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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 that peroxyacetic acid (PAA, $\text{CH}_3\text{C}(\text{O})\text{OOH}$) is one of the most important organic peroxides in the atmosphere, whose budget is potentially related to the aerosols. Here we present the first laboratory measurements of the uptake coefficient of gaseous PAA and H_2O_2 onto the ambient fine particulate matter ($\text{PM}_{2.5}$) as a function of relative humidity (RH) at 298 K. The results show that the $\text{PM}_{2.5}$, 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 $\gamma_{\text{H}_2\text{O}_2}$ increase with increasing RH. However, γ_{PAA} is more sensitive to the RH variation than is $\gamma_{\text{H}_2\text{O}_2}$, which indicates that the enhanced uptake of peroxide compounds on $\text{PM}_{2.5}$ under humid conditions is dominated by chemical processes rather than dissolution. Considering that mineral dust is one of the main components of $\text{PM}_{2.5}$, 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 $\text{PM}_{2.5}$, 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 $\text{PM}_{2.5}$, other components (e.g., inorganic soluble salts) are also important to the uptake of peroxide compounds. When the heterogeneous reaction of PAA on $\text{PM}_{2.5}$ is considered, its atmospheric lifetime is estimated to be 3.3 h on haze days and 7.6 h on non-haze days, values which agree well with the field observed result.

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

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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 HO₂) radicals (Wallington and Japar, 1990; Vaghjiani et al., 1990; Atkinson et al., 1992; Ravetta et al., 2001) and RO_x (RO and RO₂) 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 their sources and sinks. Recent studies that combined field and model data have demonstrated that in the Arctic troposphere, subtropical island, and urban atmospheres, the concentration of gaseous H₂O₂ was largely overestimated by a standard gas-phase chemical mechanism, whereas when the heterogeneous uptake of H₂O₂ and/or HO₂ 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 series of laboratory studies have ascertained the importance of the heterogeneous reaction of H₂O₂ on the model or on authentic mineral dust particles (Pradhan et al., 2010a, b; Wang et al., 2011; Zhao et al., 2011a, b, 2013; Romanias et al., 2012, 2013; Zhou et al., 2012; El Zein et al., 2014) and our recent study has indicated that H₂O₂ 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, CH₃C(O)OOH) has frequently been detected over both rural and urban 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 H₂O₂, i.e., several tens to hundreds of pptv in summer, and the maximum concentration surpasses 1 ppbv over the temperate area (Zhang et al., 2010) and the boreal forest (Phillips et al., 2013). Our field measurements of atmospheric peroxides

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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 $\text{PM}_{2.5}$ mass concentration of lower than $75 \mu\text{g m}^{-3}$. The $\text{PM}_{2.5}$ 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. To compare the experimental results for $\text{PM}_{2.5}$ sampled in non-haze and haze days, the mass of ADS and ATD on the filter was carefully controlled at 0.3 and 1.4 mg for the lower and higher mineral dust mass values, respectively.

2.2.3 Uptake experiments

A filter based flow reactor was used to measure the uptake coefficients of gaseous peroxide on aerosol particles. The schematic of this experimental apparatus is shown in Fig. 1. The reactor is composed of two perfluoroalkoxy resin filter holders (Saville Corporation) connected in parallel. One reactor contains a blank PTFE filter, and the other contains a particle loaded filter. 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 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%. All the experiments were conducted at 298 ± 2 K, ambient pressure and in the dark.

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

$$\gamma = \frac{d\{C\}/dt}{Z} \quad (1)$$

$$Z = \frac{1}{4} \omega A_{\text{es}} [C] \quad (2)$$

$$\omega = \sqrt{\frac{8RT}{\pi M_x}} \quad (3)$$

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 peroxide, molecules m^{-3} ; ω is the mean molecular speed, m s^{-1} ; R is the universal gas constant, $\text{kg m}^2 \text{s}^{-2} \text{mol}^{-1} \text{K}^{-1}$; 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 define the fractional loss of the reactant (Lf) as Eq. (4):

$$\text{Lf} = \frac{[C]_{\text{in}} - [C]_{\text{out}}}{[C]_{\text{in}}} \quad (4)$$

where $[C]_{\text{in}}$ and $[C]_{\text{out}}$ is the concentration of the reactant at the inlet and outlet of the reactor, molecules m^{-3} , respectively. Therefore, Eq. (1) can be expressed as Eq. (5):

$$\gamma = \frac{4\text{Lf}V_g}{\omega A_{\text{es}}} \quad (5)$$

where V_g is the flow rate of the reactant containing gas, $\text{m}^3 \text{s}^{-1}$.

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2.3 Analysis of peroxides

Peroxide compounds were measured by high-performance liquid chromatography (HPLC, Agilent 1200) coupled with a post-column derivatization module. 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 flow rate of 0.5 mL min^{-1} . The formed fluorescent dimer was analyzed by a fluorescence detector.

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 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. 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 ambient particles were loaded on the filter in an agglomerated state, extremely different from their status in the atmosphere, where they are highly dispersive. 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 investigating the relationship between the uptake and loaded particle mass. Equation (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

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A_{es} . Figure 2 shows the relationship between the Lf of gaseous PAA vs. 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. (6):

$$Lf = 0.15 \times \ln(M_a) + 0.47 \quad (6)$$

where M_a is the mass of the particles, mg. In the low particle mass region, the particles were highly dispersed on the filter and A_{es} increased rapidly with increasing particle mass; at high particle mass values, because the particles highly overlapped each other on the filter, A_{es} was similar to the A_{gs} of the filter. Here, we assumed that there existed 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 (\bar{Lf}) which were larger than Lf_c and the calculation method was expressed in Eq. (7). Here, we set R_{el} as 5% to terminate the iteration. The procedure of iteration was as follows: (i) start $M_{a,c}$ with 0.1 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), (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^{-2} , which was similar to the experimental result in Fig. 2., i.e., 4.90×10^{-2} . Based on the directly proportional relationship between A_{es} and Lf, A_{es} can be expressed in Eq. (8).

$$R_{el} = \frac{Lf_c}{\bar{Lf}} \quad (7)$$

$$A_{\text{es}} = \frac{A_{\text{gs}}}{L_f c} \times L_f \quad (8)$$

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

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

$$\text{For ADS} \quad A_{\text{es}} = 3.66 \times \ln(M_a) + 9.59 \quad (10)$$

$$\text{For ATD} \quad A_{\text{es}} = 3.01 \times \ln(M_a) + 10.3 \quad (11)$$

where M_a represents the filter-loaded particle mass, mg. The mass of the filter-loaded $\text{PM}_{2.5}$ and the estimated A_{es} values are listed in Table 1. A_{es} for $\text{PM}_{2.5}$ changes with the particle mass, ranging from 3.2–13.8 cm^2 ; A_{es} for ADS is 6.1 and 10.9 cm^2 , respectively; A_{es} for ATD is 6.4 and 11.2 cm^2 , respectively.

3 Results and discussion

3.1 Uptake of PAA and H_2O_2 on $\text{PM}_{2.5}$

The uptake coefficient of PAA (γ_{PAA}) on filter-loaded $\text{PM}_{2.5}$ 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 $\text{PM}_{2.5}$ with respect to increasing RH. For all the $\text{PM}_{2.5}$ samples, γ_{PAA} increases with increasing RH; at the same RH, and the γ_{PAA} values, on the nighttime $\text{PM}_{2.5}$ sample are similar to those observed on the daytime $\text{PM}_{2.5}$ sample. Additionally, even though the $\text{PM}_{2.5}$ mass collected on a haze day was significantly different from that on a non-haze day, the γ_{PAA} exhibited a similar value for these two different weather conditions (Table 2). In general, γ_{PAA} rose from $(0.89 \pm 0.26) \times 10^{-4}$ at 3% RH to $(4.41 \pm 0.92) \times 10^{-4}$ at 90% RH. The empirical equation of γ_{PAA} plotted against water activity ($a_{\text{H}_2\text{O}}$; here, $a_{\text{H}_2\text{O}} = \text{RH}/100$) (Fig. 4) can be expressed as

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Eq. (12):

$$\gamma_{\text{PAA}} = \frac{4.94 \times 10^{-5}}{1 - 0.91 \times a_{\text{H}_2\text{O}}^{0.21}} \quad (12)$$

where $a_{\text{H}_2\text{O}}$ is a variable fraction, e.g. 0.6.

We also determined the uptake coefficient of H_2O_2 on $\text{PM}_{2.5}$ over the RH range of 3 to 90 %. The measured $\gamma_{\text{H}_2\text{O}_2}$ on $\text{PM}_{2.5}$ is shown in Fig. 5. The empirical equation of $\gamma_{\text{H}_2\text{O}_2}$ as a function of $a_{\text{H}_2\text{O}}$ can be expressed as Eq. (13):

$$\gamma_{\text{H}_2\text{O}_2} = \frac{1.26 \times 10^{-4}}{1 - 0.75 \times a_{\text{H}_2\text{O}}^{0.055}} \quad (13)$$

where $a_{\text{H}_2\text{O}}$ is a variable fraction. The value of $\gamma_{\text{H}_2\text{O}_2}$, similar to γ_{PAA} , showed a positive correlation with RH, whereas the value of $\gamma_{\text{H}_2\text{O}_2}$ at low RH exceeded that of γ_{PAA} . The $\gamma_{\text{H}_2\text{O}_2}$ changed from $(3.18 \pm 0.7) \times 10^{-4}$ at 3 % RH to $(4.78 \pm 0.4) \times 10^{-4}$ at 90 % RH. The positive RH dependence of $\gamma_{\text{H}_2\text{O}_2}$ has been reported by Pradhan et al. (2010b). They have measured $\gamma_{\text{H}_2\text{O}_2}$ on authentic mineral dust particles (i.e., Gobi dust particles and Saharan dust particles). However, El Zein et al. (2014) have reported an inverse RH dependence of $\gamma_{\text{H}_2\text{O}_2}$ on the ATD particles. Even though the RH dependence of $\gamma_{\text{H}_2\text{O}_2}$ differs in different particles, its order of magnitude is generally at 10^{-4} , which is comparable to the $\gamma_{\text{H}_2\text{O}_2}$ on $\text{PM}_{2.5}$ measured in our study.

Figure 6 shows the ratio of $\gamma_{\text{PAA},90\% \text{RH}}$ to $\gamma_{\text{PAA},3\% \text{RH}}$ ($R_{\gamma_{\text{PAA}}}$). The $R_{\gamma_{\text{PAA}}}$ showed no obvious difference at different times and in different weather conditions, varying over the narrow range of 4.4 ± 0.6 to 6.3 ± 2.7 . On average, $R_{\gamma_{\text{PAA}}}$ was 5.4 ± 1.9 . Although $\gamma_{\text{H}_2\text{O}_2}$ had a positive RH dependence on $\text{PM}_{2.5}$ as well, H_2O_2 was less sensitive to RH variance compared to PAA. It is interesting to note that the ratio of $\gamma_{\text{H}_2\text{O}_2,90\% \text{RH}}$ to $\gamma_{\text{H}_2\text{O}_2,3\% \text{RH}}$ ($R_{\gamma_{\text{H}_2\text{O}_2}}$) was 1.5 ± 0.1 , which is much lower than $R_{\gamma_{\text{PAA}}}$. For peroxide compounds, if the physical process, especially the dissolution, dominated their uptake

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on $\text{PM}_{2.5}$, the $R_{\gamma_{\text{H}_2\text{O}_2}}$ should be larger than $R_{\gamma_{\text{PAA}}}$, because the Henry's law constant of H_2O_2 is 100 times that of PAA (298 K) (O'Sullivan et al., 1996). This expectation, however, is at odds with our experimental results. Hence, the physical process is not the main reason for the uptake of peroxide compounds on $\text{PM}_{2.5}$. However, for H_2O_2 , the larger value of $\gamma_{\text{H}_2\text{O}_2}$ than that of γ_{PAA} in low humidity indicated a physical process is important for the uptake of H_2O_2 onto $\text{PM}_{2.5}$ when humidity is low. In addition, the values of γ_{PAA} and $\gamma_{\text{H}_2\text{O}_2}$ on $\text{PM}_{2.5}$ were measured with increasing RH from 3 to 90 % and then the measurements were repeated but with decreasing RH from 90 to 3 % using the same sample. Interestingly, we find that the γ_{PAA} and $\gamma_{\text{H}_2\text{O}_2}$ can be repeated in these two cases with only small error bars (see Figs. 3 and 5). The independence of γ_{PAA} and $\gamma_{\text{H}_2\text{O}_2}$ on reaction time also indicated that $\text{PM}_{2.5}$ had a sustained reactivity for the uptake of peroxide compounds at different levels of humidity, which falls into the category of reactive uptake as suggested by Crowley et al. (2010). The detailed mechanism is described in Sect. 3.3.

The present study is the first investigation on the kinetics of the heterogeneous reactions of PAA and H_2O_2 on $\text{PM}_{2.5}$ particles. Recent studies have indicated the importance of mineral dust for H_2O_2 uptake (Pradhan et al., 2010a, b; Wang et al., 2011; Zhao et al., 2011a, b, 2013; Romanias et al., 2012, 2013; Zhou et al., 2012; El Zein et al., 2014). In general, the measured $\gamma_{\text{H}_2\text{O}_2}$ on $\text{PM}_{2.5}$ in our study were comparable to that measured on those mineral dusts. For PAA, however, no data regarding its kinetics on mineral dust has been available in the literature.

3.2 Uptake of PAA and H_2O_2 on mineral dust

Mineral dust is an important component of atmospheric aerosols in Beijing, and it comprises 7.1–33.4 % of $\text{PM}_{2.5}$ in different seasons (Sun et al., 2004; Yang et al., 2011; Zhang et al., 2013). To determine whether the mineral dust dominates the uptake of PAA on $\text{PM}_{2.5}$, 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

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listed in Table 2. The γ_{PAA} on ADS increased from $(0.84 \pm 0.01) \times 10^{-4}$ at 3 % RH to $(3.21 \pm 0.08) \times 10^{-4}$ at 90 % RH. The positive correlations between RH and the value of γ_{PAA} on ADS are similar to that on $\text{PM}_{2.5}$. Similar positive RH dependence was also 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 $(2.42 \pm 0.02) \times 10^{-4}$ at 3 % RH to $(0.91 \pm 0.04) \times 10^{-4}$ at 90 % RH. This negative RH dependence was similar to the previously reported $\gamma_{\text{H}_2\text{O}_2}$ on ATD and mineral oxides (e.g. $\alpha\text{-Al}_2\text{O}_3$, Fe_2O_3 , TiO_2 , SiO_2) (Pradhan et al., 2010a; Zhao et al., 2011a; Romanias et al., 2012, 2013; El Zein et al., 2014). The discrepancies in the RH dependence of γ_{PAA} are discussed in Sect. 3.3. The empirical equation of γ_{PAA} against $a_{\text{H}_2\text{O}}$ on ADS and ATD can be expressed as Eqs. (14) and (15), respectively:

$$\gamma_{\text{PAA}} = \frac{7.49 \times 10^{-5}}{1 - 0.76 \times a_{\text{H}_2\text{O}}^{0.25}} \quad (14)$$

$$\gamma_{\text{PAA}} = \frac{2.18 \times 10^{-4}}{1 + 1.08 \times a_{\text{H}_2\text{O}}^{1.06}} \quad (15)$$

where $a_{\text{H}_2\text{O}}$ 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 $\gamma_{\text{H}_2\text{O}_2}$ on ADS and ATD is shown in Fig. 7. The value of $\gamma_{\text{H}_2\text{O}_2}$, similar to γ_{PAA} , showed a positive correlation with RH on ADS particles and a negative correlation with RH on ATD particles. The value of $\gamma_{\text{H}_2\text{O}_2}$ on ADS changed from $(1.25 \pm 0.5) \times 10^{-4}$ at 3 % RH to $(4.54 \pm 0.12) \times 10^{-4}$ at 90 % RH and the value of $\gamma_{\text{H}_2\text{O}_2}$ on ATD changed from $(5.51 \pm 1.15) \times 10^{-4}$ at 3 % RH to $(1.28 \pm 0.04) \times 10^{-4}$ at 90 % RH.

3.3 Reaction mechanisms

How does PM_{2.5} take up peroxide compounds? What causes the difference between $R_{\gamma\text{PAA}}$ and $R_{\gamma\text{H}_2\text{O}_2}$? 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 chemical processes (e.g., catalytic reaction, acid-base reaction, redox reaction and thermal decomposition). In Sect. 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 of PM_{2.5} determine 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. There have been several studies of the mechanism of H₂O₂ uptake on mineral dust particles. Zhao et al. (2011) have found that the uptake of H₂O₂ on both SiO₂ and α -Al₂O₃ particles decreased with increasing RH. On SiO₂ particles, the contribution of physisorption to H₂O₂ uptake increased from 59% at 12% RH to 80% at 76% RH; on α -Al₂O₃ particles, the catalytic decomposition dominated H₂O₂ uptake even at high RH probably due to its high surface reactivity. Even though the $\gamma_{\text{H}_2\text{O}_2}$ on both SiO₂ and α -Al₂O₃ particles decreased with increasing RH, the reduction was more pronounced on the physical dominated SiO₂ particles. El Zein et al. (2014) observed a negative correlation between RH and $\gamma_{\text{H}_2\text{O}_2}$ on ATD particles and suggested that the uptake of H₂O₂ 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 some other

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pathways are important for the uptake of peroxide compounds onto $\text{PM}_{2.5}$. Based on the characteristics of peroxide compounds, acid-base reaction, redox reaction, thermal decomposition, and aqueous reaction are potential pathways.

With respect to acid-base reactions, we must consider that H_2O_2 and PAA are both weak acids ($\text{pK}_a = 11.6$ for H_2O_2 , Marinoni et al., 2011; $\text{pK}_a = 8.2$ 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 enhanced with increasing RH (Santschi and Rossi, 2006; Preszler et al., 2007; Sullivan et al., 2009). However, $\text{PM}_{2.5}$ in Beijing is acidic (e.g., $\text{pH} = 5.57$, Wang et al., 2005). Therefore acid-base reactions on $\text{PM}_{2.5}$ 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 $\text{PM}_{2.5}$. These peroxide species can react with the reducing substances on aerosol particles, especially in the presence of water. Zhao et al. (2013) found that $\gamma_{\text{H}_2\text{O}_2}$ 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 of OVOCs will be significantly enhanced by the coexistence of H_2O_2 . In addition, both PAA and H_2O_2 can undergo transition metal catalytic oxidation and release radicals, such as OH radical, RO radical and RO_2 radical (Koubek and Edwards, 1963; Lin and Gurol, 1998; Zhang et al., 1998; Hiroki and LaVerne, 2005). Petigara et al. (2002) reported that the decomposition rate of H_2O_2 was enhanced by the presence of organic matter and manganese. Therefore, the redox reactions may be important to the uptake of peroxide compounds on $\text{PM}_{2.5}$.

Third, consider the thermal decomposition. The structure of PAA, which has a hydroperoxyl group ($-\text{OOH}$) together with a carbonyl group ($\text{C}=\text{O}$), is less stable than H_2O_2 (Kunigk et al., 2012) and it more readily undergoes thermal decomposition than H_2O_2 . The bond dissociation enthalpies of PAA and H_2O_2 are 48 and 50 kcal mol^{-1} ,

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respectively (Bach et al., 1996). In addition, PAA is prone to dissociate in the presence of water. This is consistent with our experimental result that $R_{\gamma_{\text{PAA}}}$ is larger than $R_{\gamma_{\text{H}_2\text{O}_2}}$.

In considering the role of aqueous reactions, water soluble inorganic salts including sulfate and nitrate make up a substantial fraction (35–58 %) of $\text{PM}_{2.5}$ (Sun et al., 2004; Wang et al., 2005). 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, $\text{PM}_{2.5}$ 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 $(\text{NH}_4)_2\text{SO}_4$, 39 % for NH_4HSO_4 and 62 % for NH_4NO_3 at 298 K (Cziczo et al., 1997; Lightstone et al., 2000), and the DRH of $\text{PM}_{2.5}$ 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 enhance the dissolution of Fe cation (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 $\gamma_{\text{H}_2\text{O}_2}$. They found that nitrate coating on calcium carbonate particles decreased the $\gamma_{\text{H}_2\text{O}_2}$ by 30–85 % at 3 % RH, but increased $\gamma_{\text{H}_2\text{O}_2}$ by a factor of 1–8 with increasing RH from 20 to 75 %, as compared to the $\gamma_{\text{H}_2\text{O}_2}$ 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 (e.g., SiO_2 , TiO_2 , $\alpha\text{-Al}_2\text{O}_3$ and ATD) have no or few soluble salts coating. These coatings can lead to the formation of an aqueous film on the particles under humid conditions, and in a similar manner, the aqueous reactions may occur as they do on the aqueous film on $\text{PM}_{2.5}$. This observation helps explain the differences in

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RH dependence of the uptake of peroxides on aged authentic particles and pristine particles. In conclusion, 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, 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 affected by the combined effects of catalytic reactions, redox reactions, thermal decomposition, and aqueous reactions.

4 Conclusions and implications

The present study is the first to measure the uptake coefficient of gaseous PAA and H₂O₂ on ambient PM_{2.5} and on mineral dust over a wide range of RH values (3–90%). Both of γ_{PAA} and $\gamma_{\text{H}_2\text{O}_2}$ on PM_{2.5} have a positive correlation with RH. In general, both γ_{PAA} and $\gamma_{\text{H}_2\text{O}_2}$ are on the order of 10⁻⁴. γ_{PAA} shows no obvious differences between haze days and non-haze days. Both γ_{PAA} and $\gamma_{\text{H}_2\text{O}_2}$ on Asian Dust Storm (ADS) particles show a similar RH dependence compared to PM_{2.5}, but on Arizona Test Dust (ATD), both γ_{PAA} and $\gamma_{\text{H}_2\text{O}_2}$ 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 $\gamma_{\text{PAA},90\% \text{RH}}$ to $\gamma_{\text{PAA},3\% \text{RH}}$ ($R_{\gamma_{\text{PAA}}}$) is larger than the ratio of $\gamma_{\text{H}_2\text{O}_2,90\% \text{RH}}$ to $\gamma_{\text{H}_2\text{O}_2,3\% \text{RH}}$ ($R_{\gamma_{\text{H}_2\text{O}_2}}$), while the Henry's law constant of H₂O₂ is 100 times that of PAA; 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 reac-

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tions. 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 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, 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 $3.4 \times 10^6 \text{ molecule cm}^{-3}$ 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 $3.7 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (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 44.4 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 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 $\text{PM}_{2.5}$ particles are spheres and the heterogeneous reaction on $\text{PM}_{2.5}$ with gaseous PAA is a pseudo-first-order reaction. The lifetime of PAA can be

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calculated by Eq. (16) (Ravishankara, 1997):

$$\tau = \frac{[C]}{d[C]/dt} = \frac{4}{\gamma \omega A_v} \quad (16)$$

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) (Seinfeld and Pandis, 2006):

$$\frac{dN}{d \log D_p} = \sum_i^n \frac{N_i}{\sqrt{2\pi} \log \sigma_i} \exp \left(-\frac{(\log D_p - \log \overline{D_{p,i}})^2}{2 \log^2 \sigma_i} \right) \quad (17)$$

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; $\overline{D_{p,i}}$ is the geometric mean diameter, m; σ_i is the geometric SD of the i th mode. The recommended values of $N_{i,i}$, $\overline{D_{p,i}}$ and σ_i are suggested by Yue et al. (2009). The value of A_v can be calculated by Eq. (18):

$$A_v = \frac{6M_a}{\rho \overline{D_p} V} \quad (18)$$

where M_a is the mass of the $PM_{2.5}$ particles, kg; ρ is the density of the $PM_{2.5}$ particles, $1.42 \times 10^3 \text{ kg m}^{-3}$ for a haze period and $1.96 \times 10^3 \text{ kg m}^{-3}$ for a non-haze period (Hu et al., 2012); $\overline{D_p}$ 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 about 0.02% of the fine particles number (3–1000 nm) (Wu et al., 2008) and 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. The mean mass concentration is $123 \mu\text{g m}^{-3}$ on a haze day and $23 \mu\text{g m}^{-3}$

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on a non-haze day and the corresponding A_v is $4.5 \times 10^3 \mu\text{m}^2 \text{cm}^{-3}$ on a haze day and $1.2 \times 10^3 \mu\text{m}^2 \text{cm}^{-3}$ on a non-haze day, which is similar to the reported values (Wehner et al., 2008; He et al., 2010). Here, we use the mean uptake coefficient of PAA on $\text{PM}_{2.5}$ at 60% RH, i.e., $\gamma = 2.38 \times 10^{-4}$, to estimate the PAA lifetime. The calculated lifetime of PAA against heterogeneous reaction is 3.6 h on a haze day and 13.5 h on a non-haze day. After the heterogeneous reaction is considered together with the gas phase reaction and deposition, the estimated lifetime of PAA is 3.3 h on a haze day and 7.6 h on a non-haze day, values similar to the field measurement results. Thus, the heterogeneous reaction on $\text{PM}_{2.5}$ is likely to be an important removal pathway for PAA.

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 ($\text{NO} + \text{NO}_2$), such as the urban area, NO_2 will combine with acetyl peroxy ($\text{CH}_3\text{C}(\text{O})\text{OO}$) radical to form PAN by competing with HO_2 radical which will donate H to the $\text{CH}_3\text{C}(\text{O})\text{OO}$ radical to form PAA. The uptake of PAA onto the particle surface will result in a sink for the $\text{CH}_3\text{C}(\text{O})\text{OO}$ radical, hence reducing PAN, which is an important carrier of NO_x and regionally transports NO_x from the urban area to the rural and remote areas, affecting the oxidants (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

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may help 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 account of the heterogeneous reactions of peroxide compounds on aerosols.

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Table 1. Statistical summary showing the sampled mass of $\text{PM}_{2.5}$ (in unit mg), average mass concentration of $\text{PM}_{2.5}$ (in unit $\mu\text{g m}^{-3}$) and effective surface area of $\text{PM}_{2.5}$ (in unit cm^2) on haze and non-haze days.

Samples	Weather	M_a	Concentration	A_{es}
31 Jul ^a	haze	1.28	127.0	12.88
31 Jul ^b	haze	1.61	156.9	13.75
1 Aug ^a	haze	1.33	132.6	13.04
1 Aug ^b	haze	1.39	136.7	13.19
2 Aug ^a	haze	1.04	107.0	12.12
2 Aug ^b	haze	1.39	137.8	13.21
3 Aug ^a	haze → non-haze	0.60	61.7	10.09
3 Aug ^b	non-haze	0.41	41.1	8.63
4 Aug ^a	non-haze	0.10	9.2	3.15
4 Aug ^b	non-haze	0.18	16.9	5.44
5 Aug ^a	non-haze	0.26	25.6	6.85
5 Aug ^b	non-haze	0.32	32.4	7.76

Note: ^a daytime; ^b nighttime; A_{es} , effective surface area; M_a , mass of $\text{PM}_{2.5}$.

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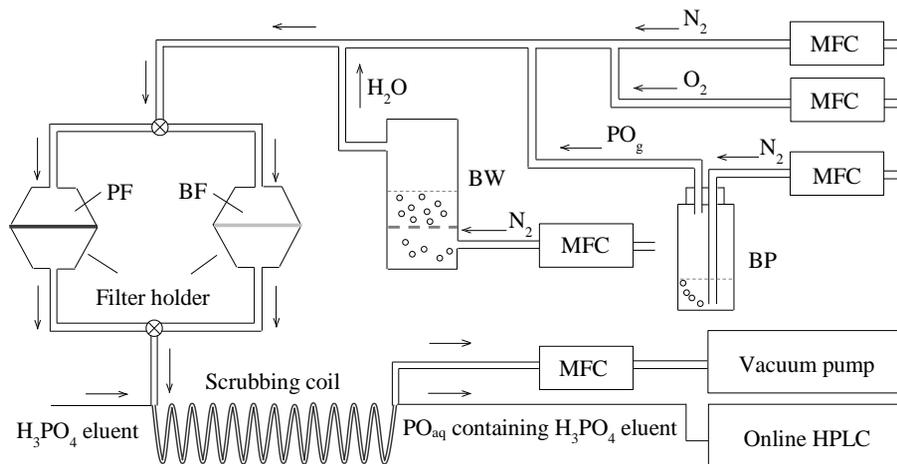


Figure 1. Schematic diagram of experimental apparatus. MFC, mass flow controller; PF, particle loaded filter; BF, blank filter; PO_g, peroxide compound in the gas phase; PO_{aq}, peroxide compound in the aqueous phase; BP, bubbler for peroxide vapor; BW, bubbler for water vapor; HPLC, high-performance liquid chromatography. The scrubbing coil, BP and BW were kept in 277 K water bath.

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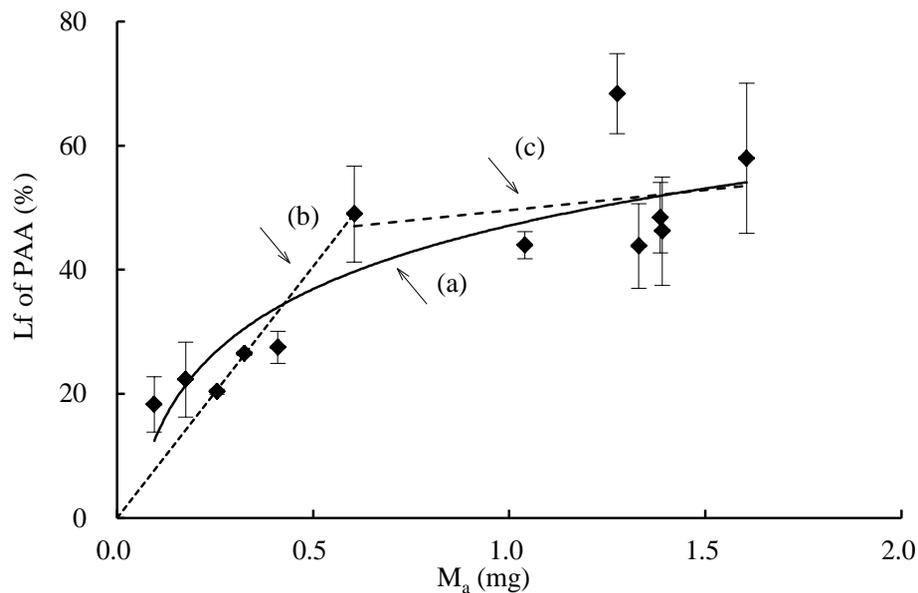


Figure 2. The trend line of fractional loss (Lf) of PAA against $PM_{2.5}$ mass (M_a) (60% RH). The error bars represent 1 SD. Solid line (a), the logarithmic trend line of Lf against M_a among all mass values; dotted line (b), the linear correlation of Lf against M_a in the low mass region; dotted line (c), the nearly constant Lf against M_a in the high mass region.

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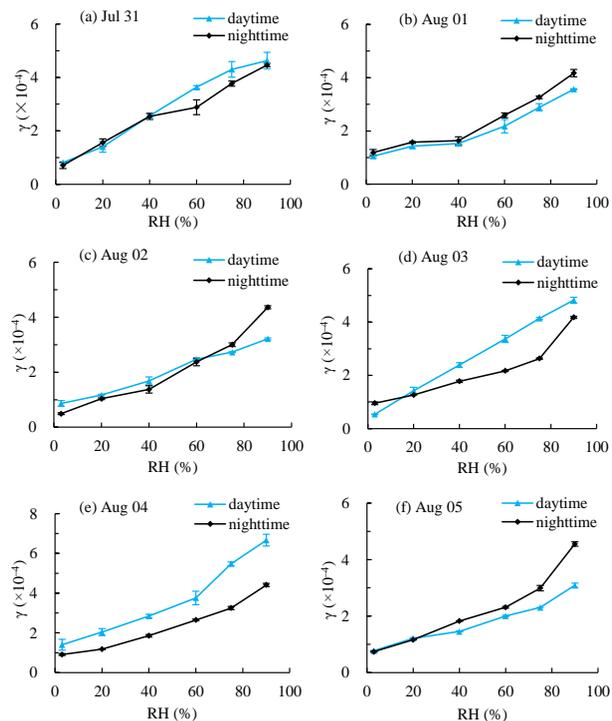


Figure 3. Profiles of uptake coefficient of gaseous PAA on $PM_{2.5}$ over a range of RH (3–90%). The $PM_{2.5}$ particles were either collected in the daytime or in the nighttime. Error bars are 1 SD.

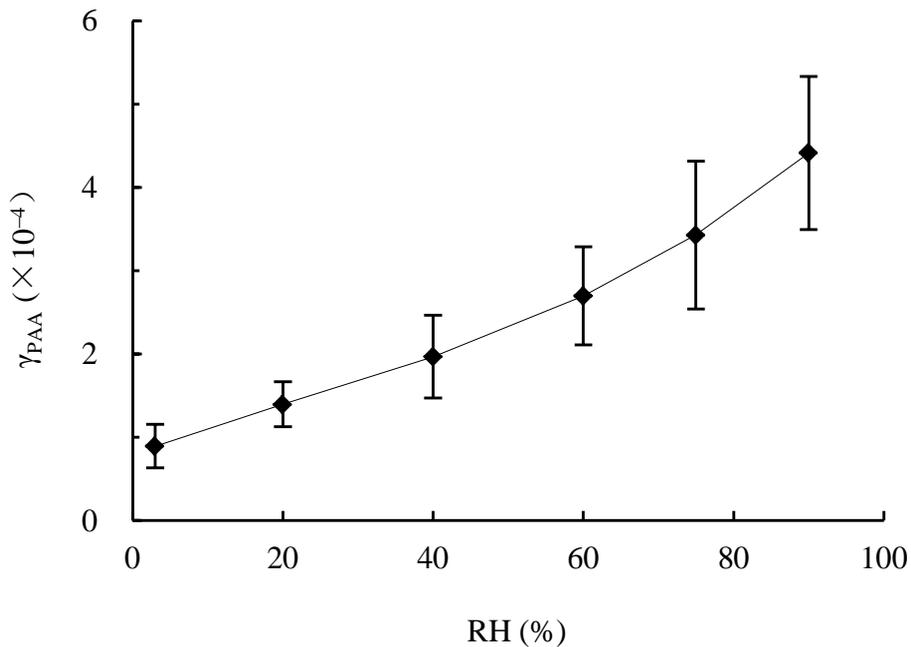


Figure 4. Uptake coefficient of PAA on $\text{PM}_{2.5}$ particles as a function of relative humidity. The error bars are 1 SD.

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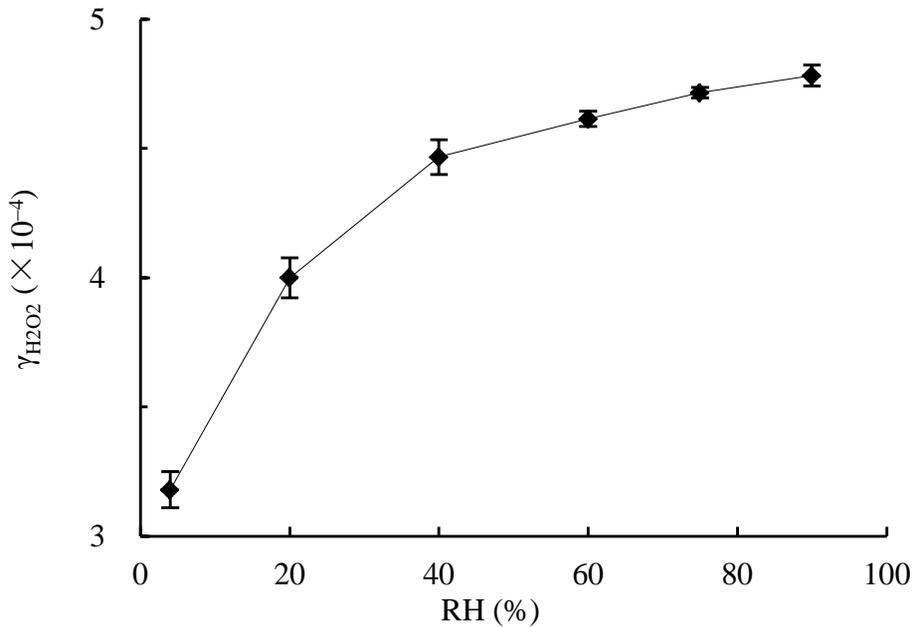


Figure 5. Uptake coefficient of H_2O_2 on $\text{PM}_{2.5}$ particles as a function of relative humidity. The error bars are 1 SD.

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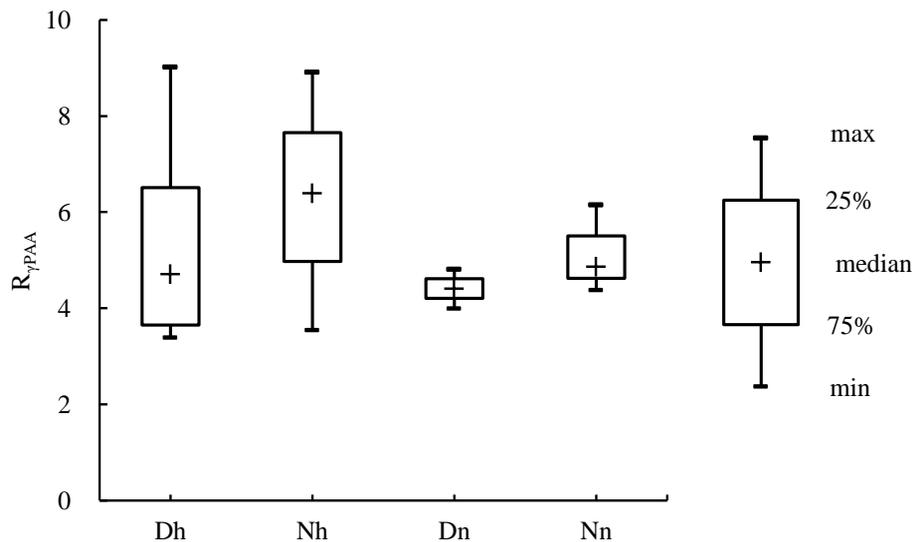


Figure 6. The ratio of γ_{PAA} at 90% RH to γ_{PAA} at 3% RH ($R_{\gamma_{\text{PAA}}}$) on $\text{PM}_{2.5}$. Dh, daytime of haze day; Nh, nighttime of haze day; Dn, daytime of non-haze day; Nn, nighttime of non-haze day.

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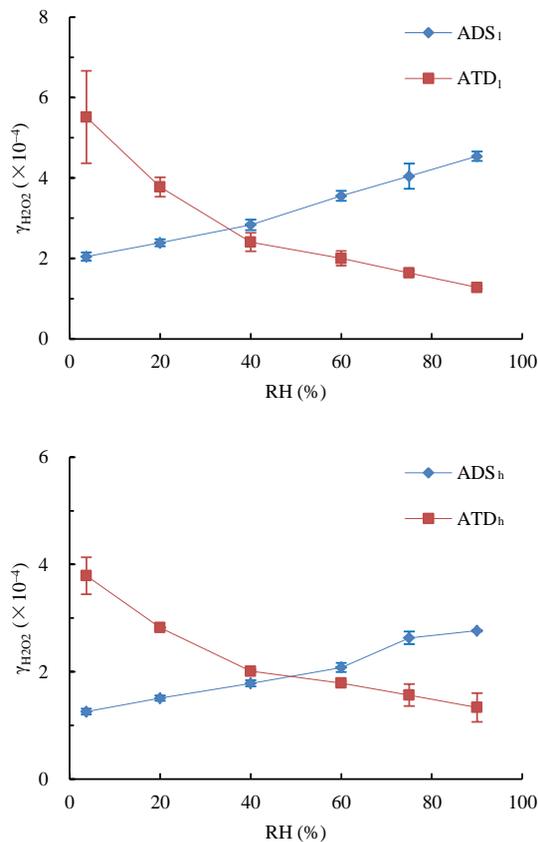


Figure 7. Uptake coefficient of H_2O_2 on ADS and ATD particles as a function of relative humidity. ADS₁ and ATD₁, the mass of mineral dust about 0.3 mg; ADS_h and ATD_h, the mass of mineral dust about 1.3 mg. The error bars are 1 SD.