Atmos. Chem. Phys., 10, 737–748, 2010
www.atmos-chem-phys.net/10/737/2010/

Atmospheric Chemistry and Physics

Peroxyacetic acid in urban and rural atmosphere: concentration, feedback on PAN-NO_x cycle and implication on radical chemistry

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Received: 2 October 2009 – Published in Atmos. Chem. Phys. Discuss.: 26 October 2009
Revised: 6 January 2010 – Accepted: 8 January 2010 – Published: 25 January 2010

Abstract. Peroxyacetic acid (PAA) is one of the most important atmospheric organic peroxides, which have received increasing attention for their potential contribution to the oxidation capacity of the troposphere and the formation of secondary aerosols. We report here, for the first time, a series of data for atmospheric PAA concentrations at urban and rural sites, from five field campaigns carried out in China in summer 2006, 2007 and 2008. For these five measurements, daytime mean (08:00–20:00 LT) PAA concentrations on sunlit days were 21.4–148.0 pptv with a maximum level of ~1 ppbv. The various meteorological and chemical parameters influencing PAA concentrations were examined using Principal Factor Analysis. This statistical analysis shows that the local photochemical production was the major source of PAA, and its concentration increased with increasing temperature, solar radiation and ozone but decreased with increasing NO_x (NO and NO_2), CO, SO_2, and relative humidity. Based on the dataset, several issues are highlighted in this study: (i) Because PAA is a product from the photochemical oxidation of some specific volatile organic compounds (VOCs) that lead to acetyl peroxy radicals, the importance of various VOCs with respect to the PAA formation is therefore ranked using the incremental reactivity method. (ii) The contribution of PAN thermal degradation to PAA formation under conditions of different NO_x concentrations is estimated based on the chemical kinetics analysis. The result shows that PAN seems to play an important role in the formation of PAA when the NO/NO_2 concentration ratio was less than 0.2 and PAA would correspondingly have feedback on the PAN-NO_x cycle. (iii) PAA and other peroxides, such as methyl hydroperoxide (MHP) and H_2O_2, usually exhibited a similar asymmetric shape typically shifted to the afternoon. However, under some conditions, H_2O_2 diurnal cycle was out of phase with MHP and PAA. The combination of linear regression and kinetics analysis indicate that the formation and removal processes of H_2O_2 may be different from those of MHP and PAA. (iv) Considering that PAA is the reservior of free radicals, its fate is expected to have an effect on the free radical budget in the atmosphere. A box model based on the CBM-IV mechanism has been performed to access its influence on the radical budget. We suggest that the detailed information on PAA in the atmosphere is of importance to better understand the free radical chemistry.

1 Introduction

Peroxyacetic acid (PAA) plays a potentially important role in atmospheric processes. As an organic peroxide oxidant, PAA contributes to the oxidation capacity of the atmosphere (Barth et al., 2007; Acker et al., 2008) and the formation of secondary sulfate (Lind et al., 1987; Stockwell, et al., 1994); as a reservoir of free radicals, PAA can reflect the free radical levels of the troposphere and indicate the extent of free radical chemistry involved at a particular location (Jackson and Hewitt, 1999; Lee et al., 2000). Furthermore, PAA is thought to have some toxic effects on ecosystem and human beings.

No significant direct emission of PAA from natural or anthropogenic sources has been found, and it is believed that the atmospheric PAA is mainly produced through the combination of peroxy radicals (Reactions R1, R2) (Lightfoot et al., 1992; Staffelbach et al., 1995). Further, a small amount of PAA can be formed by the reaction of acetyl peroxy radical ($CH_3C(O)OO$) with high concentrations of "H-atom

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Fig. 1. Map showing the location of observation sites, Beijing, Mazhuang and Backgarden.

donors" commonly found in atmospheric aqueous phase, like formate, formaldehyde, glyoxal and phenolic compounds (Reaction R3) (Faust et al., 1997). Sinks of PAA include photolysis, reaction with the hydroxy radical (OH), and loss by physical deposition to the ground (Reactions R4, R5) (Jackson and Hewitt, 1999). The photolysis of PAA releases OH (Keller et al., 2008), and the reaction between PAA and OH regenerates $CH_3C(O)OO$ (Jenkin et al., 1997), so that PAA is involved in the radical balance as both a source and a sink.

$$CH_3C(O)OO\cdot + HO_2\cdot \rightarrow CH_3C(O)OOH + O_2 \quad \text{(R1)}$$

$$CH_3C(O)OO\cdot + CH_3OO\cdot \rightarrow CH_3C(O)OOH + HCHO + O_2 \quad \text{(R2)}$$

$$CH_3C(O)OO\cdot + RH \rightarrow CH_3C(O)OOH + R\cdot \quad \text{(R3)}$$

$$CH_3C(O)OOH + hv \rightarrow CH_3C(O)O\cdot + \cdot OH \quad \text{(R4)}$$

$$CH_3C(O)OOH + \cdot OH \rightarrow CH_3C(O)OO\cdot + H_2O \quad \text{(R5)}$$

In recent years, PAA has been widely used in industry for disinfection and bleaching purposes. In many industrial and medical applications, a release of PAA can not be fully avoided (Henneken et al., 2006). It has been found that high exposure and eye contact will cause severe health problems. For the above reasons, many studies were focusing on developing reliable and commercial methods to detect its aqueous concentration (Davies and Deary, 1988; Pinkernell et al., 1996; Ruttinger and Radschuweit, 2000; Awad, et al., 2003), and to monitor its airborne concentration on a regular basis in workplace environments (Effkemann et al., 1999; Hecht et al., 2004; Henneken et al., 2006). However, field measurements of PAA are extremely sparse (Fels and Junkermann, 1993; Walker et al., 2006), and hence, the limited data restrain better understanding the role of PAA on atmospheric chemistry.

In this paper, we focus on the less studied organic peroxide, PAA, by reporting its levels during five field campaigns carried out in urban and rural sites of China, namely, Beijing-2006, Beijing-2007, Beijing-2008, Backgarden-2006, and Mazhuang-2007. The primary aim of our study is fourfold: (i) to investigate the impact of meteorological and chemical factors on the concentrations and variations of PAA in the atmosphere; (ii) to examine the relationship between PAA and PAN using chemical kinetic analysis to elucidate the feedback of PAA on PAN-NO_x cycle; (iii) to provide field evidence for potentially different sources and sinks of three peroxides, namely, hydroperoxide, methyl hydroperoxide (MHP), and PAA; and (iv) to evaluate the influence of PAA on free radicals budget using a box model based on the CBM-IV mechanism for better understanding the free radical chemistry.

2 Experimental

2.1 Measurement sites

Atmospheric PAA concentrations were investigated at three sites in China, namely, Peking University (PKU) campus in Beijing city (39.991° N 116.304° E), Mazhuang in Taian city, Shandong Province (36.150 ° N 116.133° E), and Backgarden in Guangzhou city, Guangdong Province (23.548° N 113.066° E), on the base of several regional integrated field campaigns, as shown in Fig. 1.

Beijing, the capital city of the country, is located in the north of China. The PKU campus is in the northern downtown, which is the hi-tech center of Beijing. The surroundings of campus are several electronic supermarkets, institutes, campuses, residential apartments and two major streets at its east and south which are often congested. The sampling inlet was mounted on the roof of a six-story building (~26 m aboveground). The PAA measurement was a part of air quality research campaign in Beijing (Beijing-2006, 2007, 2008) during 11 August–9 September 2006, 3–31 August 2007, and 11 July–31 August 2008. Beijing is located in temperate zone with half-moist continent monsoon climate and four distinct seasons. During the 2006 campaign, the average meteorological values (arithmetic mean±standard deviation) were: 26.1±4.6 °C ambient temperature, 65.1±20.1% ambient relative humidity, 1002±5 hPa ambient pressure, 1.6±1.4 m/s local wind speed, and the dominant wind direction was southerly/westerly. During the 2007 campaign, the average meteorological values (arithmetic mean ± standard deviation) were: 29.3±4.3 °C ambient temperature, 54.0±15.3% ambient relative humidity, 1001±6 hPa ambient pressure, 1.5±0.8 m/s local wind speed, and the dominant wind direction was southerly/westerly. During the 2008 campaign, the average meteorological values (arithmetic mean ± standard deviation) were: 28.1±5.6 °C ambient temperature, 67.0±18.5% ambient relative humidity, 998±4 hPa ambient pressure, 1.0±0.9 m/s local wind speed, and the dominant wind direction was southerly.

Guangzhou, the capital city of Guangdong Province, is located in south China. As a megacity, the increase in industry and population impacts the air quality of Guangzhou and this city is impacted by complex air pollution due to the mixture of coal burning and vehicle emissions. Backgarden is a rural site, surrounded by 20 km^2 of forest and 2.7 km^2 of lake, located in the north of the central Pearl River Delta Region (PRD) and about 60 km northwest of Guangzhou. Backgarden is a much less populated area at the outskirts of the densely populated center of the PRD and can be treated as a regional background site. Backgarden does not have significant local vehicle emission, while the biomass burning in the afternoon and cable burning in the evening might be a source of local mission. The sampling inlet was mounted on the roof of a three-story hotel building (∼14 m aboveground), which is located next to a 2.7 km^{2}reservoir in a rural resort surrounded by a large area of farmland and forest. The PAA measurement was a part of Program of Regional Integrated Experiments of Pearl River Delta Region (PRIDE-PRD) during 3–30 July 2006. The Backgarden site experiences a typical sub-tropical climate and is usually influenced by the monsoon circulation in July. During the period of PAA measurement, the observation site was mainly influenced by the western Pacific subtropical high pressure and typhoon. When controlled by the western Pacific subtropical high pressure from 19 to 23 July, the days were sunny, and the dominant wind direction at Backgarden was southerly. When influenced by typhoon from 24 to 25 July, northerly winds prevailed at the observation site. During the last days of campaign from 26 to 30 July, the local weather conditions were cloudy and rainy and the sampled air masses came mainly from the south/southeast. The average meteorological values (arithmetic mean ± standard deviation) for the campaign were: $29.5\pm 3.4\,^\circ$C ambient temperature, $76.2\pm14.4\%$ ambient relative humidity, 1001 ± 4 hPa ambient pressure, and 1.9 ± 1.2 m/s local wind speed.

Mazhuang is a rural site located 40 km southwest of Taian, a medium sized city in Shandong province, northeast of China. Taian city, the location of Mount Tai, is suffering from the acid rain pollution in recent years and the amount of rain of pH $\leq$4.5 accounted for nearly 16% of total precipitation every year. The sampling inlet was mounted on the roof of a container (∼5 m above the ground) on the playground of a primary school. It was surrounded by farmland and a national highway passed by there 1 km north. The PAA measurement was a part of Chinese atmospheric acidifying mechanism research campaign carried out during 29 June–31 July 2007. Mazhuang experiences half-moist continent monsoon climate. During the observation period, the average meteorological values (arithmetic mean ± standard deviation) were: $28.7\pm5.8\,^\circ$C ambient temperature, $70.4\pm19.6\%$ ambient relative humidity, 1001 ± 5 hPa ambient pressure, 1.2 ± 1.3 m/s local wind speed, and the dominant wind direction was southerly/southeasterly.

2.2 Measurement method for PAA

2.2.1 Instrument

For the five measurements, an automatic ground-based apparatus for hydrogen peroxide and organic peroxides measurement was set up by using a scrubbing coil collector to sample ambient air. High performance liquid chromatography (HPLC) post-column derivatization equipped with fluorescence detection was used for the analysis of PAA and other peroxides. The details about this instrument can be found in our previous work (Xu and Chen, 2005; Hua et al., 2008). The instrument was located in an air conditioned room or container and the sampling inlet was mounted on the rooftop of the building or container. The detection limits of H_2O_2, MHP, and PAA in the gas phase were about 9, 20 and 12 pptv, respectively.

2.2.2 Chemicals

H_2O_2 was purchased from Sigma-Aldrich (35% solution). PAA was synthesized from H_2O_2 and acetic acid (>99.5%, Damao), and methyl hydroperoxide was synthesized from H_2O_2 and dimethyl sufate as described in Hua et al. (2008). The concentrations of stock solutions and standard solutions were determined using $KMnO_4$ and $KI/Na_2S_2O_3$/starch every two weeks. All reagents and standard solutions were prepared with 18 MΩ Milli-Q water (Millipore), and were stored at 4 °C in a refrigerator.

2.3 Measurement method for other trace gases

PAN was determined using online GC (HP5890)-ECD (Shimadzu Mini-2) with a time resolution of 5 min operated by PKU. Briefly, ambient air was continuously sampled into a wide bore fused silica capillary gas chromatographic separation column with subsequent detection by electron capture. The detection limit of PAN was 5 pptv. The detail can be found in Wang and Zhang (2007). Other trace gases measurement methods can be seen in our previous work (Hua et al., 2008).

2.4 Modeling methodology

A box model was performed based on the Carbon Bond Mechanism-Version IV (CBM-IV), developed by M. W. Gery (1989) and updated recently. The CBM-IV mechanism includes the degradation kinetics and oxidation schemes of 43 species. In this study, we add the PAA scheme into this mechanism based on parameters evaluated by Jenkin et al. (1997) and Atkinson et al. (1999). Typical model inputs include NO_x, SO_2, CO, VOCs, water vapor, and temperature. The box model calculations were carried out using initial VOCs and NO_x concentrations, with additional VOCs and NO_x emissions every 1-h during the 72-h simulations.

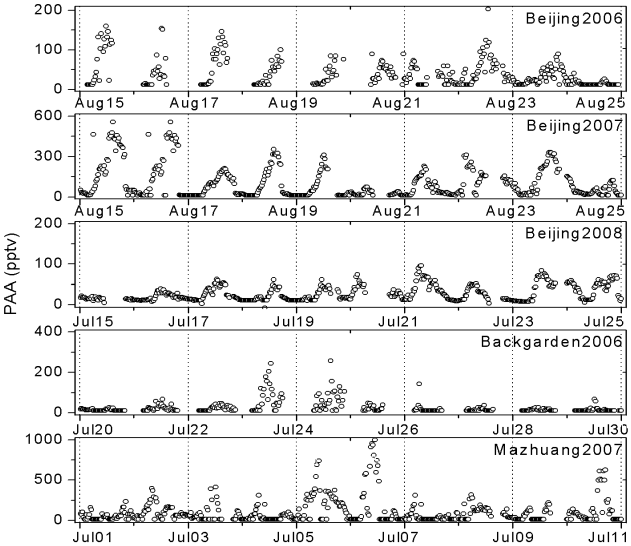

Fig. 2. Temporal profiles of atmospheric PAA concentrations during periods of five campaigns.

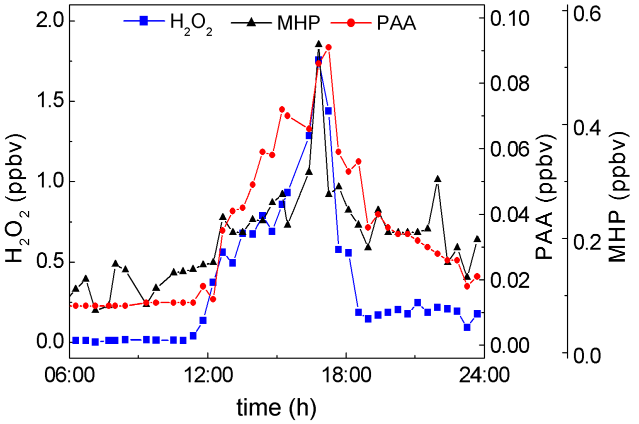

Fig. 3. Diurnal cycle for PAA, H_2O_2, and MHP in Beijing on 2 August 2008.

3 Results and discussion

3.1 General observations

Air samples for Beijing-2006, Beijing-2007, Beijing-2008, Backgarden-2006, and Mazhuang-2007 amounted to 862, 867, 2614, 354, and 1663, respectively. PAA was often present in the order of several tens of pptv level among these five campaigns, with a maximum value of ∼1 ppbv at Mazhang, 2007. In order to calculate the mean of the observed concentrations, any value below the detection limit was treated as 12 pptv. With regard to all samples, the mean (and standard deviation) concentrations during daytime (08:00–20:00 LT) were 40.7±32.8 pptv for Beijing-2006, 141.7±131.3 pptv for Beijing-2007, 43.7±51.2 pptv for Beijing-2008, 31.9±20.3 pptv for Backgarden-2006 and 148.0±156.3 pptv for Mazhuang-2007. The mean values at night (20:00–08:00 LT) were 27.9±27.3 pptv for Beijing-2006, 84.5±84.1 pptv for Beijing-2007, 27.2±39.2 pptv for Beijing-2008, 21.4±7.4 pptv for Backgarden-2006 and 85.8±93.8 pptv for Mazhuang-2007. These values are higher than or comparable with those in previous measurements that PAA was occasionally detected with a level of 10–30 pptv (Walker et al., 2006) and accounted for less than 10% of total measured peroxides (Fels and Jundermann, 1993). Temporal profiles of PAA concentrations for the five campaigns are shown in Fig. 2.

The time series of PAA, H_2O_2 and MHP on 2 August 2008, a sunny day in Beijing, were shown in Fig. 3. The diurnal profile of PAA was similar to those of H_2O_2 and MHP. This can be explained by vertical mixing and local photochemical production in a sunlit day (Möller et al., 2004, 2009). From sunrise, the inversion layer was broken and PAA was transported down by vertical mixing. The photochemical reactions began later and consequently, PAA concentration started to rise, reaching a maximum level at 17:00 LT. Its level remained relatively high in the late afternoon and decayed rapidly due to the dry deposition from the sunset to 24:00 LT. Throughout the night, there seemed to be no obvious transportation from the residual layer, which contains species that do not mix rapidly during the night with either the nocturnal boundary dayer below or the free troposphere above (Finlayson-Pitts and Pitts, 2000), to the surface layer and PAA was depleted even to zero till the early morning.

3.2 Meteorological and chemical factors related to the ambient PAA level

A statistical method, Principal Factor Analysis (PFA) is employed in order to understand the influence of chemical and meteorological parameters on the PAA concentrations. The advantage of PFA is to provide the decomposition into modes of variation that can be more easily interpretable by performing dimensionality reduction (Jolliffe et al., 2002; Ren et al., 2009). A matrix with 12 variables, including PAA, SO_2, NO, NO_2, CO, O_3, wind direction (WD), wind speed (WS), temperature (T), relative humidity (RH), total radiation (TI), and pressure (P), from 317 samples of Backgarden-2006 was analyzed. The varimax rotated factor pattern for the data set with 4 factors was arranged in descending order of variances explained, as shown in Table 1. Factor 1, which has a strong positive loading from secondary pollutants, including O_3 and PAA, while a negative loading from primary pollutants, NO, NO_2, CO and SO_2, indicates a photochemical production process. It can be associated with the photochemical aged air-masses (Tseng et al., 2009). Figure 4 shows a typical case related to Factor 1. During 19–21 July, days were sunny with slight southern breeze, intense solar radiation, high temperature and low RH at noon, PAA exhibited a high concentration

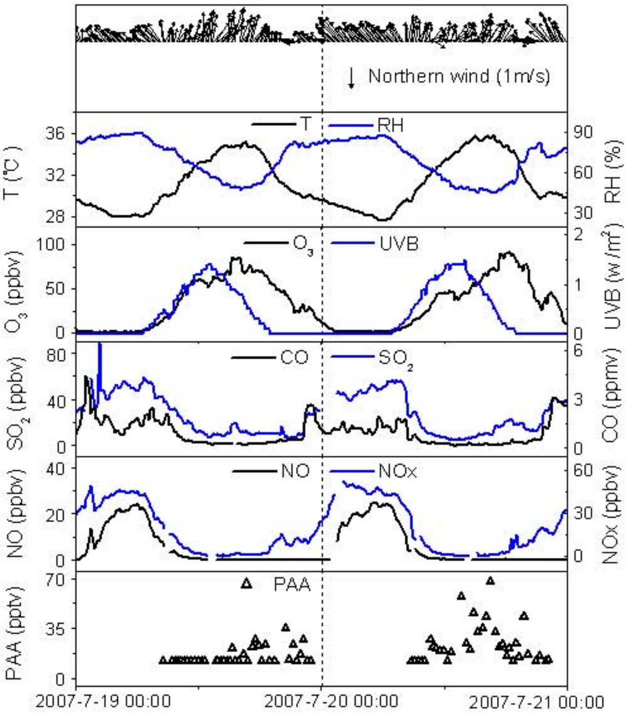

Fig. 4. Diurnal profiles of wind speed, wind direction, temperature, total irradiation, relative humidity, CO, SO_2, NO, O_3, and PAA at Backgarden from 19 to 20 July 2006.

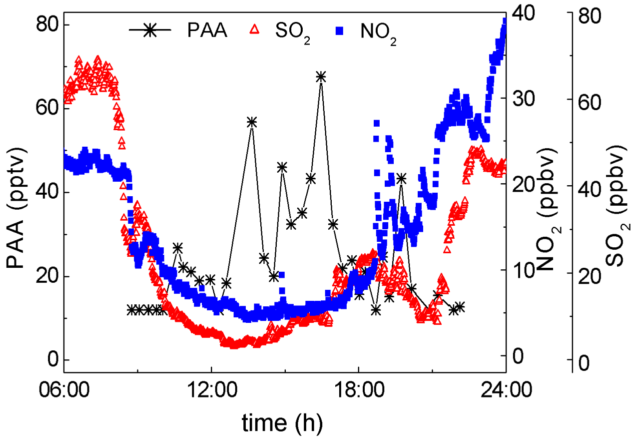

Fig. 5. Diurnal profiles of PAA, SO_2, and NO_2 at Backgarden on 21 July 2006.

Table 1. The rotated factor matrix from principal factor analysis of data at Backgarden 2006 (n=317; accumulative variance 71.8%).

Factor	1	2	3	4
PAA	**0.53**	–0.12	**–0.49**	0.10
SO_2	–0.33	**0.80**	0.14	0.31
NO	–0.19	0.14	0.02	**0.73**
NO_2	**–0.50**	**0.58**	–0.25	0.05
CO	**–0.57**	0.39	–0.14	–0.23
O_3	**0.71**	0.42	0.21	–0.04
WD	**0.62**	0.18	–0.39	–0.05
WS	–0.14	–0.49	**0.51**	0.45
T	**0.86**	0.41	0.08	–0.05
RH	**–0.88**	–0.27	–0.22	0.01
TI	**0.64**	0.09	**0.58**	0.09
P	–0.35	0.01	**0.61**	–0.49
Variance explained	34.7%	15.5%	12.7%	8.9%

due to the continuous production of free radicals in the daytime. A delay between the maximum of solar radiation and PAA concentration was observed, for the reason that the production of peroxy radicals (HO_2) and $CH_3C(O)OO$ is the subsequent step following OH formation (Gnauk et al., 1997). It is not surprising for the positive correlation between temperature and PAA because temperature affects the reaction rate and the production of radicals in the atmosphere (Jackson and Hewitt, 1999; Reeves and Penkett, 2003). Factor 2 has a strong positive loading from SO_2 and NO_2, while a negative loading from PAA. The anti-correlation between PAA and SO_2/NO_2 can be derived from Fig. 5. It can be easily explained by the photochemical history of primary and secondary pollutants in the atmosphere. In addition, the low NO_2 level condition is favorable for PAA production for the following two reasons: first, NO_2 provides a sink of OH; and second, NO_2 will compete for $CH_3C(O)OO$ with HO_2 in the atmosphere, producing peroxylacetyl nitrate (PAN). Therefore, PAA is inclined to accumulate to a high concentration when the ambient concentrations of NO_2 are low. Factor 3, which had a loading from PAA, wind speed, total radiation and pressure, indicates two possible sinks of PAA, namely, photolysis under an intense radiation and dry deposition under a shallow inversion and at a low wind speed. Previous studies have reported that the dry deposition rate of peroxide over trees will significantly increase (Walcek et al., 1987; Wesley et al., 1989). It is possible that dry deposition on the surface might act as an important sink for the loss of PAA in Backgarden, where natural plants are luxuriant. Factor 4 has a strong loading from NO but the PAA loading is rather small, suggesting that PAA levels are sensitive to the NO background. NO will compete directly with PAA production via the cross combination of RO_2 radicals if sufficient NO is present (Reactions R6, R7, and R10) (Frey et al., 2005). The NO suppression of radicals could be observed in the early morning of 24 July, see Fig. 6, when a spike in NO of over 20 ppbv possibly caused a reduction of PAA.

$$NO + HO_2\cdot \rightarrow NO_2 + \cdot OH \quad (R6)$$

$$NO + CH_3OO\cdot \rightarrow NO_2 + HCHO + HO_2\cdot \quad (R7)$$

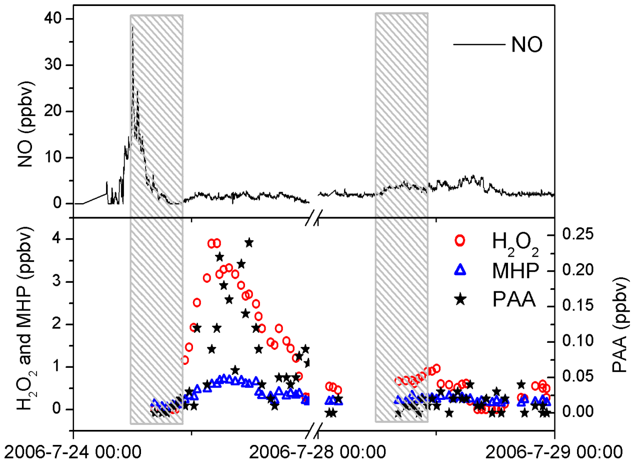

Fig. 6. Diurnal profiles of peroxides and NO at Backgarden on 24 and 28 July 2006.

3.3 Correlations with other species

3.3.1 PAA and VOCs

PAA is produced from the photochemical oxidation of some volatile organic compounds (VOCs) via $CH_3C(O)OO$ formation. Here we refer to the maximum incremental reactivity (MIR) method (Carter and Atkinson, 1989; Grosjean et al., 2002) to evaluate the PAA formation potential (PFP).

$$\mathrm{PFP} = \lim_{\Delta_{\mathrm{VOC_i}} \to 0} \left\{ \frac{\mathrm{PAA}_{(\mathrm{VOC_i}+\Delta\mathrm{VOC_i})} - \mathrm{PAA}_{(\mathrm{VOC_i})}}{\Delta\mathrm{VOC_i}} \right\},$$

where $\mathrm{PAA}_{(\mathrm{VOC_i})}$ is the maximum of PAA calculated in the "base case" simulation, $\mathrm{PAA}_{(\mathrm{VOC_i}+\Delta\mathrm{VOC_i})}$ is the maximum of PAA calculated with the test $\mathrm{VOC_i}$ added in the "base case" simulation, and $\Delta\mathrm{VOC_i}$ is the incremental change in the concentration of test $\mathrm{VOC_i}$. The "base case" was the idealized simulation for urban atmosphere at VOCs/NO_x ratio approaching 8:1. The initial concentrations of VOCs and NO_x represented their average values for Beijing-2006 (Xie et al., 2008). The chemical mechanism used to calculate PFP is CBM-IV. It is a lumped structure mechanism where organics are represented using 12 species (Dodge, 2000). PAR represents alkanes and most single-bonded carbon atoms found in other organics. Ethene is treated explicitly (as ETH); the C=C double bond in other 1-alkenes is represented using the OLE surrogate. Toluene is represented explicitly (as TOL) and the surrogate XYL is used to represent the dialkylbenzenes; the trialkylbenzenes are presented as 1 XYL+1 PAR. Formaldehyde is treated explicitly (as FORM); the carbonyl component of other aldehydes is represented using the surrogate ALD2 whose chemistry is similar to acetaldehyde. Isoprene is treated explicitly (as ISOP).

Figure 7 lists the percent contribution of each surrogate species to the total PFPs calculated by the MIR method. XYL was the most important species in terms of PAA formation, accounting for ~33% of the total PFPs. The VOCs represented by XYL surrogate mainly include dialkylbenzenes and trialkylbenzenes, whose oxidation in the atmosphere produces methylglyoxal and biacetyl that contain acetyl group (Obermeyer et al., 2009), therefore leading to PAA formation. Also important as precursor of PAA was the surrogate ISOP, accounting for ~18% of the total PFPs. Key products of isoprene, including methylglyoxal and pyruvic acid, undergoing further photochemical reactions in the atmosphere lead to $CH_3C(O)OO$. The surrogate OLE, representing alkenes, accounted for ~ 13% of the total PFPs. The oxidation of some alkenes, including propene, 2-butene and 2-pentene, produces acetaldehyde, as discussed below. FORM accounted for ~12% of the total PFPs, for the reason that the oxidation of formaldehyde gives HO_2. TOL accounted for ~9% of the total PFPs. Products of toluene oxidized by OH include methylglyoxal and HO_2. The PFP for ALD2 accounted for ~8% of the total PFPs, because the oxidation of acetaldehyde initiated by OH leads to CH_3CO and subsequently to $CH_3C(O)OO$. Other species, such as ETH and PAR (~6% and 3%, respectively, of the total PFPs), were less significant than other VOCs as precursors to PAA. The above analysis evaluates the photochemical reactivity of VOCs in terms of PAA formation. However, the observed PAA level in the atmosphere is not only dependent on the photochemical reactivity, but also the ambient concentration of each VOC. Taking Beijing-2006 field campaign as an example, the measurement results showed top 10 VOCs with relatively high concentrations were formaldehyde, acetaldehyde, toluene, benzene, isopentane, butane, dialkyl-benzenes, pentane, propane, and isoprene (Xie et al., 2008). Taking into account the photochemical reactivity of each VOC, we suggest that dialkylbenzenes, acetaldehyde, formaldehyde, and toluene were the key compounds in total VOCs contributing to the PAA formation in Beijing 2006.

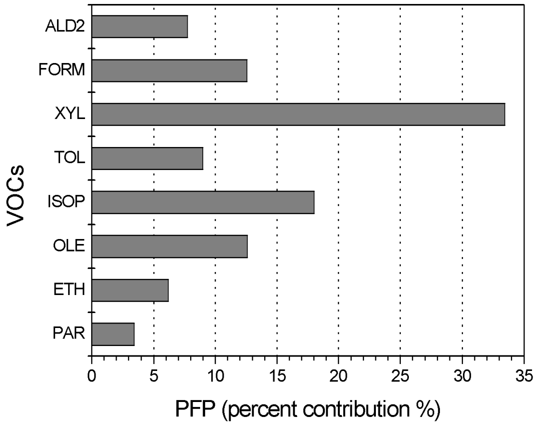

Fig. 7. Percent contribution (%) of VOCs to the PAA formation potential.

3.3.2 PAA and PAN

As mentioned above, any reaction leading to CH_3CO or $CH_3C(O)OO$ will probably contribute to the PAA formation. It is well known that PAN is thermally unstable, decomposing to produce the acetyl peroxy radical and nitrogen dioxide (Orlando et al., 1992). Therefore, PAN, which has received attention as precursor to photochemically reactive species, including free radicals (Grosjean et al., 2002; Grosjean et al., 2003), should be an important precursor of PAA. In the absence of NO, we expect the concentration of PAA to be associated with the extent of thermal degradation of PAN (Reactions R8, R9, R11), while under prevailing high NO conditions, PAA formation will be suppressed because $CH_3C(O)OO$ can be rapidly removed by NO (Reaction R10).

$$CH_3C(O)OO\cdot + HO_2\cdot \xrightarrow{k_8} CH_3C(O)OOH + O_2 \tag{R8}$$

$$CH_3C(O)OO\cdot + NO_2 \xrightarrow{k_9} CH_3C(O)OONO_2 \tag{R9}$$

$$CH_3C(O)OO\cdot + NO \xrightarrow{k_{10}} NO_2 + CO_2 + \cdot CH_3 \tag{R10}$$

$$CH_3C(O)OONO_2 \xrightarrow{k_{11}} CH_3C(O)OO\cdot + NO_2 \tag{R11}$$

Figure 8 presents the diurnal profiles of PAA and PAN at Backgarden on 24 July 2006. During that sunny day, the wind direction was northerly and veered to northwesterly in the afternoon, consistent with that of back trajectories obtained from NOAA (www.arl.noaa.gov), and the wind speed measured during daytime was ~2 m/s, ensuring that the transport distance of air mass was less than ~30 km from sunrise to the afternoon. So we suggest that the variation of PAA and PAN concentrations can be attributed, to a large extent, to the local photochemical drive. It can be seen that the daytime level of PAA is one order of magnitude on average lower than that of PAN, suggesting that Reaction (R9), which is highly dependent on the NO_2 concentration, was much more competitive than Reaction (R8) in the atmosphere. The peak time of PAA is several hours later than that of PAN, for the reason that the thermal degradation of PAN produces $CH_3C(O)OO$, which will subsequently react with HO_2 to form PAA. To better understand the correlation between PAN and PAA, the loss rate of PAN and formation rate of PAA were examined, using the same data on 24 July as an example. From Reactions (R8)–(R11), rate laws for the destruction of PAN and the formation of PAA are given by:

$$-\frac{\mathrm{dln[PAN]}}{\mathrm{dt}} = \frac{k_{10}k_{11}[\mathrm{NO}] + k_8k_{11}[\mathrm{HO_2}\cdot]}{k_8[\mathrm{HO_2}\cdot] + k_9[\mathrm{NO_2}] + k_{10}[\mathrm{NO}]};$$

$$\frac{\mathrm{d[PAA]}}{\mathrm{dt}} = \frac{k_8k_{11}[\mathrm{HO_2}\cdot][\mathrm{PAN}]}{k_8[\mathrm{HO_2}\cdot] + k_9[\mathrm{NO_2}] + k_{10}[\mathrm{NO}]},$$

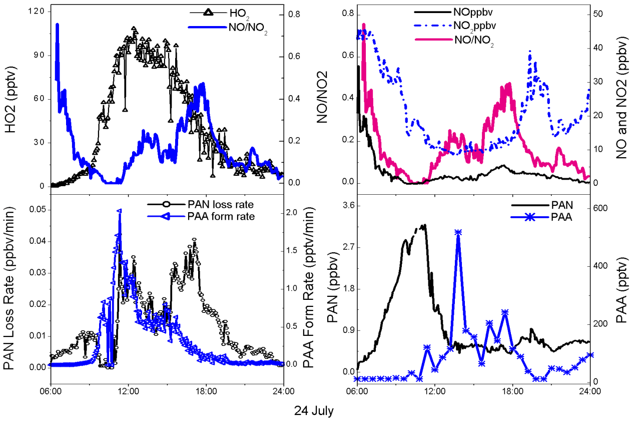

Fig. 8. Diurnal variations of PAN loss rate, PAA formation rate, together with concentrations of PAA, PAN, NO, NO_2 and HO_2 at Backgarden on 24 July 2006.

where $[HO_2\cdot]$, [NO], $[NO_2]$, and [PAN] are ambient concentrations, $k_8=4.3\times10^{-13}$ exp (1040/T) cm^3 $molecule^{-1}$ s^{-1}, $k_9=1.2\times10^{-11}\times(T/300)^{-0.9}$ cm^3 $molecule^{-1}$ s^{-1}, $k_{10}=7.8\times10^{-12}$ exp (300/T) cm^3 $molecule^{-1}$ s^{-1}, and $k_{11}=5.4\times10^{16}$ exp(−13 830/T) s^{-1} (Atkinson et al., 1999). The results of the calculations are shown in Fig. 8. The PAN loss rate is not only dependent on temperature, but also on the NO/NO_2 concentration ratio because high NO concentrations enhance indirectly the thermal degradation of PAN (see Reactions R10 and R11), thereby preventing the recombination of $CH_3C(O)OO$ with NO_2 to form PAN (McFadyen and Cape, 2005). The PAA formation rate is a function of both HO_2 concentration and NO/NO_2 concentration ratio because although the thermal degradation of PAN increases with increasing NO/NO_2 concentration ratio at a given temperature, a high level of NO will compete with HO_2 for $CH_3C(O)OO$ produced by the thermal degradation of PAN. It should be noted that the amount of $CH_3C(O)OO$ produced from VOCs oxidation was not considered in the above discussion and the steady-state concentration of $CH_3C(O)OO$ was significantly underestimated, resulting in higher loss rate for PAN and lower formation rate for PAA. Therefore, d[PAN]/dt and d[PAA]/dt represent the upper limit of PAN loss rate and the lower limit of PAA formation rate, respectively. When the NO/NO_2concentration ratio was approaching zero (09:50–10:30 LT), the loss rate of PAN and the formation rate of PAA were comparable. When $NO/NO_2 \leq 0.05$ and $[HO_2] > 20$ pptv (10:30–11:00 LT), the loss rate of PAN was nearly ten times higher than the formation rate of PAA, suggesting that under low NO/NO_2 concentration ratio, the PAA formation is an important pathway to remove $CH_3C(O)OO$, thus accelerating the thermal degradation rate of PAN. When $0.05 < NO/NO_2 \leq 0.2$ and $[HO_2] > 90$ pptv (11:00–12:00 LT), the formation rate of PAA was ten times lower than the loss rate of PAN. It indicates that a certain amount of HO_2 will compete for $CH_3C(O)OO$ with NO_x, suppressing the reproduction of PAN and leading to an enhanced PAA level. When $NO/NO_2 > 0.2$, the loss rate of PAN was several orders of magnitude higher than the formation rate of PAA, even though the HO_2 concentration remained a high level and

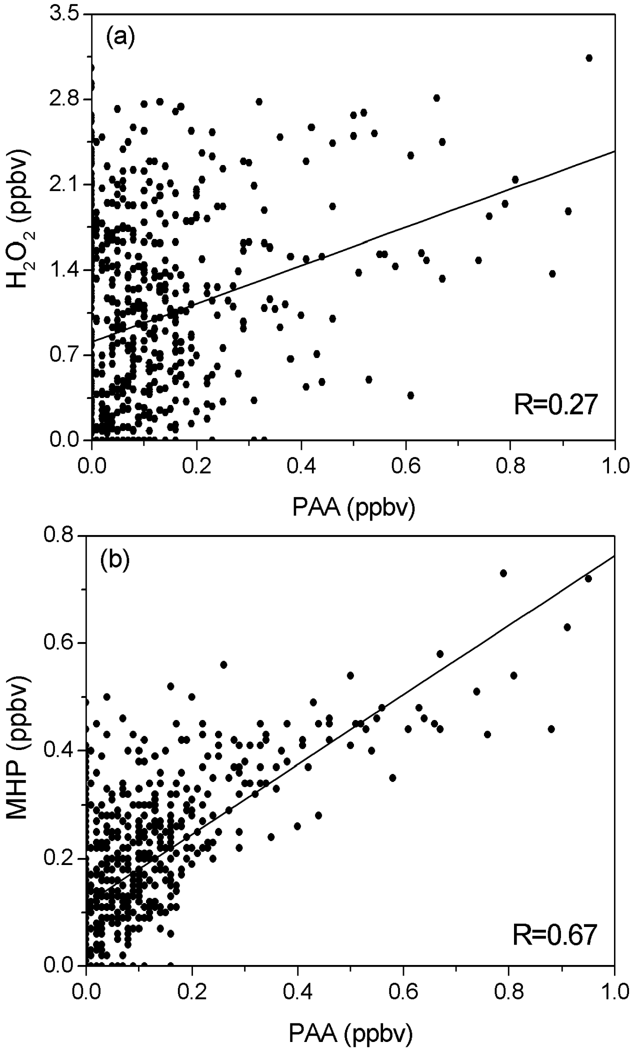

Fig. 9. Hourly averaged scatter plots of PAA vs. H_2O_2 and PAA vs. MHP at Mazhuang in July 2007.

accordingly, the contribution of PAN thermal degradation to the PAA formation was considered to be minor. In conclusion, we suggest that under low NO/NO_2 concentration ratio conditions, the reaction between HO_2 and $CH_3C(O)OO$ will be significant, producing an enhanced level of PAA, which will correspondingly have feedback on the thermal decomposition of PAN.

3.3.3 PAA–H_2O_2−MHP relationship

As shown in Fig. 3, PAA generally presented the same diurnal profile as both H_2O_2 and MHP in a sunlit day, indicative of a similar photochemical formation mechanism of these three peroxides. However, the linear regression for data in July 2007 at Mazhuang, see Fig. 9, shows that the positive correlation between PAA and MHP was stronger than that between PAA and H_2O_2, suggesting that the budget of H_2O_2 was potentially different from those of MHP and PAA at Mazhuang site. Figure 10 depicts the hourly averaged concentrations of PAA, H_2O_2 and MHP, together with simultaneously measured concentrations of primary pollutants on 6 July at Mazhuang site. The most striking feature is that H_2O_2 diurnal cycle was out of phase with MHP and PAA. Its concentrations were extremely low, even under detection limit, during 07:00–10:00 LT and 17:00–19:00 LT, but remained a high level during 03:00–06:00 LT and 21:00–23:00 LT. The most possible reason for the low concentrations of H_2O_2 in the daytime was the air mass fluctuation, which resulted in an increase of primary pollutants and a decrease of secondary pollutants in air. In addition, the removal of H_2O_2 by SO_2 should be considered because they exhibited a strong anti-correlation during 17:00–19:00 LT. The fraction of H_2O_2 undergoing the aqueous reaction with SO_2 was calculated to be negligible when there was no rain or fog. We suggest that the oxidation of S(IV) initiated by H_2O_2 on the surface of aqueous aerosols may provide evidence to explain this inverse correlation, because the surface reaction may be more important and more ubiquitous than the reaction in the bulk of wet aerosols, especially for the rapid reactions (Chen et al., 2008; Zhang et al., 2009). The elevated H_2O_2 at night can be probably ascribed to its particular sources. First, it has been proved that the ozonolysis of alkenes contributes to the production of H_2O_2 at night (Becker et al., 1990; Gäb et al., 1995; Grossmann et al., 2003; Möller, 2009). During 03:00–06:00 LT, O_3 dropped down to several ppbv, while a

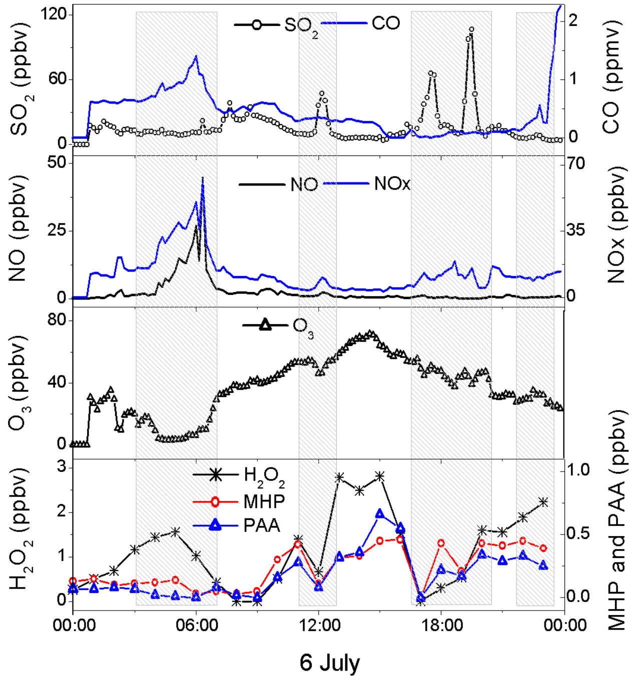

Fig. 10. Diurnal variations of PAA, H_2O_2, MHP, and primary pollutants at Mazhuang on 6 July 2007.

peak of H_2O_2 occurred simultaneously. Since the elevation of H_2O_2 and O_3 levels are usually observed synchronously when convective or regional-scale transport of the air mass affects the local gas concentrations (Balasubramanian et al., 1997; Takami et al., 2003), this H_2O_2 peak can be attributed to the local ozonolysis production. Second, several previous studies have reported the subsidence of H_2O_2 from aloft where chemical production occurs at night (Takami et al., 2003; Ganzeveld, et al., 2006). The elevated level of H_2O_2 during 21:00–23:00 LT can be explained by the downward transport of H_2O_2 from upper atmosphere, although more evidence should be needed.

3.4 Implication on free radical chemistry

PAA can be considered as the reservoir of radicals. If PAA undergoes photochemical reactions, the radicals will be released, but if PAA undergoes the dry/wet deposition, it will certainly become a sink of radicals. Here we present a preliminary evaluation with respect to the influence of PAA on the radical budget using a box model with CBM-IV mechanism. The following two versions are implemented: Version-1 (including PAA kinetics) and Version-2 (excluding PAA kinetics). The initial VOCs and NO_x concentrations input were representative of average concentrations in early morning in Beijing-2006. The simulation was carried out on a 24-h basis and we chose the period from 24 h to 48 h for analysis. The modeling results in terms of the OH, HO_2 and $CH_3C(O)OO$ concentrations are shown in Fig. 11. There are three scenarios constrained by NO_x emissions: Scenario 1 (base case simulation), Scenario 2 (simulation with 20% NO_x emission decreased), and Scenario 3 (simulation with 50% NO_x emission decreased). Apparently, when PAA kinetics was applied to the CBM-IV mechanism, both HO_2 and $CH_3C(O)OO$ concentrations simulated would decrease correspondingly, and the extent of these two radicals undergoing PAA formation pathway depends on the NO_x level. Take the Scenario 3 as an example, PAA accounted for up to ∼10% and ∼20% homogeneous loss of HO_2 and $CH_3C(O)OO$, respectively, indicating that PAA is an important sink of HO_2 and $CH_3C(O)OO$ under low NO_x condition. In particular, the impact of PAA on $CH_3C(O)OO$ is much more evident than HO_2.

It is well known that the oxidation of VOCs by OH initiates radical cycling via HO_x (=OH+HO_2) and NO_x (=NO+NO_2) chemistry in the troposphere (Emmerson et al., 2007; Lelieveld et al., 2008; Sheehy et al., 2008; Dusanter et al., 2009; Hofzumahaus et al., 2009). Particularly speaking, the photo-chemical oxidation of some specific VOCs generates $CH_3C(O)OO$, which can either react with NO_2 to form PAN, or react with NO and NO_3 to form CH_3O radicals in the polluted atmosphere (Tyndall et al., 2001). The CH_3O radical reacts with oxygen to produce HO_2, which will readily react with NO to generate recycled OH. However, in regions where NO_x levels are low, the fraction of $CH_3C(O)OO$ undergoing the above pathway will decrease because there is no sufficient NO_x to sustain the HO_x–NO_x cycling. As such, a significant amount of $CH_3C(O)OO$ and HO_2 will be removed due to the formation of PAA, leading to the termination of these radicals. The comparison between Version 1 and Version 2 indicates that PAA is potentially an important sink of $CH_3C(O)OO$ under low NO_x condition. To calculate the fraction of $CH_3C(O)OO$ undergoing PAA formation pathway in different regions, a more detailed mechanism constrained by the observed concentrations of various species is needed.

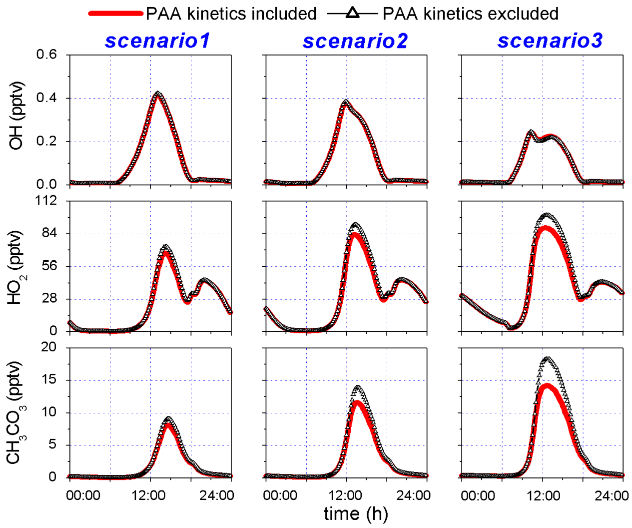

Fig. 11. The box model simulation of concentrations of free radicals before and after the PAA kinetics added to the CBM-IV mechanism (scenario 1 represents the base case simulation; scenario 2 represents the simulation with 20% NO_x emission decreased; scenario 3 represents the simulation with 50% NO_x emission decreased).

Very recently, the organic peroxy radicals and peroxides are found to be important intermediate species for explaining the OH radical missing source (Lelieveld et al., 2008) and the observed formation of organic aerosols (Paulot et al., 2009). Therefore, we think that the knowledge on PAA and other organic peroxides, in regard to their concentration, formation mechanism and role in the cycle of free radicals and the formation of secondary aerosols in the atmosphere is urgently needed.

4 Conclusions

Atmospheric PAA at both urban and rural sites of China were measured during the following five campaigns, namely, Beijing-2006, Beijing-2007, Beijing-2008, Backgarden-2006, and Mazhuang-2007. PAA was often present in the order of several tens of pptv level, with a maximum value of ∼1 ppbv. Meteorological and chemical parameters in related to PAA are analyzed using the Principal Factor Analysis (PFA) method, indicating that its concentration will increase with enhancing temperature and total radiation, but decrease with enhancing SO_2, NO, NO_2, and relative humidity. The importance of various VOCs in terms of PAA formation potential is ranked using the maximum incremental reactivity (MIR) method, and the result shows that the acetyl-containing compounds, including dialkylbenzene, trialkylbenzene, isoprene, alkenes, and acetaldehyde, are important precursors of PAA. The contribution of PAN to the PAA formation is estimated on the basis of chemical kinetics. We find that when the NO/NO_2 concentration ratio is lower than 0.2, PAN is an important contributor to PAA and the formation of PAA will have feedback on the existed PAN-NO_x cycle by consuming acetyl peroxy radicals. The correlation between PAA and the other two peroxides (H_2O_2 and MHP) is analyzed. Finally, the influence of PAA on the radials budget is preliminarily accessed using a box model on the basis of CBM-IV mechanism. The simulation results suggest that under low NO_x level conditions, PAA can be regarded to an important sink of acetyl peroxy radicals. We suggest that the PAA scheme should be considered in the current chemical mechanism due to its impact on the HO_x and RO_x budget and the study for PAA kinetics constitutes important tasks in gaining insight into the free radical chemistry and the formation of secondary aerosols.

Acknowledgements. The authors gratefully thank the National Natural Science Foundation of China (grants 40875072 and 20677002), and the Project of Development Plan of the State Key Fundamental Research of MOST of China (grant 2005CB422203), for their financial support. The authors would like to thank L. M. Zeng group and M. Hu group (Peking University) for their O_3, SO_2, NO_x, and CO data and meteorological data; J. B. Zhang group (Peking University) for PAN data; S. J. Fan group (Sun Yet-sen University) for meteorological data; Y. Kondo group (Research Center for Advanced Science and Technology, the University of Tokyo) for NO_x data; and A. Hofzumahaus group (Institute für Chemie and Dynamic der Geosphäre II: Troposphäre, Forschungszentrum Jülich) for HO_2 data.

Edited by: L. Carpenter

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