). Li and Shao (2009) used the transmission electron microscopy (TEM) observation to ascertain that even the most hydrophobic particles (e.g., mineral dust, some organics, fly ash, soot) can be coagulated or coated with hygroscopic components (e.g., nitrates, sulfates) on haze days.

Based on the relative humidity (RH) data during our sampling period, the average

RH during daytime is (63±9)%, ranging from 51% to 91%; and the average RH during nighttime is (83±8)%, ranging from 72% to 94% (website: http://classic.wunderground.com/). Under the condition of such high RH, $PM_{2.5}$ particles might agglomerate severely on the filter, and the gas is difficult to go through the internal layers. In summary, we suggest using the estimation method in this study to calculate the value of A_{es}. Although this A_{es} is probably close to the lower limit, it can fit well with the observation results. The quantification of A_{es} still has large uncertainty. How to estimate the precise value of A_{es} is still a challenge. More works are still needed in future researches.

Although the experiment method in this study is different from that used by Bedjanian et al., a mass-dependent uptake of peroxides was evidently observed. Specifically, the uptake of peroxides increases linearly with mass in low mass regime and is independent of the mass in high mass region.

The agglomeration of particles on the filter has a strong impact on A_{es} of particles for the uptake of peroxides. In the low-mass regime, agglomeration of particles is not important, and the uptake is linearly correlated with the particle mass. As the particle mass keep growing, the agglomeration of particles becomes gradually important, and the increase of A_{es} with the particle mass is less effective than that in the low-mass regime. When the particle mass reaches a critical mass, the particles agglomerate severely with each other, and the A_{es} of particles does not increase apparently with the particle mass but rather approach a plateau. Therefore, a conceptual framework for the estimation of A_{es} similar to the study by Bedjanian et al. can be applied to the present study.

We have measured the Lf of ADS and ATD as a function of mass, i.e., 0.18, 0.37, 0.81, 1.05, 1.16, 1.63, 1.86 and 2.46 mg for ADS and 0.27, 0.48, 0.83, 1.07, 1.36, 1.58, 1.76, 2.02, 2.57 and 3.00 mg for ATD. We have added these into the revised manuscript.

As per your suggestion, we have used A_{ps} of $PM_{2.5}$ particles to and A_{BET} of ADS and ATD particles to estimate the lower limit of γ on the corresponding particles. The results are listed in Table 3 (in the revised manuscript).

Scientific/technical comments and questions

1. P5716L23, were these aqueous solutions?

A: Yes, they are aqueous solutions. We have changed “solution” to “aqueous solution”.

2. P5717L10, how were the concentrations of PAA/H_2O_2 determined? Reference should be made here to Section 2.3.

A: H_3PO_4 solution (5×10^{-3} M) was used to scrub gaseous peroxides in a glass scrubbing coil. The collection efficiency was 85% for PAA and 100% for H_2O_2 (Hua et al., 2008; Liang et al., 2013). Then the peroxide-containing scrubbing solution was rapidly sent to an online high-performance liquid chromatography (HPLC) instrument. The method was described in detailed in Sect. 2.3.

3. P5718L6, how were the ADS particles collected?

A: ADS particles were collected at PKU campus in April 17, 2006 after a strong dust storm. The ADS particles deposited on a glass plate and then were collected and kept in a glass bottle. We have added this information into the revised manuscript.

4. P5718L8, a brief description of the resuspension apparatus (rotating brush generator?) should be provided.

A: We have added the description of resuspension apparatus in the revised manuscript as “The resuspension apparatus consists of three parts, i.e., glass inlet, stainless filter holder and vacuum pump. First, we put a known amount of mineral dust particles into the glass inlet and then turned off the inlet. Secondly, we turned on the vacuum pump and a negative pressure was then formed in this resuspension system. Finally, we turned on the inlet, and the particles were resuspended with the help of airflow and collected onto the filter”.

5. P5718L25, some information regarding the timescale/resolution of an uptake measurement should be provided here. If the RH was “continuously” increasing, then presumably the uptake values shown in Figure 3 were obtained over a range of RH? Or, was the RH stepped to the values shown in Figure 3, and then held at those values for long enough to achieve (and measure) a steady-state peroxide concentration (and thus steady-state uptake coefficient)? How often were measurements of peroxide concentrations made?

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. The RH was then changed to a different value with no any treatment for the filter samples. The resolution of PAA and H_2O_2 concentration measurements corresponds to the HPLC retention time of PAA and H_2O_2, which is 8.9 min and 4.0 min, respectively, and the concentrations of PAA and H_2O_2 are measured every 10 min and 5 min, respectively. We have added a detailed description into the revised manuscript.

6. P5722L18-20, if the uptake coefficient is scaled to A_{es}, why would there be dependence on $PM_{2.5}$ mass?

A: We didn't state the uptake coefficients are dependent on $PM_{2.5}$ mass. What we said is that although the $PM_{2.5}$ mass varied significantly on haze days and non-haze days, there was no obvious difference between the uptake coefficients.

7. P5722L21, I would suggest plotting this empirical fit in Figure 4 rather than just connecting the mean uptake values (and would suggest the same for Figure 5).

A: Yes. We have revised it and combined the previous two figures into one (see Fig. 4 in the revised manuscript).

8. P5723L13-16, the El Zein et al. (JPCA) paper cited here reported an inverse dependence of the initial γ value, rather than the steady-state value, on relative humidity. In addition, the steady-state uptake coefficients reported in this study were calculated using BET surface areas. So I'm not sure how appropriate this comparison is from both a qualitative/quantitative perspective.

On this note, I would suggest including a summary table showing how the uptake coefficients/RH dependencies obtained in this study fit into those obtained previously.

A: We have deleted the comparison here. We have added a summary table showing the value of γ_{H2O2} and its RH dependence on mineral dust in literature data. Table 4 (in the revised manuscript) shows the summary of γ_{H2O2} and its RH dependence on mineral dust in literature data. Apart from γ_{H2O2} on authentic Gobi dust, authentic Saharan dust and aged particles, all γ_{H2O2} values show a negative RH dependence.

9. P5723L17, to me, it looks as though the samples obtained on haze days were much more variable than those obtained on non-haze days.

A: Yes, the $R_{\gamma PAA}$ values are more variable on haze days than those obtained on non-haze days. However, by taking an average, $R_{\gamma PAA}$ has no obvious difference at different times and under different weather conditions. We have changed as

“Although the $R_{\gamma PAA}$ values are more variable on haze days than those obtained on non-haze days, the average value of $R_{\gamma PAA}$ show no obvious difference at different times and under different weather conditions”.

10. P5723L17-22, were uptake measurements of both PAA and H_2O_2 made on the same samples? I_S it possible that previous exposure of samples to PAA could have influenced H_2O_2 uptake? If not, which samples were used for H_2O_2 uptake measurements? Or, were PAA/H_2O_2 uptake measurements made simultaneously? This needs to be clarified in the text.

A: Yes, the uptake coefficients of PAA and H_2O_2 were measured on the same $PM_{2.5}$ samples. We measured the uptake coefficients of PAA first, and then those of H_2O_2. We have compared the measured uptake coefficient of H_2O_2 on two $PM_{2.5}$ samples: one had been used to measure the uptake coefficient of PAA and the other had not been used for any measurements. The results showed that the relative error between γ_{H2O2} on these two samples was 0.97−7.37% at different RH (3−90%). Therefore, there is no obvious difference between the uptake coefficients of H_2O_2 on used and unused $PM_{2.5}$ samples. We have added a detailed description of this into the revised manuscript.

11. P5724L4-6, I don’t see how the larger value of γ for H_2O_2 at lower RH implies a physical process.

A: Thank you for pointing out this. In this study, we suggest that chemical process dominate the uptake of peroxide rather than physical process and $R_{y,PAA}$ is larger than $R_{y,H2O2}$. However, γ_{H2O2} at low RH is larger than γ_{PAA}, we once considered this might suggest the importance of physical process in low humidity. Now, we find this statement is not appropriate and we have deleted it in the revised manuscript.

12. P5724L9-10, what do the error bars in Figure 3 represent, exactly? If there are only two data points (ascending and descending RH values), I think that the spread in data would be better represented using different symbols for the ascending/descending γ values.

A: These error bars represent relative standard deviation of γ_{PAA} values on $PM_{2.5}$ with the ascending and descending RH. In the revised manuscript, we have used different symbols for γ values obtained with ascending and descending RHs (see Fig. 3 in the revised manuscript).

13. P5725L1, again, what do these errors represent? In addition, these values appear

to be for ADS_l. The PAA uptake coefficient for ADS_h at 3% RH is higher than that for ADS_l, while the opposite is true for ATD (i.e. the uptake coefficient for ATD_l is higher than that for ATD_h). If these uptake coefficients are scales to A_{es} (or some proxy for it), then why are the values for high/low loadings so different?

A: These errors represent standard deviation of γ on mineral dust of the ascending and descending RH. The difference of γ between ADS_l, ADS_h and ATD_l, ATD_h are mainly caused by two reasons: the uncertainty of the A_{es} estimation and the experimental error. We have calculated the uptake coefficients of peroxides on ADS and ATD by the BET area to represent its lower limit in the revised manuscript (see Table 3).

14. P5725L18, "The value of γ_{H2O2} on ADS changed from $(1.25\pm0.5)\times10^{-4}$ at 3% RH to $(4.54\pm0.12)\times10^{-4}$ at 90% RH". I don't see this trace on Fig.7 at all! In addition, the presentation of values for both "high" and "low" dust loadings is confusing in the absence of explanation of differences/similarities between results obtained at the surface of these samples.

A: This value is the average of γ_{H2O2} values at low and high mass loading. We have changed it to "By taking the average of γ values at low and high mass loading, γ_{H2O2} on ADS increases from $(1.10\pm0.31)\times10^{-4}$ at 3% RH to $(2.44\pm0.69)\times10^{-4}$ at 90% RH". Although the values of γ_{H2O2} at low and high mass loading are not identical, all γ_{H2O2} values on ADS show a positive correlation with RH, and all γ_{H2O2} values on ATD show a negative correlation with RH. We have added this information and an explanation of the differences/similarities of γ values into the revised paragraph.

15. P5727L7, does this value represent a bulk pH? It may be possible that some individual particles are basic, and that measured uptake to $PM_{2.5}$ is an average value that includes contributions from both unreactive and reactive particles types.

A: Yes, this value is a bulk pH. We have measured compositions of $PM_{2.5}$ (see Table 5 in the revised manuscript). The concentrations of acidic ions such as SO_4^{2-} and NO_3^- make up 60.9% of $PM_{2.5}$ on haze days, and 41.3% on non-haze days. Even though there are some basic components, we believe they are already neutralized or acidified. However, in any cases, the measured uptake to $PM_{2.5}$, as you pointed out, is an average value that includes contributions from both unreactive and reactive particles types.

16. P5728L1-2, is there a reference for this?

A: Thank you for pointing out this. We have added a reference to the revised manuscript.

17. P5728L14, the Rubasinghege et al. paper looks at the acid-induced dissolution of α-FeOOH in solutions (PH 2) of HNO_3, HCl, and H_2SO_4, and investigates the effect of the anion on dissolution. Would these effects still be valid at the pH values in the aerosol samples used in these experiments?

A: Rubasinghege et al. (2010) have pointed out that in the presence of light, acids with pH=2 promote iron dissolution. While in the dark, the total iron dissolution is related to the strength and coordination mode of anions. Because sulfate and nitrate are both polyatomic oxyanions, they have bidentate and bridging coordination mode, and both of these modes can enhance iron dissolution. In our study, we detected high concentration of SO_4^{2-} and NO_3^- in $PM_{2.5}$ and ADS particles, and our study was carried out in the absence of light. Therefore, we think the presence of SO_4^{2-} and NO_3^- in $PM_{2.5}$ and ADS particles can potentially enhance iron dissolution.

We have changed the sentence "anions can enhance the dissolution of Fe cation" to "anions can potentially enhance the dissolution of Fe cation".

18. P5729L8-10, I think that this statement is too definitive, and should be qualified somewhat, since no specific direct evidence for each of these pathways exists.

A: We have added "probably" into this statement to make it less definitive.

19. P5731L16-20, I am not sure that I understand the purpose of this passage. Presumably these larger particles are of crustal origin and contribute to PAA uptake?

A: The estimation of mean diameter of $PM_{2.5}$ is based on the literature. This literature only measured the size distribution of PM_1. So, this passage aimed to evaluating the contribution of PM_1-$PM_{2.5}$ to the total mean diameter of $PM_{2.5}$.

Minor typos/usage errors

1. P5714L6, "the aerosols" should perhaps read "aerosol-phase processes"?

Also, it's not entirely clear to me from this sentence what the field observations suggest: that PAA is important? That the PAA budget is potentially influenced by aerosol processes? I'm assuming you mean the latter, but the sentence should be revised to make this clearer.

A: We have changed "the aerosols" to "aerosol-phase processes". The field studies have suggested that PAA is important organic peroxide with typical concentration of several tens to hundreds of pptv, and its budget in the atmosphere is potentially influenced by aerosol processes. We have rewritten the sentence to make it clearer.

2. P5714L7, “onto the ambient” should read “onto ambient”

A: We have revised it.

3. P5714L9, “at the uptake coefficient” should read “with an uptake coefficient”

A: We have revised it.

4. P5714L14, I would specify that mineral dust is one of the main components of $PM_{2.5}$ “in this region”

A: We have changed the previous sentence to “Considering that mineral dust is one of the main components of $PM_{2.5}$ in Beijing”.

5. P5715L10-15, to my understanding, the Mao et al. and Liang et al. articles cited here focus primarily on the influence of HO_2 uptake (and, specifically, on HO_2 uptake mechanism that don’t produce H_2O_2). I think that inclusion of these papers-and, by extension, the transition metal-catalyzed HO_2 uptake story- here is somewhat of a distraction.

A: We have deleted the Mao et al. and Liang et al. articles here.

6. P5715L15-20, with reference to the previous comment, what do these studies show regarding the relative contribution of direct H_2O_2 uptake to H_2O_2 concentrations (i.e. vs. HO_2-mediated H_2O_2 loss)? I think that it would make sense here to more clearly describe the conclusions of the studies that have “ascertained the importance” of this process.

A: Thank you for your constructive suggestion. We have revised it as “a series of laboratory studies have addressed the importance of the heterogeneous reaction of H_2O_2 on model or authentic mineral dust particles (Pradhan et al., 2010a; Pradhan et al., 2010b; Wang et al., 2011; Zhao et al., 2011a; Zhao et al., 2011b; Romanias et al., 2012; Zhou et al., 2012; Romanias et al., 2013; Zhao et al., 2013; El Zein et al., 2014). For example, Pradhan et al. (2010a) have indicated that the heterogeneous reaction of H_2O_2 on dust aerosols could compete with its photolysis and significantly affect HO_x radical budget. Romanias et al. (2012, 2013) have confirmed that the heterogeneous reaction of H_2O_2 on mineral dust had an important effect on the fate of HO_x radicals. El Zein et al. (2014) also suggested that the lifetime of H_2O_2 removed by heterogeneous reaction was comparable with its photolysis on severe dust storm period. Our recent study has indicated that H_2O_2 could enhance the uptake of oxygenated volatile organic compounds (OVOCs) onto the surface of mineral dust particles (Zhao et al., 2014)".

7. P5715L16, "on the model" should read "on model"

A: We have revised it.

8. P5715L28, this is too broad: which temperate areas?

A: We have changed "temperate area" to "Mazhuang, a rural site in Shandong Province, China".

9. P5716L1, "that the heterogeneous" should read "that heterogeneous", i.e. "the" is not necessary.

A: We have deleted "the".

10. P5716L3-4, this sentence is awkwardly phrased, and should perhaps be revised to more clearly indicate that PAA is used as representative organic peroxide.

A: We have rewritten this sentence as "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%)".

11. P5716L9, should read "kinetics of H_2O_2 uptake on $PM_{2.5}$"

A: We have revised it.

12. P5716L10, "to ensure the constant" should read "to ensure a constant"

A: We have revised it.

13. P5717L15, "particle loaded" should be read "particle-loaded"-there are also a number of other instances in the manuscript where hyphens are missing from compound adjectives

A: We have revised them.

14. P5717L17, "PKU located" should read "PKU is located"

A: We have revised it.

15. P5718L9, “sampled in” should read “sampled on”

A: We have revised it.

16. P5718L14, “gaseous peroxide” should read “gaseous peroxides”

A: We have revised it.

17. P5718L19-22, I think it would be clearer if this were places after equation 4, since, from what I understand, $[C]_{in}$ in this equation was approximated by $[C]_{out}$, blank.

A: We have moved this sentence to the place after equation 4.

18. P5720L7, “at the flow rate” should read “at a flow rate”

A: We have revised it.

19. P5720L14, “challenge for the γ determination” should be read “challenge for the determination of γ”

A: We have revised it.

20. P5721L22, should this be 4.89×10^{-1}?

A: Yes, we have corrected it.

21. P5722L15-17, this sentence is unclear and should be rephrased.

A: We have rephrased this sentence to make it clearer.

22. P5723L14, “on the ATD” should read “on ATD”.

A: We have deleted “the”.

23. P5726L5, “to the physical processes” should read “to physical processes”.

A: We have deleted “the”.

24. P5728L12, “for the aqueous reaction” should read “for aqueous reactions”.

A: We have deleted “the”.

25. P5728L15, “by the Fe catalysis” should read “by Fe catalysis”.

A: We have deleted “the”.

26. P5728L16, the Mishra reference is missing```but I don’t necessarily think that its conclusions are valid for application here, since PAA/H_2O_2 are weak acids.

A: Thank you for your constructive suggestion. PAA and H_2O_2 are weak acids, so their dissociation is quite limited. We have deleted this citation.

27. P5730L5, “The field observations” should read “Field observations”.

A: We have revised it.

28. P5731L15, what value was used for the mean diameter of the total particles?

A: $\overline{Dp}$ is 114.6 nm for haze days $PM_{2.5}$ particles and 62.4 nm for non-haze $PM_{2.5}$ particles. We have added it into the revised manuscript.

29. P5732L16, “the urban area” should read “urban areas”

A: We have revised it.

30. P5732L21, “from the urban area” should read “from urban areas”; “affecting the oxidants” should read “affecting oxidant”.

A: We have revised them.

31. Figure 5, the y-axis should be expanded (i.e. it should start at zero).

A: We have revised it.

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Heterogeneous reaction of peroxyacetic acid and hydrogen peroxide on ambient aerosol particles under dry and humid conditions: kinetics, mechanism and implications

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Abstract. Hydrogen peroxide (H_2O_2) and organic peroxides play important roles in the cycle of oxidants and the formation of secondary aerosols in the atmosphere. Recent field observations ~~suggest~~have suggested that the budget of peroxyacetic acid (PAA, ~~CH_3~~CH_3C(O)OOH) is ~~one of the most important organic peroxides in the atmosphere, whose budget is~~ potentially related to the ~~aerosols~~aerosol-phase processes, especially to secondary aerosol formation. Here we present the first laboratory measurements of the uptake coefficient of gaseous PAA and H_2O_2 onto ~~the~~ ambient fine particulate matter ($PM_{2.5}$) as a function of relative humidity (RH) at 298 K. The results show that the $PM_{2.5}$, which was collected in an urban area, can take up PAA and H_2O_2 at the uptake coefficient (γ) of 10^{-4}, and both γ_{PAA} and γ_{H2O2} increase with increasing RH. ~~However,~~The value of γ_{PAA} at 90% RH is 5.4 ±1.9 times of that at 3% RH whereas γ_{H2O2} at 90% RH is 2.4 ±0.5 times of that at 3% RH, which suggests that PAA is more sensitive to the RH variation than is ~~γ_{H2O2}, which indicates~~H_2O_2. Considering the larger Henry's law constant of H_2O_2 than that of

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PAA, while the less RH sensitivity of H_2O_2, we suggest that the enhanced uptake of peroxide compounds on $PM_{2.5}$ under humid conditions is dominated by chemical processes rather than dissolution. Considering that mineral dust is one of the main components of $PM_{2.5}$ in Beijing, we also determined the uptake coefficients of gaseous PAA and H_2O_2 on authentic Asian Dust Storm (ADS) and Arizona Test Dust (ATD) particles. Compared to ambient $PM_{2.5}$, ADS shows a similar γ value and RH dependence in its uptake coefficient for PAA and H_2O_2, while ATD gives a negative dependence on RH. The present study indicates that in addition to the mineral dust in $PM_{2.5}$, other components (e.g., inorganic soluble salts) are also important to the uptake of peroxide compounds. When the heterogeneous reaction of PAA on $PM_{2.5}$ is considered, its atmospheric lifetime is estimated to be 3.~~3~~0 h on haze days and 7.~~6~~1 h on non-haze days, values which ~~agree well~~are in good agreement with the field ~~observed result~~observations.

1 Introduction

Peroxide compounds, including hydrogen peroxide (H_2O_2) and organic peroxides, play an important role in the chemistry of the atmosphere, because they serve as oxidants for the conversion of S(IV) to S(VI) in the atmospheric aqueous phase, resulting in the formation of sulfate aerosol (Calvert et al., 1985; Lind et al., 1987; Stein and Saylor, 2012). Peroxide species also serve as a reservoir for HO_x (OH and HO_2) radicals (Wallington and Japar, 1990; Vaghjiani et al., 1990; Atkinson et al., 1992; Ravetta et al., 2001) and RO_x (RO and RO_2) radicals (Lightfoot et al., 1991; Reeves and Penkett, 2003). Moreover, recent laboratory studies have indicated that peroxide compounds, especially organic peroxides, significantly contribute to the formation and aging of secondary organic aerosols (SOA) (Claeys et al., 2004; Docherty et al., 2005; Surratt et al., 2006; Paulot et al., 2009; Huang et al., 2013; Xu et al., 2014).

The ~~atmospheric concentration of~~ peroxide compounds ~~depends on~~ are mainly produced by the bimolecular reaction of HO_2 and RO_2 radicals (e.g. R1 and R2), and their minor sources ~~and sinks.~~include the ozonolysis of alkenes and biomass burning

(Lee et al., 2000).

$$HO_2 + HO_2 (+ H_2O) \rightarrow H_2O_2 + O_2 \tag{R1}$$

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

Their traditional removal pathways include reacting with OH radicals, photolysis and deposition (Lee et al., 2000). Recent studies ~~that~~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 ~~Arctic troposphere,~~ subtropical island~~, and urban atmospheres~~, the concentration of gaseous H_2O_2 was largely overestimated by a standard gas-phase chemical mechanism~~, whereas~~. Whereas when the heterogeneous uptake of H_2O_2 and/or HO_2 radicals on the surface of aerosols was accounted for in the model, the observed and modeled values were in better agreement ~~(de Reus et al., 2005; Mao et al., 2010; Liang et al., 2013). A~~. In addition, a series of laboratory studies have ~~ascertained~~addressed the importance of the heterogeneous reaction of H_2O_2 on ~~the~~ model or ~~on~~ authentic mineral dust particles (Pradhan et al., 2010a; Pradhan et al., 2010b; Wang et al., 2011; Zhao et al., 2011a; Zhao et al., 2011b; Romanias et al., 2012; Zhou et al., 2012; Romanias et al., 2013; Zhao et al., 2013; El Zein et al., 2014). For example, Pradhan et al. (2010a) have indicated that the heterogeneous reaction of H_2O_2 on dust aerosols could compete with its photolysis and significantly affect HO_x radical budget. Romanias et al. (2012, 2013) have confirmed that the heterogeneous reaction of H_2O_2 on mineral dust had an important effect on the fate of HO_x radicals. El Zein et al. ~~) and our~~(2014) also suggested that the lifetime of H_2O_2 removed by heterogeneous reaction was comparable with its photolysis on severe dust storm period. Our recent study has indicated that H_2O_2 could enhance the uptake of oxygenated volatile organic compounds (OVOCs) onto the surface of mineral dust particles (Zhao et al., 2014).

To the best of our knowledge, to date, there has been no laboratory experimental evidence for the importance of the heterogeneous reactions of organic peroxides in the atmosphere. As an important organic peroxide, peroxyacetic acid (PAA, ~~CH_3~~CH_3C(O)OOH) has been frequently ~~been~~ detected over both rural and urban

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areas (Lee et al., 1995; Hua et al., 2008; He et al., 2010; Zhang et al., 2010; Liang et al., 2013; Phillips et al., 2013). The typical concentration of PAA is comparable to that of H_2O_2, i.e., several tens to hundreds of pptv in summer, and the maximum concentration surpasses 1 ppbv over the ~~temperate area~~Mazhuang, a rural site in Shandong Province, China (Zhang et al., 2010) and the boreal forest (Phillips et al., 2013). Our field ~~measurements of atmospheric peroxides~~observation results have suggested that~~ the~~ heterogeneous reactions on aerosol particles might be an important removal pathway for PAA in the atmosphere (Zhang et al., 2010; Liang et al., 2013). ~~We therefore undertook a study of~~Therefore, we undertake PAA ~~concerning the heterogeneous reactions of~~as representative organic ~~peroxides on aerosol particles. In the present study, we~~ peroxide to investigate the kinetics and ~~discuss~~ mechanisms of ~~the~~its heterogeneous reactions ~~of gaseous PAA~~ on ambient $PM_{2.5}$ as well as mineral dust particles over a wide range of relative ~~humidity values~~humidities (3–90%). We ~~have~~ also ~~estimated~~estimate the contribution of heterogeneous reactions to ~~the~~ PAA budget in the atmosphere. As a comparison, we ~~also~~ investigate the kinetics of H_2O_2 uptake on $PM_{2.5}$.

2 Experimental

2.1 Reagents and materials

Hydrogen peroxide (H_2O_2~~ (~~, Alfa Aesar, 35% water solution), acetic acid (CH_3COOH, Xilong Chemical Co., LTD, 99.8%), and sulfuric acid (H_2SO_4, Beijing Chemical Plant, 95–98%) were used to prepare the PAA solutions. *Ortho*-Phosphoric acid (H_3PO_4, Fluka, 85%); hemin (Sigma, ≥ 98%), *p*-hydroxyphenylacetic acid (POPHA~~) (~~, Alfa Aesar, 99%), ammonia solution ($NH_3{\cdot}H_2O$, Beijing Tongguang Fine Chemicals Company, 25.0–28.0%), ammonium chloride (NH_4Cl, Beijing Chemical Works, ≥ 99.5%), N_2 ~~(≥~~gas (≥ 99.999%, Beijing Haikeyuanchang Practical Gas Company Limited, Beijing, China), O_2 ~~(≥~~gas (≥ 99.999%, Beijing Haikeyuanchang Practical Gas Company Limited, Beijing, China) and polytetrafluoroethylene (PTFE) filter membrane (Whatman Inc., ~~46.2~~47 mm in diameter) were also used in the experiments. Asian Dust Storm particles (ADS

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particles, the BET surface area is 6.1 m^2 g^{-1}) and Arizona Test Dust particles (ATD particles, Al Ultrafine test dust, Powder Technology, the BET surface area is 16.5 m^2 g^{-1}) were used. ADS particles were collected at PKU campus in April 17, 2006 after a strong sand storm. The ADS particles deposited on a glass plate and then were collected and kept in a glass bottle.

2.2 Apparatus and procedures

2.2.1 Generation of gaseous PAA and H_2O_2

PAA aqueous solution was synthesized by mixing H_2O_2 aqueous solution with acetic acid aqueous solution, using H_2SO_4 as a catalyst (Dul'neva and Moskvin, 2005; Zhao et al., 2007). The mixing aqueous solution was kept in the dark for 24 h at room temperature to make sure PAA reached its maximum balanced concentration. The PAA concentration in this primary solution (S1) was 1.3 M, which was stored at 277 K in the dark before use. At the beginning of every experiment, a PAA solution (S2) (4×10^{-5} M) was prepared by diluting S1 with ultrapure water and then 100 mL S2 was added into a 1 L bubbler. The S2 in the bubbler, kept in a 277 K water bath in the dark, was bubbled by a N_2 flow at a rate of 70 mL min^{-1} to generate gaseous PAA. The PAA-containing N_2 flow was then mixed with an O_2 flow and water vapor flow generated by another bubbler. The resulting gas mixture (reactant gas) was introduced into the filter-based flow reactor as described in ~~Sect.~~Section 2.2.3. 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). The method was described in detailed in Section 2.3. The concentration of PAA was 300±30 pptv in the gas mixture. To ensure ~~the~~a constant concentration of gaseous PAA, the bubbling solution of PAA was renewed every day. The generation of gaseous H_2O_2 was similar to that of PAA. The concentration of the bubbling solution of H_2O_2 was 1.14×10^{-3} M. The resulting H_2O_2 concentration was 510±40 pptv in the gas mixture.

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2.2.2 Preparation of particle~~-~~-loaded filters

The PM$_{2.5}$ samples were collected on the roof of a six-story teaching building (26 m above the ground) at the campus of Peking University (PKU), Beijing, China. PKU is located in the northwest downtown area, with two major traffic arteries passing by. An ambient particulate sampler (TH–16A, Wuhan Tianhong Instruments Co., Ltd) was used to collect the PM$_{2.5}$ particles on the PTFE filters with four parallel channels operating simultaneously and the sampling flow of each channel was 16.7 standard L min^{-1}. The PM$_{2.5}$ samples were collected for 6 days, from 31 July ~~31st,~~ 2014 to 6 August~~ 6th,~~ 2014. Sampling was conducted twice a day for 11.5 h each time (daytime, 9:00–20:30 LT; nighttime, 21:00–08:30 LT). During the sampling period, 31 July ~~31st~~ to 3 August ~~3rd~~ were haze days and 3 August ~~3rd~~ to 5 August ~~5th~~ were non-haze days. Haze is caused by a large amount of fine particles (e.g. dust, smoke, salt) with RH less than 90% and makes the visibility less than 10 km (Li, 2010). Here, we differentiated non-haze days from haze days based on two criteria. One was the visibility of a mountain (by eye) which is about 10 km away from the sampling site. The other was the national ambient air quality standard grade II in China, i.e., average PM$_{2.5}$ mass concentration of lower than 75 μg m^{-3}. The PM$_{2.5}$ particle-loaded filters were sealed and kept at 255 K before use. ~~Asian Dust Storm (~~ADS~~)~~ and ~~Arizona Test Dust (~~ATD~~)~~ particles were separately used to prepare the mineral dust particle~~-~~-loaded filters.~~ ADS particles were collected at PKU campus in April 2006 and kept in a glass bottle in the dark.~~ Mineral dust particles were resuspended using a custom-built resuspension apparatus and then collected on the PTFE filters. The resuspension apparatus consists of three parts, i.e., glass inlet, stainless filter holder and vacuum pump. First, we put a known amount of mineral dust particles into the glass inlet and then turned off the inlet. Secondly, we turned on the vacuum pump and a negative pressure was then formed in this resuspension system. Finally, we turned on the inlet, and the particles were resuspended with the help of airflow and collected onto the filter. To compare the experimental results for PM$_{2.5}$ sampled ~~in~~on non-haze and haze days, the mass of ADS ~~and~~or ATD on the

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filter was carefully controlled at 0.3 mg and 1.~~4~~3 mg for the lower and higher ~~mineral dust~~particle mass~~ values~~, respectively.

2.2.3 Uptake experiments

A filter based flow reactor was used to measure the uptake coefficients of gaseous ~~peroxide~~peroxides on aerosol particles. The schematic of this experimental apparatus is shown in ~~Fig.~~Figure 1. The reactor is composed of two perfluoroalkoxy resin filter holders (Savillex Corporation) connected in parallel. One reactor contains a blank PTFE filter, and the other contains a particle~~–~~-loaded filter. The tubing system is made of Teflon tubes. The peroxide containing gas mixture (20% O_2 + 80% N_2) was used at a flow rate of 2.7 standard L min^{-1} and was introduced into the blank reactor or the particle~~–~~-loaded reactor via two unreactive stainless steel valves. ~~Since no obvious uptake of peroxide on the blank filter occurred, the reactant concentration at the outlet of the blank reactor can be treated as the initial concentration at the inlet of the reactor for the uptake on aerosols.~~ After exiting the reactor, the peroxide containing gas was directed into a glass scrubbing coil in a 277 ±0.1 K water bath, in which a H_3PO_4 solution (5×10^{-3} M) was used as the eluent to scrub the peroxide at a rate of 0.2 mL min^{-1}. The same particle~~–~~-loaded filter was used to measure the uptake coefficient at a continuously increasing RH ranging from 3% to 90% and then the measurement was repeated in reverse, at a decreasing RH from 90% to 3%. We have compared the uptake coefficients of PAA on the exposed $PM_{2.5}$ filter which has been used in the PAA uptake experiments and the unexposed $PM_{2.5}$ filter which has not been used for any experiments at 60% RH, and no obvious difference was observed between the two uptake coefficients (Table 1). Therefore, we think the reuse of the filter for experiments at different RH has no significant effect on the results.

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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. Then the RH was directly changed to another RH without any treatment for the filter samples. All the experiments were conducted at 298 ±2 K, ambient pressure

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and in the dark.

The uptake coefficients of gaseous peroxide can be calculated using the following equations (Molina et al., 1996; Zhao et al., 2010):

$$\gamma=\frac{d\{C\}/dt}{Z} \tag{1}$$

$$Z=\frac{1}{4}\omega A_{es}[C] \tag{2}$$

$$\omega=\sqrt{\frac{8RT}{\pi M_x}} \tag{3}$$

where $\{C\}$ is the total uptake of gaseous peroxide by particle surfaces, molecules; Z is the collision frequency, molecules s^{-1}; $[C]$ is the ~~gaseous~~ concentration of the molecule number of gaseous peroxide, molecules m^{-3}; ω is the mean molecular speed, m s^{-1}; R is the universal gas constant, kg m^2 s^{-2} mol^{-1} K^{-1}; T is the Kelvin temperature, K; A_{es} is the effective surface area of particles, m^2; M_x is the molecular weight, kg mol^{-1}. The uptake onto the particles is equal to the loss of the gaseous reactant and this gas phase loss can be calculated by the difference between the reactant concentrations at the inlet and outlet of the reactor. Here, we ~~defined~~define the fractional loss of the reactant (Lf) as Eq. (4):

$$Lf=\frac{[C]_{in}-[C]_{out}}{[C]_{in}} \tag{4}$$

where $[C]_{in}$ and $[C]_{out}$ is the concentration of the reactant at the inlet and outlet of the reactor, molecules m^{-3}, respectively. Since no obvious uptake of peroxide on the blank filter occurred, the reactant concentration at the outlet of the blank reactor can be treated as the initial concentration at the inlet of the reactor for the uptake on aerosols. Therefore, Eq. (1) can be expressed as Eq. (5):

$$\gamma=\frac{4\times Lf\times V_g}{\omega A_{es}} \tag{5}$$

where V_g is the flow rate of the reactant containing gas, m^3 s^{-1}. The values of γ on

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$PM_{2.5}$, ADS and ATD particles in the next test are calculated by the A_{es} estimated in Section 2.4.

2.3 Analysis of Peroxides, Soluble Species and Elements

Peroxide compounds were measured by ~~high performance liquid chromatography (~~HPLC~~, Agilent 1200)~~ coupled with a post-column derivatization module. The length of the column is 150 mm (Alltima AQ 5μ). The details of this method have been reported in our previous study (Hua et al., 2008). Briefly, this method is based on the determination of the fluorescent dimer produced by the reaction of POPHA and peroxides with the catalysis of hemin. The HPLC mobile phase was H_3PO_4 solution (pH=3.5) at ~~the~~a flow rate of 0.5 mL min^{-1}. The formed fluorescent dimer was analyzed by a fluorescence detector. 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 used ultrasonic method to extract the soluble compounds in particles samples. Each sample was ultrasonic in ice water with 10 mL Milli-Q water for 30 min. The extracted soluble compounds were measured by ion chromatography (IC, Dionex ICS2000 and ICS2500). The analytical column for cation and anion was Dionex CS 12A and Dionex AS 11, respectively. Here, the measured compounds include eight inorganic ions (i.e., K^+, Ca^{2+}, Na^+, Mg^{2+}, NH_4^+, Cl^-, NO_3^- and SO_4^{2-}) and four organic acids (i.e., formic acid, acetic acid, pyruvic acid and oxalic acid).

We used acid digestion to extract elements in particles through microwave digestion system (CEM MARS, USA). Elements in the extractions were measured by inductively coupled plasma mass spectroscopy (ICP-MS, Thermo X series). The measured elements include Na, Mg, Al, P, K, Ca, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Se, Mo, Cd, Ba, Tl, Pb, Th and U.

2.4 Estimation of effective surface area

The effective surface area (A_{es}) is a key factor in the uptake of a specific compound from the gas phase onto aerosol particles. The uptake coefficient (γ) estimated by the geometric filter surface area (A_{gs}) is several orders of magnitude higher than that by the Brunauer-Emmett-Teller (BET) surface area (Shen et al., 2013). To date, accurate estimation of A_{es} of the particle sample has been a challenge for the ~~γ~~ determination of γ. Bedjanian et al. (2013) have measured the uptake of HO_2 radicals on ATD particles and showed a pseudo-logarithmic relationship between the uptake and the particle mass. ~~They have suggested that in the high mass region where uptake coefficient was independent of particle mass, the geometric surface area could be used to calculate the uptake coefficients. In the present study, the~~In the present study, ambient particles were loaded on the filter in an agglomerated state, extremely different from their status in the atmosphere, where they are highly ~~dispersive~~dispersed. Obviously, both the geometric surface area and the BET surface area can not represent the A_{es} of the ambient particle samples on the filter. Here~~,~~ we estimated A_{es} by investgating the relationship between the uptake and loaded particle mass. ~~Equation~~Eq. (5) shows that the fractional loss (Lf) of a specific gaseous reactant due to the uptake of the filter-loaded particles was directly proportional to A_{es}. The value of A_{es} should depend on the loaded particle mass. Therefore, we used the relationship between Lf and particle mass (M_a) to estimate the value of A_{es}. Figure 2 shows the relationship between the Lf of gaseous PAA ~~vs.~~versus the loaded particle mass. Although Lf appeared to have a linear relationship with particle mass in the low particle mass region, it generally fitted with the logarithmic function of particle mass, with a correlation coefficient r=0.88. This empirical logarithmic relationship is given in ~~Eq~~Eqs. (6) to (8):

For $PM_{2.5}$ $$Lf=0.15\times ln\,(\cancel{M_a}M_a) + 0.47 \qquad (6)$$

For ADS $$Lf=0.099\times \ln\,(M_a) + 0.26 \qquad (7)$$

For ATD $$Lf=0.058\times \ln(M_a)+ 0.20 \qquad (8)$$

where M_a is the mass of the particles, mg. The mass used for measuring the Lf of ADS is 0.18, 0.37, 0.81, 1.05, 1.16, 1.63, 1.86 and 2.46 mg, respectively. The mass for measuring the Lf of ATD is 0.27, 0.48, 0.83, 1.07, 1.36, 1.58, 1.76, 2.02, 2.57 and 3.00 mg, respectively. In the low particle mass region, the particles were highly

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dispersed on the filter and A_{es} increased rapidly with increasing particle mass; ~~at~~in high particle mass ~~values, because the~~region, particles highly overlapped and agglomerated with each other on the filter, and A_{es} was ~~similar~~closer to ~~the~~ A_{gs} ~~of the filter.~~(12.43 cm^2). Here, we ~~assumed~~assume that there ~~existed~~exists a critical particle mass ($M_{a,c}$) for which A_{es} is equal to A_{gs}. When the particle mass is greater than $M_{a,c}$, A_{es} tends to be constant, i.e., the A_{gs} ~~of the filter (Bedjanian et al., 2013).~~. For $M_{a,c}$, the corresponding fractional loss of PAA is Lf_c. We use an iterative method to determine $M_{a,c}$. The termination criterion of this iterative method was the relative error (R_{el}) of Lf_c towards the average of all the Lf values ($\overline{Lf}$) which were larger than Lf_c and the calculation method was expressed in Eq. (~~7~~9). Here, we set R_{el} as 5% to terminate the iteration. The procedure of iteration was as follows: (i) start $M_{a,c}$ with 0.10 mg; (ii) calculate a series values of Lf by inputting a range of M_a (0.01 to 2.00 mg) into Eq. (6); (iii) calculate R_{el} by the calculated values of Lf and Eq. (~~7~~9); (iv) if R_{el} is larger than 5%, reset $M_{a,c}$ with an added mass of 0.01 mg (i.e., 0.11 mg); (v) repeat steps (ii-iv) until R_{el} is less than 5%, and then obtain the expected $M_{a,c}$ and Lf_c. The calculated Lf_c was 4.89×10$^{-\cancel{2}1}$, which was similar to the experimental result in Fig. 2., i.e., 4.90×10$^{-\cancel{2}1}$. Based on the directly proportional relationship between A_{es} and Lf, A_{es} can be expressed in Eq. (~~8~~10).

$$R_{el}=\frac{Lf_c}{\overline{Lf}}$$ (~~7~~9)

$$A_{es}=\frac{A_{gs}}{Lf_c}\times Lf$$ (~~8~~10)

The estimation of A_{es} for filter-loaded PM$_{2.5}$, ADS and ATD particles can be expressed as the respective logarithmic functions in ~~Eq. (9), Eq. (10) and Eq.~~Eqs. (11) to (13):

For PM$_{2.5}$ $A_{es}=3.75\times ln\ (\cancel{M_a}M_a)+12.0$ (~~9~~11)

For ADS $A_{es}=3.66\times ln\ (\cancel{M_a}M_a)+9.59$ ~~(10~~ (12)

For ATD $A_{es}=3.01\times ln\text{-}(M_a)\cancel{+}+10.3$ (~~11~~13)

where M_a represents the filter-loaded particle mass, mg. The mass of the filter-loaded

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$PM_{2.5}$ and the estimated A_{es} values are listed in Table ~~1~~2. A_{es} for $PM_{2.5}$ changes with the particle mass, ranging from 3.2–13.8 cm^2; A_{es} for ADS is 6.1 cm^2 and 10.9 cm^2, respectively; A_{es} for ATD is 6.4 cm^2 and 11.2 cm^2, respectively. The uptake coefficients on $PM_{2.5}$ particles, ADS and ATD particles below are all calculated with these A_{es} values.

3. Results and discussion

3.1 Uptake of PAA and H_2O_2 on $PM_{2.5}$

The uptake coefficient of PAA (γ_{PAA}) on ~~filter-loaded~~ $PM_{2.5}$ particles was measured over a wide range of RH~~, from dry condition~~ (3~~% RH) to high humidity (~~–90~~% RH).~~%). Figure 3 shows the γ_{PAA} profile on $PM_{2.5}$ with respect to increasing/decreasing RH. ~~For all the $PM_{2.5}$ samples,~~ γ_{PAA} increases with increasing RH~~; at the same RH,~~ on both daytime and ~~the γ_{PAA}~~ nighttime $PM_{2.5}$ samples. The values~~,~~ of γ_{PAA} on ~~the~~ nighttime $PM_{2.5}$ ~~sample is~~samples are similar to ~~that observed~~those on ~~the~~ daytime $PM_{2.5}$ ~~sample~~samples. Additionally, ~~even though~~although the mass of $PM_{2.5}$ ~~mass~~ collected on a haze day ~~was~~is significantly different from that on a non-haze day, the γ_{PAA} ~~exhibited a~~values are similar ~~value for~~under these two different weather conditions (Table ~~2~~3). In general, γ_{PAA} ~~rose~~rises from $(0.89 \pm 0.26) \times 10^{-4}$ at 3% RH to $(4.41 \pm 0.92) \times 10^{-4}$ at 90% RH. Table 3 also lists the lower limit of γ_{PAA} on $PM_{2.5}$, which are calculated using the total surface area of the particles using size distribution (see the details in Section 4, Eq. 21 and Eq. 22). The lower limit is on the order of 10^{-6}–10^{-5}. The empirical equation of γ_{PAA} plotted against water activity (a_{H2O}; here, a_{H2O} ~~=~~ =RH/100) ~~(Fig. 4)~~ can be expressed as Eq. ~~(12):~~(14) and the measured and modelled γ_{PAA} on $PM_{2.5}$ are shown in Fig. 4.

$$\gamma_{PAA}=\cancel{\frac{4.94\times10^{-5}}{1-0.91\times a_{H2O}^{0.21}}}\frac{4.94\times10^{-5}}{1-0.91\times a_{H2O}^{0.21}} \qquad (\cancel{12}14)$$

~~where a_{H2O} is a variable fraction, e.g. 0.6.~~

We also determined the uptake ~~coefficient~~coefficients of H_2O_2 on $PM_{2.5}$ over the RH range of 3% to 90%. ~~The~~ Before this experiment, we compared the measured

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~~γ_{H2O2} on $PM_{2.5}$ is shown in Fig.~~ uptake coefficients of H_2O_2 on two $PM_{2.5}$ samples, one had been used to measure the uptake coefficient of PAA and the other had not been used for any measurements. The results show that the relative error between the above two experiments was 1.0−7.4% among different RH (3−90%). Therefore, there is no obvious difference between the uptake coefficients of H_2O_2 on used and unused $PM_{2.5}$~~.~~ samples. Figure 5 shows the γ_{H2O2} on $PM_{2.5}$ which had been used to measure γ_{PAA}, over 3−90% RH. The empirical equation of γ_{H2O2} as a function of a_{H2O} can be expressed as Eq. ~~(13):~~(15) and the measured and modelled γ_{H2O2} on $PM_{2.5}$ is shown in Fig. 4.

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$$\gamma_{H2O2}=\cancel{\frac{1.26\times10^{-4}}{1-0.75\times a_{H2O}^{0.055}}}\frac{5.32\times10^{-4}}{1-0.82\times a_{H2O}^{0.13}}$$

(~~13~~15)

~~where a_{H2O} is a variable fraction.~~ The value of γ_{H2O2}, similar to γ_{PAA}, ~~showed~~shows a positive correlation with RH~~, whereas the~~. The average value of γ_{H2O2} ~~at low RH exceeded that of γ_{PAA}. The γ_{H2O2} changed~~changes from (~~3.18~~1.12 ±0.~~07~~20) ×10^{-4} at 3% RH to (~~4.78~~2.70 ±0.~~04~~37) ×10^{-4} at 90% RH. The positive RH dependence of γ_{H2O2} has been reported by Pradhan et al. (2010b). They have measured γ_{H2O2} on authentic mineral dust particles (i.e., Gobi dust particles and Saharan dust particles). ~~However,~~Table 4 summarizes the literature result of γ_{H2O2} and its RH dependence on different type of mineral dust in literature data. Apart from γ_{H2O2} on authentic Gobi dust, authentic Saharan dust and aged particles, all γ_{H2O2} values show a negative RH dependence~~ El Zein et al. (2014) have reported an inverse RH dependence of γ_{H2O2} on the ATD particles. Even though the RH dependence of γ_{H2O2} differs in different particles, its order of magnitude is generally at 10^{-4}, which is comparable to the γ_{H2O2} on $PM_{2.5}$ measured in our study~~.

Figure 6 shows the ratio of $\gamma_{PAA,\ 90\%\ RH}$ to $\gamma_{PAA,\ 3\%\ RH}$ ($R_{\gamma PAA}$~~). The~~) and $\gamma_{H2O2,\ 90\%\ RH}$ to $\gamma_{H2O2,\ 3\%\ RH}$ ($R_{\gamma H2O2}$). Although the $R_{\gamma PAA}$ ~~showed~~values are more variable on haze days than those on non-haze days, the average value of $R_{\gamma PAA}$ shows no obvious difference at different times and ~~in~~under different weather conditions, varying over

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the narrow range of 4.4±0.6 to 6.3±2.7. On average, $R_{\gamma PAA}$ ~~was~~is 5.4±1.9. It is interesting to note that $R_{\gamma H2O2}$ is 2.4±0.5 (see Fig. 6), which is much lower than $R_{\gamma PAA}$. Although γ_{H2O2} ~~had~~has a positive RH dependence on $PM_{2.5}$ as well, H_2O_2 ~~was~~is less sensitive to RH variance compared to PAA. ~~It is interesting to note that the ratio of $\gamma_{H2O2, 90\% RH}$ to $\gamma_{H2O2, 3\% RH}$ ($R_{\gamma H2O2}$) was 1.5±0.1, which is much lower than $R_{\gamma PAA}$.~~ For peroxide compounds, if ~~the~~ physical process, especially the dissolution, ~~dominated~~dominates their uptake on $PM_{2.5}$, the $R_{\gamma H2O2}$ should be larger than $R_{\gamma PAA}$, because the Henry's law constant of H_2O_2 is 100 times that of PAA (298 K) (8.47×10^2 M atm^{-1} for PAA and 8.43×10^4 M atm^{-1} for H_2O_2) (O'Sullivan et al., 1996). This expectation, however, is at odds with our experimental results. Hence, ~~the~~ we speculate that physical process is not the main ~~reason~~pathway for the uptake of peroxide compounds on $PM_{2.5}$~~. However, for H_2O_2, the larger value of γ_{H2O2} than that of γ_{PAA} in low humidity indicated a physical process is important for the uptake of H_2O_2 onto $PM_{2.5}$ when humidity is low~~. In addition, the values of γ_{PAA} and γ_{H2O2} on $PM_{2.5}$ were measured with increasing RH from 3% to 90% and then the measurements were repeated ~~but~~by using the same sample with decreasing RH from 90~~%~~ to 3~~% while using the same sample.~~%. Interestingly, we find that the γ_{PAA} and γ_{H2O2} can be well repeated in these two cases ~~with only small error bars~~ (see Fig. 3 and Fig. 5). The independence of γ_{PAA} and γ_{H2O2} on reaction time also ~~indicated~~indicates that $PM_{2.5}$ ~~had~~has a sustained reactivity for the uptake of peroxide compounds at different ~~levels of humidity~~RH, which falls into the category of reactive uptake as suggested by Crowley et al. (2010). The detailed mechanism is described in ~~Sect.~~Section 3.3.

The present study is the first investigation on the kinetics of the heterogeneous reactions of PAA and H_2O_2 on $PM_{2.5}$ particles. Recent studies have already indicated the importance of mineral dust for H_2O_2 uptake (Pradhan et al., 2010a; Pradhan et al., 2010b; Wang et al., 2011; Zhao et al., 2011a; Zhao et al., 2011b; Romanias et al., 2012; Zhou et al., 2012; Romanias et al., 2013; Zhao et al., 2013; El Zein et al., 2014). ~~In general, the measured γ_{H2O2} on $PM_{2.5}$ in our study were comparable to that~~

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~~measured on those mineral dusts.~~ 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 $PM_{2.5}$.

3.2 Uptake of PAA and H_2O_2 on mineral dust

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Mineral dust is an important component of atmospheric aerosols in Beijing, ~~and~~ it comprises ~~7.1–33.4~~6.0% and 6.2% of $PM_{2.5}$ ~~in different seasons~~on haze days and non-haze days, which is similar to the reported values (7.1%−12.9%) (Sun et al., 2004; Yang et al., 2011; Zhang et al., 2013). To determine whether the mineral dust dominates the uptake of PAA on $PM_{2.5}$, we measured the γ_{PAA} on two kinds of mineral dust particles, i.e., ADS and ATD particles. ~~ADS is a kind of authentic Asian dust collected in Beijing, while ATD is a kind of widely used standard test dust.~~ The measured γ_{PAA} values are listed in Table ~~2. The~~3. γ_{PAA} on low mass ADS ~~increased~~(ADS$_l$) increases from (0.84±0.01)×10^{-4} at 3% RH to (3.21±0.08)×10^{-4} at 90% RH and γ_{PAA} on high mass ADS (ADS$_h$) increases from (1.37±0.02)×10^{-4} at 3% RH to (2.62±0.01)×10^{-4} at 90% RH. On the surface of ATD, however, γ_{PAA} shows a negative RH dependence, from (2.42±0.02)×10^{-4} at 3% RH to (1.17±0.03)×10^{-4} at 90% RH on low mass ATD (ATD$_l$) and decreasing from (1.86±0.01)×10^{-4} at 3% RH to (0.91±0.04)×10^{-4} at 90% RH on high mass ATD (ATD$_h$). Table 3 also lists the lower limit of γ_{PAA} on ADS and ATD, which are calculated by the BET surface area of the particles. The lower limits of γ_{PAA} on ADS and ATD are on the order of 10^{-6}–10^{-5}. The positive correlations between RH and ~~the value of~~ γ_{PAA} on ADS are similar to that on $PM_{2.5}$. Similar positive RH dependence ~~was~~has also been observed for the uptake of H_2O_2 on authentic Gobi dust ~~and~~, Saharan dust (Pradhan et al., 2010b~~). On the surface of ATD, however, γ_{PAA} showed a negative RH dependence, decreasing from (2.42±0.02)×10^{-4} at 3% RH to (0.91±0.04)×10^{-4} at 90% RH.~~) and aged $CaCO_3$ particles (Zhao et al., 2013). This negative RH dependence ~~was~~on ATD is similar to the previously reported γ_{H2O2} on ATD and mineral oxides (e.g. α-Al_2O_3, Fe_2O_3, TiO_2, SiO_2) (Pradhan et al., 2010a; Zhao et al., 2011a; Romanias et al., 2012~~;~~ ~~Romanias et al.;~~, 2013; El Zein et al., 2014). The reasons for the discrepancies in the

RH dependence of γ_{PAA} are discussed in Sect. 3.3. The empirical equation of γ_{PAA} against a_{H2O} on ADS and ATD can be expressed as Eq. (~~14~~16) and ~~Eq. (15~~(17), respectively:

$$\gamma_{PAA}=\cancel{\frac{7.49\times10^{-5}}{1-0.76\times a_{H2O}^{0.25}}}\frac{7.49\times10^{-5}}{1-0.76\times a_{H2O}^{0.25}} \qquad (\cancel{14}16)$$

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$$\gamma_{PAA}=\cancel{\frac{2.18\times10^{-4}}{1+1.08\times a_{H2O}^{1.06}}}\frac{2.18\times10^{-4}}{1+1.08\times a_{H2O}^{1.06}} \qquad (\cancel{15}17)$$

~~where a_{H2O} is a variable fraction.~~

We also determined the uptake coefficient of H_2O_2 on ADS and ATD over the RH range of 3~~%~~ to 90%. The measured γ_{H2O2} on ADS and ATD is shown in Fig. 7. The value of γ_{H2O2}, similar to γ_{PAA}, ~~showed~~shows a positive correlation with RH on ADS particles and a negative correlation with RH on ATD particles. ~~The value~~By taking the average of γ values at low and high mass loading, γ_{H2O2} on ADS ~~changed~~increases from (1.~~25~~10 ±0.~~05~~31) ×10⁻⁴ at 3% RH to (~~4.54~~2.44 ±0.~~12~~69) ×10⁻⁴ at 90% RH and the ~~value of~~ γ_{H2O2} on ATD ~~changed~~decreases from (~~5.51 ±1.15~~3.11 ±0.34) ×10⁻⁴ at 3% RH to (~~1.28 ±~~0.~~04~~87 ±0.06) ×10⁻⁴ at 90% RH. Although the values of γ_{H2O2} at low and high mass loading are not identical, all γ_{H2O2} values on ADS show a positive correlation with RH, and all γ_{H2O2} values on ATD show a negative correlation with RH. A_{es} for ADS_l and ADS_h is 6.1 cm^2 and 10.9 cm^2, respectively; A_{es} for ATD_l and ATD_h is 6.4 cm^2 and 11.2 cm^2, respectively.

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The empirical equation of γ_{PAA} against a_{H2O} on ADS and ATD can be expressed as Eq. (18) and (19), respectively:

$$\gamma_{H2O2}=\frac{9.97\times10^{-5}}{1-0.63\times a_{H2O}^{0.59}} \qquad (18)$$

$$\gamma_{H2O2}=\frac{3.33\times10^{-4}}{1+3.02\times a_{H2O}^{1.07}} \qquad (19)$$

It is noted that although the γ values of H_2O_2 and PAA on mineral dust particles obtained with the low mass loading are not the same with those with high mass loading, they have the same RH dependence. The difference among ADS_l, ADS_h, ATD_l and ATD_h are mainly caused by two reasons: the uncertainty of the A_{es} estimation method and the experimental error.

3.3 Reaction mechanisms

~~How does PM$_{2.5}$ take up peroxide compounds? What causes the difference between $R_{\gamma PAA}$ and $R_{\gamma H2O2}$? What is the reason for the opposing observations of the RH dependence on authentic particles and test particles?~~ In general, the uptake of a gas onto particles can be attributed to ~~the~~ physical processes (e.g., physisorption and dissolution) and/or chemical processes (e.g., catalytic reaction, acid-base reaction, redox reaction and thermal decomposition). In ~~Sect.~~Section 3.1, we have provided evidence that the chemical processes dominate the uptake of peroxide compounds on PM$_{2.5}$. Here, we discuss the potential chemical pathways.

The ~~components~~composition of PM$_{2.5}$ ~~determine~~determines the relative importance of physical and chemical processes. In general, PM$_{2.5}$ is mainly composed of mineral dust, sulfate, nitrate, ammonium compounds, soot, and organic matter (Eldred et al., 1997; He et al., 2001; Hueglin et al., 2005; Sun et al., 2006; Huang et al., 2014). ~~Mineral dust is an important component of PM$_{2.5}$, as shown by Zhang et al. (2013) who have determined the mean proportion of mineral dust in Beijing PM$_{2.5}$ as 23.5%, ranging from 8.2% to 33.4% in different seasons.~~ In this study, we have measured the concentrations of elements and soluble ions in PM$_{2.5}$ samples. The results are shown in Table 5. The concentration of mineral dust was estimated by multiplying 14.3 by the concentration of Al element, the ratio was suggested by Zhang et al. (2013) for PM$_{2.5}$ in urban Beijing. The estimated mineral dust accounts for 6.0 ±4.3% and 6.2 ±3.1% of PM$_{2.5}$ mass concentration on haze days and non-haze days, respectively. The concentration of SO_4^{2-} is 42.26 ±7.88 μg m^{-3} on haze days, which is about seven times of that on non-haze days. The concentration of NO_3^- and Cl^- on haze days are also about 6.9−7.3 times of those on non-haze days.

There have been several studies of the mechanism of H_2O_2 uptake on mineral dust particles. Zhao et al. (~~2011~~2011a) have found that the uptake of H_2O_2 on both SiO_2 and α-Al_2O_3 particles decreased with increasing RH. On SiO_2 particles, the contribution of physisorption to H_2O_2 uptake increased from 59% at 12% RH to 80% at 76% RH; on α-Al_2O_3 particles, the catalytic decomposition dominated H_2O_2 uptake even at high RH probably due to its high surface reactivity. ~~Even though~~Although the γ_{H2O2} on both SiO_2 and α-Al_2O_3 particles decreased with increasing RH, the reduction was more pronounced on the physical dominated SiO_2 particles. El Zein et al. (2014) observed a negative correlation between RH and γ_{H2O2} on ATD particles and suggested that the uptake of H_2O_2 on ATD particles was a catalytic process and it was not limited by site-filling. Thus, the catalytic reaction of mineral dust might be important to the uptake of peroxide compounds on $PM_{2.5}$. But this reaction alone cannot explain the positive RH dependence for the γ on $PM_{2.5}$. ~~We therefore considered that~~Therefore, some other pathways ~~are~~may also important ~~for~~to the uptake of peroxide compounds onto $PM_{2.5}$. Based on the characteristics of peroxide compounds, in addition to catalytic reaction, acid-base reaction, redox reaction, thermal decomposition, and aqueous reaction are considered as the potential pathways.

With respect to acid-base reactions, we must consider that H_2O_2 and PAA are both weak acids (pK_a=11.6 for H_2O_2, Marinoni et al., 2011; pK_a=8.2 for PAA, Evans and Upton, 1985) and can react with alkaline substances. A number of studies have demonstrated that the heterogeneous reaction of an acidic vapor on alkaline materials ~~are~~is enhanced with increasing RH (Santschi and Rossi, 2006; Preszler et al., 2007; Sullivan et al., 2009). However, $PM_{2.5}$ in Beijing is acidic (e.g., pH=5.57, Wang et al., 2005). ~~Therefore~~The concentrations of acidic ions such as SO_4^{2-} and NO_3^{-} make up 60.9% of $PM_{2.5}$ mass on haze days, and 41.3% on non-haze days (see Table 5). Even though there are some basic components (such as NH_4^+ and $CaCO_3$), we believe they are already neutralized or acidified. Therefore, acid-base reactions on $PM_{2.5}$ may not be important for the uptake of H_2O_2 and PAA.

Both PAA and H_2O_2 have strong oxidative capacity~~, suggesting that redox reactions may be important to account for their reactive uptake on $PM_{2.5}$. These peroxide species~~ and can react with the reducing substances on aerosol particles, especially in the presence of water. Zhao et al. (2013) found that γ_{H2O2} on sulfite-coated calcium carbonate particles is 3–10 times higher than that on the pristine calcium carbonate particles. This enhancement increased with increasing RH. In addition, ~~Zhao et al. (2014) have suggested the heterogeneous oxidation~~transition metals make up 0.9% of ~~OVOCs will be significantly enhanced by the coexistence of H_2O_2. In addition, both~~$PM_{2.5}$ mass on haze days and 1.2% on non-haze days. Both PAA and H_2O_2 can undergo ~~transition metal~~ catalytic ~~oxidation and release radicals~~reactions with transition metals, leading to the formation of highly reactive species, such as OH~~ radical~~, RO ~~radical~~ and RO_2 ~~radical~~radicals (Koubek and Edwards, 1963; Lin and Gurol, 1998; Zhang et al., 1998; Hiroki and LaVerne, 2005). Nawrot et al., (2009) have studies $PM_{2.5}$ samples in 20 European locations and suggested that H_2O_2 would decompose and form OH radicals in the presence of transition metals (i.e. Cu, Fe, Mn, Pb, V and Ti). Petigara et al. (2002) have reported that the decomposition rate of H_2O_2 ~~was~~is enhanced by the presence of organic matter and manganese. Therefore, the redox reactions may be important to the uptake of peroxide compounds on $PM_{2.5}$.

~~Third, consider the thermal decomposition. The structure of~~It is noted that PAA, which has a hydroperoxyl group (–OOH) ~~together with~~and a carbonyl group (C=O), is less stable than H_2O_2 (Kunigk et al., 2012) and ~~it~~can more readily ~~undergoes~~undergo thermal decomposition~~ than H_2O_2~~. The O–O bond dissociation enthalpies at 298 K of PAA and H_2O_2 are 48 kcal mol^{-1} and 50 kcal mol^{-1}, respectively (Bach et al., 1996). In addition, PAA is prone to ~~dissociate~~hydrolysis in the presence of water~~.~~ (Reaction 3 and Reaction 4) (Yuan et al., 1997). This is consistent with our experimental result that $R_{\gamma PAA}$ is larger than $R_{\gamma H2O2}$.

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$CH_3C(O)OOH + H_2O \rightarrow CH_3C(O)OH + H_2O_2$ (R3)

$CH_3C(O)OO^- + H_2O_2 \rightarrow CH_3C(O)O^- + H_2O + O_2$ (R4)

In considering the role of aqueous reactions, water soluble inorganic salts including sulfate and nitrate make up a substantial fraction (35–58%) of $PM_{2.5}$ (Sun et al., 2004; Wang et al., 2005). As shown in Table 5, the concentration of Cl^-, NO_3^- and SO_4^{2-} accounts for 61.9% and 42.0% of $PM_{2.5}$ mass on haze days and non-haze days, respectively. These salts can greatly increase the water content of the particles under humid conditions. When RH exceeds the deliquescence relative humidity (DRH) of ~~the salt~~these inorganic salts, $PM_{2.5}$ may be covered with an aqueous film on the particle surface or exist in a liquid phase state. The DRH is suggested to be 79% for $(NH_4)_2SO_4$, 39% for NH_4HSO_4 and 62% for NH_4NO_3 at 298K (Cziczo et al., 1997; Lightstone et al., 2000), and the DRH of $PM_{2.5}$ is even lower than that of the individual salt particles (Seinfeld and Pandis, 2006). Under humid conditions, the deliquesced particles and/or the aqueous film on the particle surface becomes a medium for ~~the~~ aqueous reaction. In this aqueous phase, soluble salts will release anions. The anions can potentially enhance the dissolution of Fe ~~cation~~mineral (Rubasinghege et al., 2010), resulting in a larger uptake of peroxide compounds by ~~the~~ Fe catalysis (Chevallier et al., 2004; Pignatello et al., 2006). ~~Besides, Mishra et al. (2012) have found that in the presence of anions, the dissociation of gaseous HNO_3 into droplets is markedly enhanced. As an acidic gas, both PAA and H_2O_2 might have dissociation mechanisms similar to HNO_3.~~ Furthermore, Zhao et al. (2013) have provided experimental evidence for the effect of a soluble salt on γ_{H2O2}. They found that nitrate ~~coating~~coated on calcium carbonate particles decreased the γ_{H2O2} by 30–85% at 3% RH, but increases γ_{H2O2} by a factor of 1–8 with increasing RH from 20~~%~~ to 75%, as compared to the γ_{H2O2} on the uncoated particles. Mineral dust can undergo atmospheric aging from its emission, which modifies its surface with coating sulfates and nitrates (Sullivan et al., 2007). The aged authentic mineral dust particles (e.g., ADS dust, Gobi dust and Saharan dust) are coated with salts, while the ~~pristine particles~~ mineral oxide (e.g., SiO_2, TiO_2~~,~~ and α-Al_2O_3) and ATD~~)~~ particles have no or few soluble salts coating. ~~These~~For example, in this study, the

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measured concentration of SO_4^{2-} in ADS and ATD particles was 20.3 μg mg^{-1} and 0.2 μg mg^{-1}, respectively. The coatings on the particles can lead to the formation of ~~an~~a surface aqueous film~~ on the particles under humid conditions, and in a similar manner,~~, in which the aqueous reactions may occur~~ as they do on the aqueous film on PM$_{2.5}$~~. This observation helps explain the differences in RH dependence of the uptake of peroxides on aged authentic particles and ~~pristine~~unaged mineral oxide and ATD particles. In ~~conclusion~~short, the aqueous reactions that occur in the aqueous film or liquid particles formed by the deliquescence of soluble salts may play important roles in the uptake of peroxide compounds on PM$_{2.5}$ and aged mineral dust particles.

In summary, the chemical processes rather than physical processes dominate the heterogeneous reaction of peroxide compounds on PM$_{2.5}$ and aged mineral dust particles. The inorganic soluble components in authentic particles play an important role in the uptake of peroxide compounds. The uptake of peroxide compounds on PM$_{2.5}$ is probably affected by the combined effects of catalytic reactions, redox reactions, thermal decomposition, and aqueous reactions.

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4 Conclusions and Implications

The present study is the first to measure the uptake coefficient of gaseous PAA and H_2O_2 on ambient PM$_{2.5}$ and on mineral dust over a wide range of RH values (3–90%). Both of γ_{PAA} and γ_{H2O2} on PM$_{2.5}$ have a positive correlation with RH. In general, both γ_{PAA} and γ_{H2O2} are on the order of 10^{-4}. The γ_{PAA} ~~shows~~values show no obvious differences between haze days and non-haze days. Both γ_{PAA} and γ_{H2O2} on Asian Dust Storm (ADS) particles shows a similar RH dependence compared to PM$_{2.5}$, but on Arizona Test Dust (ATD), ~~ADS showed~~both γ_{PAA} and γ_{H2O2} show a negative RH dependence. This observation provides evidence that in addition to the mineral dust, other components in PM$_{2.5}$, such as soluble inorganic salts and organic compounds may greatly contribute to the uptake of peroxide compounds. The ratio of $\gamma_{PAA,\ 90\%\ RH}$ to $\gamma_{PAA,\ 3\%\ RH}$ ($R_{\gamma PAA}$) is larger than the ratio of $\gamma_{H2O2,\ 90\%\ RH}$ to $\gamma_{H2O2,\ 3\%\ RH}$ ($R_{\gamma H2O2}$), while the Henry's law constant of H_2O_2 is 100 times that of PAA;

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besides, authentic particles show a sustained surface reactivity for the uptake of peroxide compounds. These two experimental results suggest that compared with the physical processes, the chemical process dominates the uptake of peroxide compounds onto $PM_{2.5}$ and aged mineral dust. The potential chemical processes include catalytic reactions, redox reactions, thermal decomposition and aqueous reactions. The heterogeneous processes of H_2O_2 have already been taken into account as an important removal pathway (de Reus et al., 2005; Liang et al., 2013). To the best of our knowledge, there has been almost no consideration of the heterogeneous removal pathways for organic peroxides.

~~The field~~Field observations have shown that the atmospheric lifetime of PAA is 4.1–5.8 h in summer in Beijing (Zhang et al., 2010; Liang et al., 2013). To explain this ~~lifetime~~result, we at first considered the traditional removal mechanism for PAA, including the gas phase chemical reactions (OH radical reaction and photolysis) and deposition (Jackson and Hewitt, 1999). The concentration of OH radicals has a positive correlation with solar ultraviolet irradiation and changes in different seasons. The mean concentration of OH radicals on non-haze summer day was estimated as 3.4×10^{6} molecule cm^{-3} in the 35–45 °N area (Bahm and Khalil, 2004), where Beijing is located. In addition, the concentration of OH radicals on a haze day is one fourth of that on a non-haze day (Liang et al., 2013). The reaction rate constant of OH radical with PAA is 3.7×10^{-12} cm^3 $molecule^{-1}$ s^{-1} (Jenkin et al., 1997; Saunders et al., 2003). Hence, the lifetime of PAA against the OH radical reaction is 88.3 h on a haze day and 22.1 h on a non-haze day. Using the reported cross sections of PAA by Orlando and Tyndall (2003), the lifetime of PAA against photolysis is about 28 d on haze days and 21 d on non-haze days. In these studies, we assume that the planetary boundary layer is 1000 m and the dry deposition of PAA is 0.27 cm s^{-1} (Wesely, 1989; Hall et al., 1999), both on haze and non-haze days. The lifetime of PAA against dry deposition is 4.3 d. The estimated overall lifetime of PAA is 44.2 h on a haze day and 17.6 h on a non-haze day. Obviously, this lifetime is much longer than the field observation results, especially on haze days, indicating that the

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heterogeneous reaction of PAA on ambient particles would be a removal pathway for gaseous PAA.

In order to estimate the PAA lifetime with respect to the heterogeneous reactions, we assume that all $PM_{2.5}$ particles are spheres and the heterogeneous reaction of PAA on $PM_{2.5}$ ~~with gaseous PAA~~ is a pseudo-first-order reaction. The lifetime of PAA can be calculated by Eq. (~~16~~20) (Ravishankara, 1997):

$$\tau=\frac{[C]}{\mathrm{d}[C]/\mathrm{dt}}=\frac{4}{\gamma\omega A_\mathrm{v}} \qquad (\cancel{16}20)$$

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where A_v is the surface area per unit volume of $PM_{2.5}$, m^2 m^{-3}. Assuming each mode of aerosol fine particles is a log-normal distribution, the particles number can be expressed as Eq. (~~17~~21) (Seinfeld and Pandis, 2006):

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$$\frac{dN}{dlog\mathrm{Dp}}=\sum_{\mathrm{i}}^{\mathrm{n}}\cancel{\frac{N_i}{\sqrt{2\pi}log\sigma_i}}\frac{N_i}{\sqrt{2\pi}\log\sigma_i}exp\Big(-\cancel{\frac{(log\mathrm{Dp}-log\overline{\mathrm{Dp}_i})^2}{2log^2\sigma_i}}\frac{(\log\mathrm{Dp}-\log\overline{\mathrm{Dp}_\mathrm{i}})^2}{2\log^2\sigma_i}\Big) \qquad (\cancel{17}21)$$

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where i = 1, 2, 3 corresponding to the nucleation mode (3–20 nm), Aiken mode (20–100 nm), and accumulation mode (100–1000 nm), respectively; N_i is the number concentration; $\overline{Dp_i}$ is the geometric mean diameter, m; σ_i is the geometric standard deviation of the ith mode. The recommended values of $N_\mathrm{t,i}$, $\overline{Dp_i}$ and σ_i are suggested by Yue et al. (2009). The value of A_v can be calculated by Eq. (~~18~~22):

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$$A_\mathrm{v}=\cancel{\frac{6\mathrm{M}_a}{\rho\overline{Dp}V}}\frac{6M_a}{\rho\overline{\mathrm{Dp}}V} \qquad (\cancel{18}22)$$

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where M_a is the mass of the $PM_{2.5}$ particles, kg; ρ is the density of the $PM_{2.5}$ particles, 1.42×10^3 kg m^{-3} for a haze period and 1.96×10^3 kg m^{-3} for a non-haze period (Hu et al., 2012); $\overline{Dp}$ is the mean diameter of the total particles, m; V is the volume of sampling air, m^3. The number percentage of coarse mode particles (1000–2500 nm) is less than 0.02% of the fine particles number (3–1000 nm) (Wu et al., 2008) and

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the corresponding surface area of the coarse mode is about 0.4% of the total surface area. Therefore, the surface area of the coarse mode particles (1000–2500 nm) could be negligible and $\overline{Dp}$ is 114.6 nm for haze days $PM_{2.5}$ particles and 62.4 nm for non-haze $PM_{2.5}$ particles. The mean mass concentration is 123 μg m^{-3} on a haze day and 23 μg m^{-3} on a non-haze day and the corresponding A_v is 4.5×10^3 μm^2 cm^{-3} on a haze day and 1.2×10^3 μm^2 cm^{-3} on a non-haze day, which is similar to the ~~reported values~~literature results (Wehner et al., 2008; He et al., 2010). Here, we use the mean uptake coefficient of PAA on $PM_{2.5}$ at 60% RH, i.e., γ=2.~~38~~70 $\times10^{-4}$, to estimate the ~~PAA~~ lifetime of PAA. The calculated lifetime of PAA against heterogeneous reaction is 3.~~6~~2 h on a haze day and ~~13.5~~11.9 h on a non-haze day~~. After the~~, which are more important than photolysis and decomposition and can compete with OH reaction on haze days. Considering heterogeneous reaction~~ is considered together with the~~, gas phase reaction and deposition, the estimated lifetime of PAA is 3.~~3~~0 h on a haze day and 7.~~6~~1 h on a non-haze day, ~~values~~which is similar to the field measurement results. Thus, the heterogeneous reaction on $PM_{2.5}$ is likely to be an important removal pathway for PAA.

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The fate of peroxide compounds on aerosols will greatly impact the budget of peroxide compounds themselves as well as the cycle of radicals in the atmosphere. The formation of PAA and H_2O_2 is related to the self-reaction of HO_2 radical and the reaction of HO_2 radical with RO_2 radical, while the photolysis of PAA and H_2O_2 release HO_x radical and RO_x radical. Therefore, peroxide compounds can be treated as a temporary reservoir of HO_x radicals and RO_x radicals. Besides, PAA has a close relation with peroxyacetyl nitrate (PAN). In ~~areas of~~ high NO_x ($NO+NO_2$~~),~~) areas, such as ~~the~~ urban ~~area~~areas, NO_2 will combine with acetyl peroxy ($CH_3C(O)OO$) radical to form PAN by competing with HO_2 radical which will donate H to the $CH_3C(O)OO$ radical to form PAA. The uptake of PAA onto the particle surface will result in a sink for the $CH_3C(O)OO$ radical, hence reducing PAN, which is an important carrier of NO_x and regionally transports NO_x from ~~the~~ urban ~~area~~areas to ~~the~~ rural and remote areas, affecting ~~the oxidants~~oxidant (e.g. O_3 and OH radical) distribution there (Fischer et al., 2014). Moreover, through the heterogeneous uptake, the peroxide compounds are introduced onto the surface of particles, which might enhance the atmospheric aerosol oxidative capacity and then change the composition of the aerosols. For example, Zhao et al. (2014) have suggested that the coexistence of H_2O_2 could enhance heterogeneous oxidation of OVOCs and the yield of organic acids, such as formic acid and acetic acid. Moreover, peroxide compounds, have the potential to enhance the heterogeneous reaction of SO_2 and promote sulfate formation. Hence, the heterogeneous reaction of peroxide compounds on aerosols may help to explain the high concentration of sulfates during haze episodes when other oxidants (e.g., OH radicals) are limited. Therefore, we suggest that the current atmospheric models should take into account~~ of~~ the heterogeneous reactions of peroxide compounds on aerosols.

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Table 1. ~~Statistical summary showing the sampled mass of $PM_{2.5}$ (in unit mg), average mass concentration of $PM_{2.5}$ (in unit μg m^{-3}) and effective surface area of $PM_{2.5}$ (in unit cm^2) on haze and non-haze days.~~Comparison of γ_{PAA} on exposed and unexposed $PM_{2.5}$ filters (60% RH).

Sample~~Samples~~	Exposed $PM_{2.5}$ particles~~Weather~~	~~M_a~~Unexposed $PM_{2.5}$ particles	~~Concentration~~	~~A_{es}~~
~~07/31[a]~~	~~haze~~	~~1.28~~	~~127.0~~	~~12.88~~
~~07/31[b]~~	~~haze~~	~~1.61~~	~~156.9~~	~~13.75~~
~~08/~~Aug 01[a]	~~haze~~2.08 ×10^{-4}	2.03 ×10^{-4}~~1.33~~	~~132.6~~	~~13.04~~
~~08/01-[b]~~Aug 01[b]	~~haze~~2.29 ×10^{-4}	2.23 ×10^{-4}~~1.39~~	~~136.7~~	~~13.19~~
~~08/02[a]~~	~~haze~~	~~1.04~~	~~107.0~~	~~12.12~~
~~08/02[b]~~	~~haze~~	~~1.39~~	~~137.8~~	~~13.21~~
~~08/03[a]~~Aug 05[a]	~~haze→ non-haze~~2.30 ×10^{-4}	~~0.60~~ ~~61.7~~ 2.40 ×10~~.09~~$^{-4}$		
~~08/03[b]~~	~~non-haze~~	~~0.41~~	~~41.1~~	~~8.63~~
~~08/04[a]~~Aug 05[b]	~~non-haze~~ ~~0.~~2.45 ×10^{-4}	~~9.~~2.33 ×10^{-4}	~~3.15~~	
~~08/04[b]~~	~~non-haze~~	~~0.18~~	~~16.9~~	~~5.44~~
~~08/05[a]~~	~~non-haze~~	~~0.26~~	~~25.6~~	~~6.85~~
~~08/05[b]~~	~~non-haze~~	~~0.32~~	~~127.0~~	~~7.76~~

Note: [a]~~,~~ daytime; [b]~~,~~ nighttime; ~~A_{es}, ~~exposed $PM_{2.5}$ particles, which has been used in the PAA uptake experiments; unexposed $PM_{2.5}$ filter which has not been used for any experiments.

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带格式的：段落间距段后：0.5 行，行距：单倍行距

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Table 2. Summary of the collected mass and effective surface area~~; M_a, mass of $PM_{2.5}$~~ of $PM_{2.5}$ on the filter, and its ambient average mass concentrations on haze and non-haze days.

Samples ~~RH-(%)~~	Weather ~~$PM_{2.5h}$~~	~~$PM_{2.5h}$~~ M_a (mg)	Concentration ~~ADS_h~~ (μg·m^{-3})	~~ADS_l~~ A_{es} (cm^2)	~~ATD_h~~	~~ATD_l~~

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Jul31a	haze	1.28	127.0	12.88
Jul31b	haze	1.61	156.9	13.75
Aug_01a	haze	1.33	132.6	13.04
Aug_01b	haze	1.39	136.7	13.19
Aug	haz	1.04	107.0	12.12

-02a e

Aug-02b haze

1.39 137.8 13.21

~~2.42±0.02~~ ~~1.86±0.01~~

~~0.81±~~

~~3~~Aug-03a haze→non-haze

0.~~98±0.27~~60 ~~0.84±0.01~~61.7 ~~1.37±0.02~~10.09

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带格式的： 行距：**单**倍行距

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~~0.26~~

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~~1.37±0.20~~non-haze ~~2.15±0.05~~ ~~1.44±0.03~~

20Aug_03b

带格式的：孤行控制

带格式的：行距：单倍行距

41.1.~~26±0.03~~

~~1.78±0.0~~38.63

~~10~~.41~~±0.38~~

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40Aug_04

~~1.95±0.05~~

~~1.65±0.08~~

9.2.~~11±0.06~~

~~1.27±0.03~~

带格式的：孤行控制

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带格式的：行距：单倍行距

~~1.99±~~0.5210

~~1.81±0.03~~3.15

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a ~~2~~ non-haze

~~2.26 ±0.08~~ ~~2.39 ±0.04~~ ~~1.62 ±0.01~~

~~2.76 ±0.~~ ~~54~~

~~60~~ Aug-04

~~2.63 ±~~ 0. ~~70~~ 18

~~1.~~ 16 ~~±0.02~~ .9

5.44

b non-haze

~~75~~ A ~~3.4~~

0.26

~~3.42 ±~~ ~~2.60 ±~~ ~~2.55 ±0.01~~ ~~1.47 ±0.01~~ 1

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插入的单元格

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ug-05[a]	~~3±0.63~~non-haze		~~1.~~25.6	~~0.03~~6.85			
	~~4.20±0.58~~				~~2.62±0.01~~	~~1.17±0.03~~	~~0.91±0.04~~
~~90~~Aug-05[b]	non-ha	0.32	32.4~~.63±1.30~~	~~3.21±0.08~~7.76			

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Note: ~~$PM_{2.5n}$, non~~ [a] daytime; [b] nighttime; A_{es}, effective surface area; M_a, mass of $PM_{2.5}$.

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Table 3. The uptake coefficients γ (×10^{-4}) of PAA on $PM_{2.5}$, ADS, and ATD under different relative humidity conditions. The values in the brackets are the lower limit of γ (×10^{-5}).

RH	$PM_{2.5h}$	$PM_{2.5n}$	ADS_l	ADS_h	ATD_l	ATD_h
3%	0.81 ±0.26 (0.23 ±0.06)^{a}	0.98 ±0.27 (0.54 ±0.24)^{a}	0.84 ±0.01 (2.19 ±0.27)^{b}	1.37 ±0.02 (1.72 ±0.02)^{b}	2.42 ±0.02 (3.45 ±0.03)^{b}	1.86 ±0.01 (0.93 ±0.02l)^{b}
20%	1.37 ±0.20 (0.40 ±0.11)^{a}	1.41 ±0.38 (0.78 ±0.33)^{a}	1.26 ±0.03 (3.27 ±0.38)^{b}	1.78 ±0.03 (2.24 ±0.04)^{b}	2.15 ±0.05 (3.07 ±0.07)^{b}	1.44 ±0.03 (0.72 ±0.05)^{b}
40%	1.95 ±0.52 (0.58 ±0.24)^{a}	1.99 ±0.52 (1.11 ±0.46)^{a}	1.65 ±0.08 (4.28 ±0.5)^{b}	2.11 ±0.06 (2.66 ±0.08)^{b}	1.81 ±0.03 (2.59 ±0.04)^{b}	1.27 ±0.03 (0.64 ±0.03)^{b}
60%	2.76 ±0.54 (0.83 ±0.32)^{a}	2.63 ±0.70 (1.47 ±0.63)^{a}	2.26 ±0.08 (5.86 ±0.70)^{b}	2.39 ±0.04 (3.01 ±0.06)^{b}	1.62 ±0.01 (2.31 ±0.02)^{b}	1.16 ±0.02 (0.58 ±0.01)^{b}
75%	3.43 ±0.63 (1.03 ±0.38)^{a}	3.42 ±1.25 (1.92 ±1.00)^{a}	2.60 ±0.03 (6.74 ±1.25)^{b}	2.55 ±0.01 (3.21 ±0.01)^{b}	1.47 ±0.01 (2.1 ±0.002)^{b}	1.07 ±0.03 (0.53 ±0002)^{b}
90%	4.20 ±0.58 (1.24 ±0.41)^{a}	4.63 ±1.30 (2.60 ±1.09)^{a}	3.21 ±0.08 (8.32 ±1.30)^{b}	2.62 ±0.01 (3.30 ±0.01)^{b}	1.17 ±0.03 (1.67 ±0.04)^{b}	0.91 ±0.04 (0.45 ±0.03)^{b}

Note: $PM_{2.5h}$, haze day $PM_{2.5}$; $PM_{2.}$~~$_{5h,}$~~$_{5n}$, non-haze day $PM_{2.5}$; ADS_h and ATD_h, the mass of mineral dust about 1.3 mg; ADS_l and ATD_l, the mass of mineral dust about 0.3 mg; ^{a} uptake coefficient calculated by total surface area of the particles using size distribution, representing the lower limit; ^{b} uptake coefficient calculated by BET area, representing the lower limit; the errors represent the relative standard deviation between γ on particles of ascending and descending RH.

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Table 4. Summary of the uptake coefficients of H_2O_2 on mineral dust particles in literature data.

Substrate	RH dependence	Uptake coefficient	Method	Reference
TiO_2	N	$(1.53\pm0.11)\times10^{-4}$–$(5.04\pm0.58)\times10^{-4}$	AFT-CIMS	Pradhan et al. (2010a)
Gobi dust Saharan dust	P	$(3.33\pm0.26)\times10^{-4}$–$(6.03\pm0.42)\times10^{-4}$ $(6.20\pm0.22)\times10^{-4}$–$(9.42\pm0.41)\times10^{-4}$	AFT-CIMS	Pradhan et al. (2010b)
Al_2O_3 SiO_2	N N	$(1.21\pm0.04)\times10^{-8}$–$(0.76\pm0.09)\times10^{-7}$ $(1.55\pm0.14)\times10^{-8}$–$(0.61\pm0.06)\times10^{-7}$	T-FTIR	Zhao et al. (2011b)
HNO_3-Al_2O_3 SO_2-Al_2O_3	N (<75%); P (>75%) P	$\gamma_{aged}/\gamma_{pristine}=0.5$–$1.1$ $\gamma_{aged}/\gamma_{pristine}=1.2$–$1.9$	T-FTIR	Zhao et al. (2011a)
SiO_2 Al_2O_3 Fe_2O_3 MgO	–	$\gamma_0=(5.22\pm0.9)\times10^{-5}$ $\gamma_0=(1.00\pm0.11)\times10^{-4}$ $\gamma_0=(9.70\pm1.95)\times10^{-5}$ $\gamma_0=(1.66\pm0.23)\times10^{-4}$	Knudsen cell-QMS	Wang et al. (2011)
TiO_2	N	$\gamma_{0,dark}=\frac{4.1\times10^{-3}}{1+RH^{0.65}}$	CWFT-QMS	Romanias et al. (2012)
SiO_2 $CaCO_3$	–	$\gamma_0=\frac{\exp(934.5/T-12.7)}{1+\exp(934.5/T-12.7)}-$ $\gamma_0=\frac{\exp(1193.0/T-11.9)}{1+\exp(1193.0/T-11.9)}-$	Knudsen cell-QMS	Zhou et al. (2012)
HNO_3-$CaCO_3$ SO_2-$CaCO_3$	P P	$\gamma_{aged}/\gamma_{pristine}=1$–$8$ $\gamma_{aged}/\gamma_{pristine}=3$–$10$	T-FTIR	Zhao et al. (2013)
Al_2O_3 Fe_2O_3	N N	$\gamma_0=\frac{1.10\times10^{-3}}{1+RH^{0.93}}$ $\gamma_0=\frac{1.05\times10^{-3}}{1+RH^{0.73}}$	CWFT-QMS	Romanias et al. (2013)
TiO_2	N	$\gamma_0=\frac{4.8\times10^{-4}}{1+RH^{0.66}}$	CWFT-QMS	El Zein et al. (2014)

Note: N, negative RH dependence; P, positive RH dependence; γ_0, initial uptake coefficient; AFT, aerosol flow tube; CIMS, chemical ionization mass spectrometer; T-FTIR, transmission-Fourier Transform Infrared spectroscopy; QMS, quadrupole mass spectrometer;

CWFT, coated-wall flow tube.

Table 5. The average concentration of ions, organic acids and elements of $PM_{2.5}$ on haze and non-haze days.

Species	haze day	non-haze day
SO_4^{2-}[a]	42.3 ±7.88	5.95 ±5.88
NO_3^{-}[a]	23.2 ±16.8	3.18 ±2.92
Cl^{-}[a]	1.07 ±1.48	0.15 ±0.12
NH_4^{+}[a]	6.11 ±1.22	1.51 ±1.01
K^{+}[a]	1.10 ±0.27	0.26 ±0.16
Na^{+}[a]	0.49 ±0.15	0.24 ±0.11
HO(O)CC(O)OH[a]	0.83 ±0.06	0.21 ±0.10
HC(O)OH[a]	0.20 ±0.09	0.07 ±0.06
$CH_3C(O)OH$[a]	0.19 ±0.16	0.16 ±0.32
$CH_3C(O)C(O)OH$[a]	0.04 ±0.01	0.01 ±0.01
K[a]	0.62 ±0.16	0.17 ±0.11
Al[a]	0.45 ±0.36	0.10 ±0.09
Ca[a]	0.44 ±0.16	0.30 ±0.14
Mg[a]	0.10 ±0.04	0.05 ±0.03
P[a]	0.19 ±0.12	0.14 ±0.19
Fe[a]	0.60 ±0.14	0.17 ±0.10
Ti[a]	0.04 ±0.01	0.03 ±0.03
Mn[a]	0.03 ±0.01	0.01 ±0.01
Cu[a]	0.03 ±0.02	0.01 ±0.01
Zn[a]	0.18 ±0.08	0.03 ±0.02
V[a]	0.01 ±0.01	0.01 ±0.01
Pb[a]	0.08 ±0.02	0.01 ±0.01
Ba[b]	10.22 ±3.06	3.68 ±1.76
Cr[b]	8.55 ±2.58	4.16 ±2.49
Se[b]	4.56 ±1.60	1.28 ±0.95
Ni[b]	4.54 ±1.88	0.44 ±0.30
As[b]	4.30 ±2.64	5.57 ±3.63
Mo[b]	1.16 ±0.50	0.42 ±0.20
Tl[b]	1.12 ±0.41	0.14 ±0.10
Cd[b]	1.09 ±0.32	0.22 ±0.17
Co[b]	0.40 ±0.10	0.19 ±0.08
U[b]	0.04 ±0.01	0.02 ±0.02
Th[b]	0.03 ±0.02	0.01 ±0.02

Note: [a] the unit is μg m^{-3}; [b] the unit is ng m^{-3}.

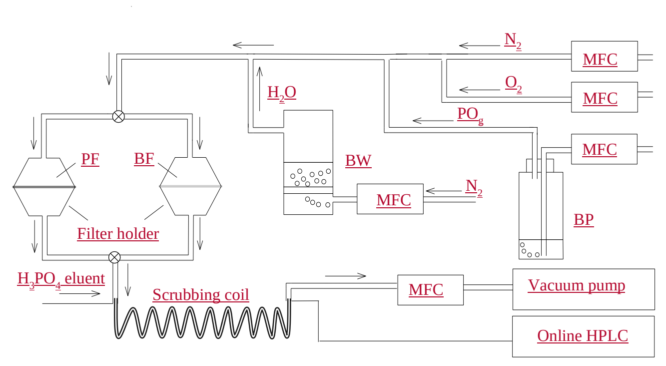

Fig. 1. Schematic diagram of experimental apparatus. MFC, mass flow controller; PF, particle~~-~~-loaded filter; BF, blank filter; PO$_g$, gaseous peroxide compound; BP, bubbler for peroxide vapor; BW, bubbler for water vapor; HPLC, high-performance liquid chromatography. The scrubbing coil, BP and BW were kept in 277 K and 298 K water bath, respectively.

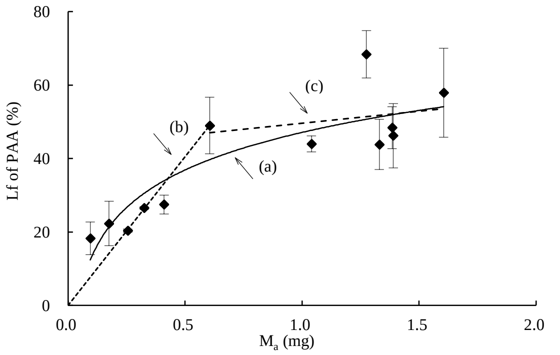

Fig. 2. The trend line of fractional loss (Lf) of PAA against PM2.5 mass (*M*$_a$) (60% RH). ~~The error~~Error bars ~~represent~~are 1 standard deviation. Solid line **(a)**, the logarithmic trend line of Lf against *M*$_a$ among all mass values; dotted line **(b)**, the linear correlation of Lf against *M*$_a$ in the low mass region; dotted line **(c)**, the nearly constant Lf against *M*$_a$ in the high mass region.

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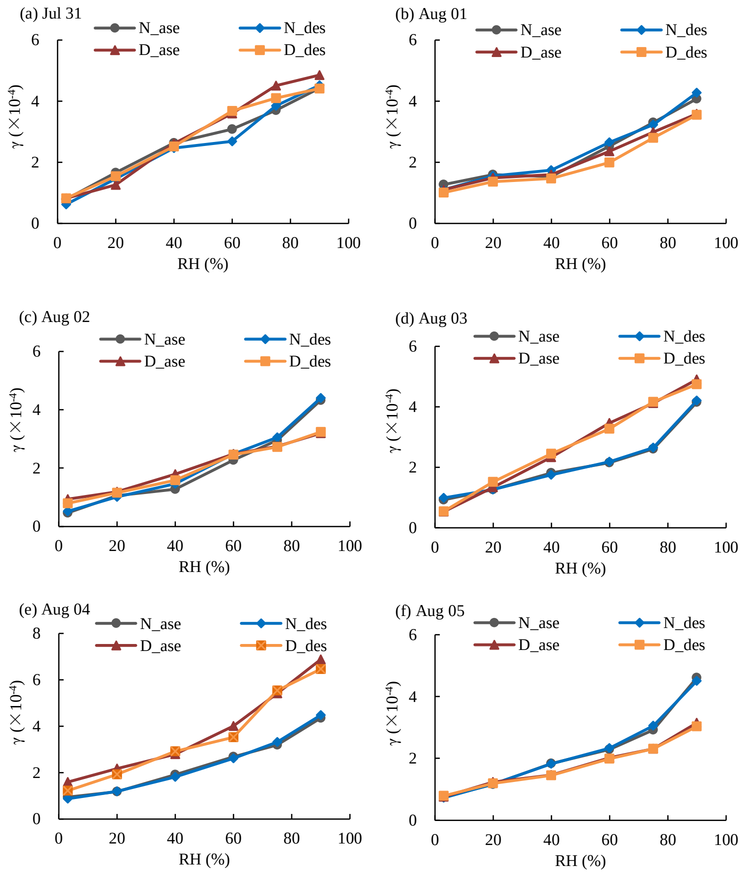

Fig. 3. Profiles of uptake coefficient of gaseous PAA on $PM_{2.5}$ over a range of RH (3–90~~%). The~~ %); N_ase, γ_{PAA} was measured with ascending RH on nighttime $PM_{2.5}$ particles~~ were either collected in the daytime or in the nighttime. Error bars are 1 standard deviation.~~

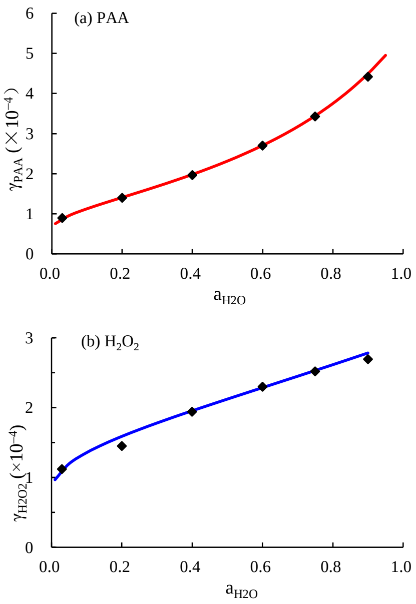

Fig. ~~5. Uptake coefficient of~~ **4.** The uptake coefficients of PAA and H_2O_2 on $PM_{2.5}$ particles ~~as~~. The red line and the blue line in figure (a ~~function~~) and (b) represent the empirical fit of ~~relative humidity. The error bars are 1 standard deviation~~ γ_{PAA} and γ_{H2O2}, respectively.

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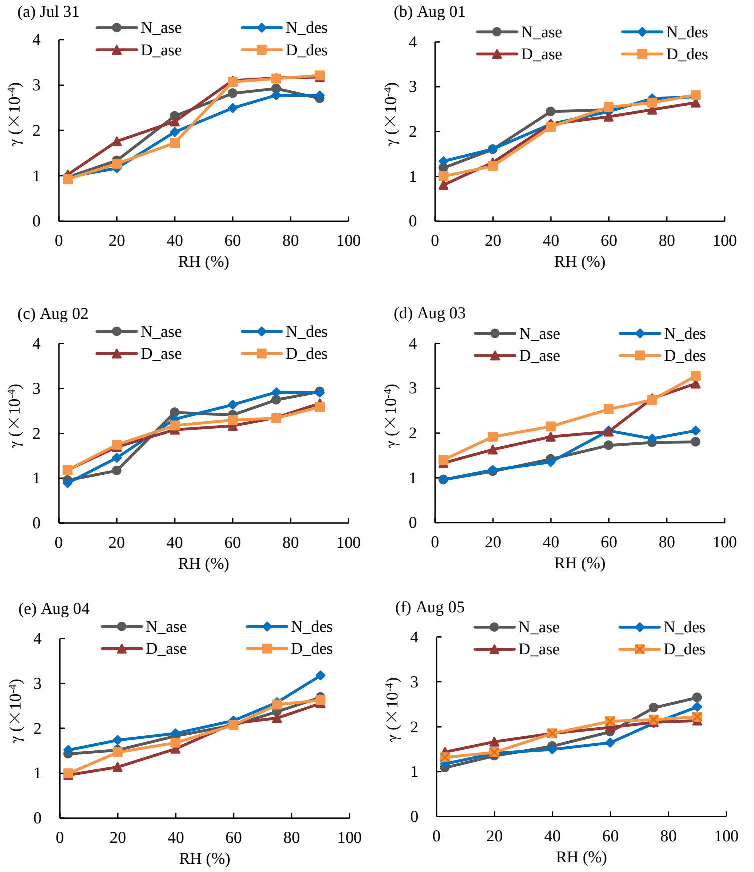
(a) Jul 31
(b) Aug 01
(c) Aug 02
(d) Aug 03
(e) Aug 04
(f) Aug 05
N_ase
N_des
D_ase
D_des
γ (×10⁻⁴)
RH (%)
0
1
2
3
4
0
20
40
60
80
100

Fig.

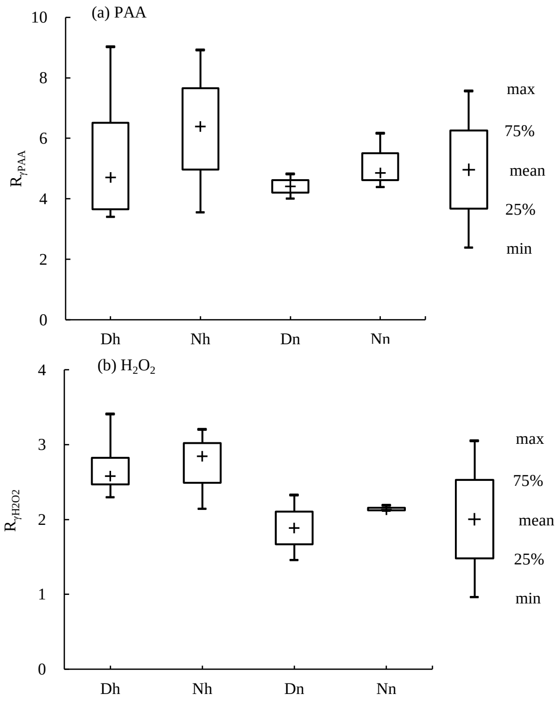

Fig. 6. The ratio of γ~~PAA~~ at 90% RH to γ~~PAA~~ at 3% RH ($R_{\gamma \mathrm{PAA}}$ and $R_{\gamma \mathrm{H2O2}}$) on $PM_{2.5}$. Dh, daytime of haze day; Nh, nighttime of haze day; Dn, daytime of non-haze day; Nn, nighttime of non-haze day.

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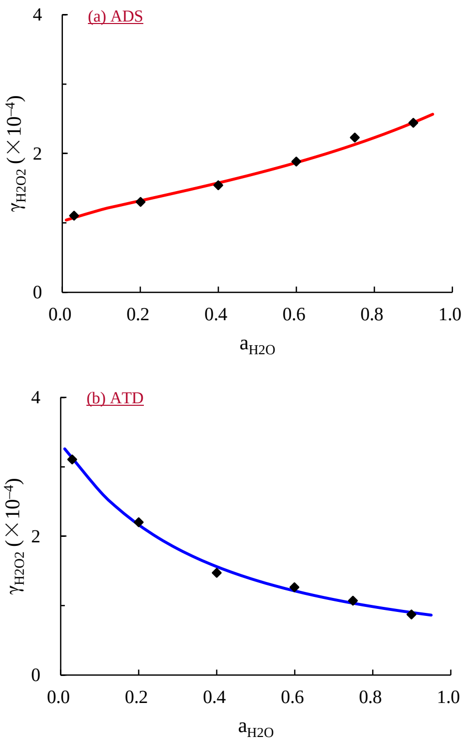

Fig. 7. Uptake coefficient of H_2O_2 on ADS and ATD particles~~ as a function of relative humidity. ADS$_{I}$~~. The red line and ~~ATD$_{I}$, ~~the ~~mass of mineral dust about 0.3 mg; ADS$_{II}$~~blue line in figure (a) and ~~ATD$_{II}$;~~(b) represent the ~~mass of mineral dust about 1.3 mg. The error bars are 1 standard deviation.~~empirical fit of γ_{H2O2} on ADS and ATD particles, respectively.

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