Atmos. Chem. Phys. Discuss., 9, C9297–C9312, 2010
www.atmos-chem-phys-discuss.net/9/C9297/2010/

Atmospheric Chemistry and Physics Discussions

Interactive comment on "Peroxyacetic acid in urban and rural atmosphere: concentration, feedback on PAN$-$NO$_x$ cycle and implication on radical chemistry" *by* X. Zhang et al.

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Received and published: 6 January 2010

Response to Reviewer 1

Thanks for your effort and constructive comments. Here are our responses to your comments:

(Q1) General Comments: This paper presents data regarding one of the first studies of peroxyacetic acid in Chinese urban and rural areas, the data in the paper are interesting, and merit publication. However, some explanations for the observed phenomena were not convincing, even with mistakes. This reviewer recommends publication after a number of revisions being implemented, and these are discussed below.

(A1) We highly appreciate your general comments. The questions you mentioned here are answered specifically as follows.

(Q2) Page 22583, line 16, “A small. . .” should be “a small. . .”

(A2) Yes, we have revised this.

(Q3) Page 22584, line 2, the “vËİ” in equation R4 should be “hv”

(A3) Yes, we have revised this.

(Q4) Page 22584, line 12-14, the two sentences seems to be repetition, are suggested to be changed as “However, field measurements of PAA are extremely sparse, and hence, the limited data restrain better understanding the role of PAA on atmospheric chemistry.”

(A4) Yes, we have rewritten the two sentences according to the reviewer’s suggestions.

(Q5) Page 22585, line 12-13, I think the information about No.4 subway is useless.

(A5) Yes, we have deleted this sentence.

(Q6) Page 22587, line 3, “China” should be “Chinese”.

(A6) Yes, we have revised this.

(Q7) Page 22587, line 18-19, it is better to provide the individual detection limit for the peroxides, because the most data shown in your figures (such as Figure 3) are below 30 pptv, even below than 10 pptv.

(A7) In this study, the detection limit of PAA in HPLC system was defined as three times the standard deviation of the PAA standard solution (7.1×10^{-8} mol/L). We have added this information in the revised manuscript. The detection limits of H_2O_2, MHP, and PAA in the gas phase were about 9, 20 and 12 pptv, respectively.

(Q8) Page 22588, line 14-17, why did you only emphasize the concentration character of PAA at Mazhang? The zero treatment for the values below the detection limit will largely underestimate the mean concentration of PAA, because PAA was often present at several-decade pptv level, and the data below the detection limit accounted for large proportion to their total data. It is better to use the detection limit value for these below the detection limit.

(A8) We did not express line 14-17 clearly. We have changed this sentence into "PAA was often present in the order of several tens of pptv level among these five campaigns, with a maximum value of $\sim$ 1 ppbv at Mazhang, 2007."

Yes, we have accepted the reviewer's suggestions and have used the detection limit value for the data below the detection limit. We have recalculated the PAA average concentrations during daytime/nighttime, and have redrawn the related figures, namely, Figure 2, 3, 4, 5, 6, 8, 9 and 10 in the revised manuscript.

(Q9) Page 22588, line 23-24, I don't think the description of this sentence is proper, because no data of previous measurement was present, while most of their values are much lower than the data (0.1-0.3 ppbv) occasionally measured by Walker et al., 2006. "that" is better changed to "these".

(A9) We have checked the reference (Walker et al., 2006). According to their report, significant levels of PAA (100–300 pptv) were observed in the INTEX-NA aircraft campaign (Crounse et al., 2005, private communication). Based on their observed H_2O_2 concentration ratio of aircraft (Crounse et al.) to ground-based (Walker et al.) measurements, Walker et al. gave an estimation for the near-surface PAA level in 10–30 pptv, although they did not detect PAA on the ground. These estimated values were comparable with the PAA level we observed. We have revised this sentence.

Reference:

Walker, S. J., Evans, M. J., Jackson, A. V., Steinbacher, M., Zellweger, C., and McQuaid, J. B.: Processes controlling the concentration of hydroperoxides at Jungfraujoch Observatory, Switzerland, Atmos. Chem. Phys., 6, 5525 - 5536, 2006.

(Q10) Page 22589, line 4-5, with only exception for two days at Mazhang (Figure 2), the concentration of PAA is comparable to that in Beijing 2007. Therefore, it is not proper for the conclusion that PAA levels in Mazhuang were much higher than those in Beijing and Backgarden.

(A10) Yes, as the reviewer suggested, it is not proper to conclude PAA levels in Mazhuang were much higher than those in Beijing and Backgarden. In fact, the average concentration of PAA in the daytime in Mazhuang 2007 was higher than those in other places. We have deleted these sentences in the revised manuscript.

(Q11) Page 22589, line 6-14, PAA formation in the real atmosphere is very complex as discussed in the manuscript, only emphasizing one factor is not convincing, e.g. the concentration of NO in Beijing must be much higher than that at Mazhuang, but the concentrations of PAA during the most investigating days in 2007 are comparable to that at Mazhuang; the sunlight intensity in 2008 was much higher than that in 2006, but the PAA concentrations in Beijing 2008 were much lower than those in 2006. In the experimental section, the authors mentioned that their field measurements in Beijing were conducted from 11 July to 31 August, why didn't the authors make the comparison by using the data from same month?

(A11) Yes, we agree with the reviewer that atmospheric PAA formation mechanisms are very complex. PAA concentration is a function of a series of physical and chemical factors. It is not convincing to discuss one factor influencing its concentration here, so we deleted the related discussions.

For some field problems like electricity power failure and instruments maintenance, it is not easy to obtain a complete set of PAA data for ten successive days. Moreover, we should make sure that data of other pollutants, which were sometimes absent because of instrument problems, were also available when we chose a period for PAA analysis. So unfortunately, we could not make the comparison by using the data from same month.

In Aug 2008, when the 2008 Olympic Games were held in Beijing, the PAA concentrations were extremely low because there were showers almost every night. So we think the observed PAA data in August can not represent its usual level in summer.

(Q12) Page 22589, line 18-22, the low level of PAA during night may be ascribed to fast dry deposition (the humidity at night is usually higher than in daytime) and less formation channels. The conclusion of “there seemed to be no transportation from the residual layer” isn’t proper. What’s the residual layer? May be boundary layer? The sharp decrease of the peroxides in late afternoon (18:00) as shown in Figure 3 revealed fast sink for them, and the relatively high concentrations of them from sunset to midnight may be ascribed to the transportation from the upper atmosphere.

(A12) Residual layer contains the species that were well-mixed in the boundary layer during the day but that do not mix rapidly during the night with either the nocturnal boundary layer below or the free troposphere above (Finlayson-Pitts and Pitts, 2000).

We agree with the reviewer that beginning at night, PAA is removed by dry deposition. Besides, since we did not observe the elevated level of peroxides throughout the night of 2 Aug 2008, Beijing, we suggest that “there seemed to be no transportation from the residual layer.” The main reason for the above statement is that during the calm sunny summer night, 2 Aug 2008, the inversion layer usually built up by the rapid cooling of the earth’s surface after the sunset and therefore, there was no transportation of PAA from the residual layer to the surface layer. We have rewritten this paragraph, as follows.

“The time series of PAA, H_2O_2 and MHP on 2 Aug 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

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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 to the surface layer and PAA was depleted even to zero till the early morning."

(Q13) Page 22590, line 4-5, what's the character of photochemical aged air-masses? Why did you assign factor 1 to be associated with the photochemical aged air-masses? The flowing description didn't give any clue for readers.

(A13) The character of photochemical aged air-masses is that primary pollutants undergo photochemical oxidation, resulting in a significant amount of secondary pollutants formation, during the transport of air-masses. Someone used VOC concentration ratios to calculate photochemical age of an air mass, defined as the time integrated exposure of an air mass to OH radical (Kleinman et al., 2003).

Factor 1 has a strong positive loading from ozone, which is a typical secondary pollutant, and has a negative loading from NO, NO_2, CO, and SO_2. It has been found that air masses during ozone episodes belong to the more aged category (Tseng et al., 2009). Moreover, a previous study also observed a strong correlation between H_2O_2 and O_3, and ascribed it to the transport of polluted air masses (Takami et al., 2003). So we assigned Factor 1 to be associated with the photochemical aged air-masses. We have explained this in the revised manuscript.

References:

Kleinman, L. I., Daum, P. H., Lee, Y. N., Nunnermacker, L. J., Springston, S. R., Weinstein-Lloyd, J., Hyde, P., Doskey, P., Rudolph, J., Fast, J., and Berkowitz, C.: Photochemical age determinations in the Phoenix metropolitan area, J. Geophys. Res., 108(D3), 10.1029/2002JD002621, 2003.

Takami, A., Shiratori, N., Yonekura, H., and Hatakeyama, S.: Measurement of hydroperoxides and ozone in Oku-Nikko area, Atmos. Environ., 37, 3861 - 3872, 2003.

Tseng, K. H., Wang, J. L., Cheng, M. T., and Tsuang, B. J.: Assessing the relationship between air mass age and summer ozone episodes based on photochemical indices, Aerosol and Air Quality Res., 9 (2), 149 - 171, 2009.

(Q14) Page 22590, line 13-14, it's a common phenomenon that the secondary pollutants (such as O3) exhibit anti-correlation with the primary pollutants, and hence, the following discussions were meaningless.

(A14) We agree with the reviewer that secondary pollutants exhibit anti-correlation with the primary pollutants for the reason that the latter was almost the photo-chemical precursor of the former.

Although it has been proved that PAA can oxidize SO_2 in the aqueous phase (Lind et al., 1987), the consumption of PAA by its reaction with SO_2 in the aqueous phase was calculated to be minus in a typical sunny day, as seen in Section 3.3.3. Se we have deleted the related discussion about the anti-correlation between PAA and SO_2.

As for the relationship between NO_2 and PAA, the suppression of NO_2 on PAA formation should also be considered because NO_2 can react with $CH_3C(O)OO$ radical, producing PAN. The reaction rate coefficients for the formation of PAN and PAA were estimated to be 1.2×10^{-12} cm^3 molecule^{-1} s^{-1} and 1.0×10^{-11} cm^3 molecule^{-1} s^{-1} at 298 K, respectively (Atkinson et al., 1996). Therefore, NO_2 will compete $CH_3C(O)OO$ with HO_2 in the atmosphere.

We have revised related discussions in the revised manuscript.

References:

Atkinson, R., Baulch, D. L., Cox, R. A., Hampson, R. F. Jr., Kerr, J. A., Rossl, M. J. and Troe, J.: Evaluated kinetic and photochemical data for atmospheric chemistry, organic species: supplement VII, J. Phys. Chem. Ref. Data, 28, 191 - 393, 1999.

Lind, J. A., Lazrus, A. L., and Kok, G. L.: Aqueous phase oxidation of sulfur by hydrogen peroxide and methyl hydroperoxide and peroxyacetic acid, J. Geophys. Res., 92, 4171

- 4177, 1987.

(Q15) Page 22590, line 23-26, the near-Uv absorption cross sections of PAA in 290-300nm are extremely high, photolysis of PAA in the atmosphere is one of its important sink channels, but intensive sunlight also produces more radicals including CH_3(O)COO and HO2 which accelerate PAA formation. The authors mentioned in section 3.1 that the elevated PAA level in 2007 can be attributed to the stronger solar radiation, and then, their PFA analysis seemed to be inconsistent with their observed phenomenon.

(A15) Based on the photolysis parameter of PAA (Jenkin et al., 1996), the photolysis rate constant at 12:00 LT of 24 July at Backgarden was estimated to be k = 3.5 $\times$ 10^{-6} s^{-1}. For the major PAA formation pathway, the combination of CH_3(O)COO and HO_2, the reaction rate coefficient k = 1.0 $\times$ 10^{-11} cm^3 $molecule^{-1}$ s^{-1} = 1.5 $\times$ 10^4 ppm^{-1} min^{-1} at 298 K (Atkinson et al., 1996). Take the day 24 July at Backgarden as an example, the concentrations of HO_2 and PAA at 12:00 LT were measured as 0.09 ppbv and 0.05 ppbv, respectively. Assuming that the concentration of CH_3(O)COO was 0.005 ppbv (based on the RO_x data from online measurement by chemical amplification operated by X.Q. Li of Peking University, private communication), then the formation and loss rate of PAA were estimated as 1.1 $\times$ 10^{-4} ppb s^{-1} and 1.7 $\times$ 10^{-7} ppb s^{-1}, respectively. Obviously, the formation rate of PAA was much higher than its loss rate, indicating that under the intense irradiation at noon, PAA was accumulated. This was associated with Factor 1 (accounting for 34.7% accumulative variance) in PFA analysis, from which both total irradiation (TI) and PAA have positive loading. Therefore, we suggested that during most days of Backgarden, atmospheric PAA behavior can be explained by Factor 1.

However, from Factor 3, we can see that PAA has a negative loading while TI has a positive loading, indicating that the PAA loss rate due to its photolysis was higher than its formation rate when concentrations of free radicals were low. So we suppose that under some specific meteorological conditions, photolysis of PAA is one of its important sinks, resulting in the decrease of its concentration in the atmosphere. In fact, more evidence should be found to support this point.

In fact, Factor 1 and Factor 3 are not incompatible with each other. Each of them represents a typical meteorological condition, under which PAA exhibits different variations in the atmosphere.

References:

Atkinson, R., Baulch, D. L., Cox, R. A., Hampson, R. F. Jr., Kerr, J. A., Rossl, M. J. and Troe, J.: Evaluated kinetic and photochemical data for atmospheric chemistry, organic species: supplement VII, J. Phys. Chem. Ref. Data, 28, 191 - 393, 1999.

Jenkin, M. E., Saunders, S. M., and Pilling M. J.: The tropospheric degradation of volatile organic compounds: a protocol for mechanism development, Atmos. Environ., 31, 81 - 104, 1997.

(Q16) Page 22591, line 4-6, there was no data in the early morning of 24 July. All data presented by the authors indicated that PAA concentrations in the early morning were extremely low (even under their stated detection limit), how to conclude that “when a spike in NO of over 20 ppbv possible caused a reduction of PAA”. In R6 should include the reaction of RO2 radical with NO.

(A16) The comparison of 24 July and 28 July can provide us evidence in terms of the suppression of NO on the peroxides formation. During most days of our measurement in Backgarden, there was usually a spike of NO in the early morning (6:00-9:00), see Fig. 1. As a result of the high concentration of NO, the values of all peroxides in the morning were close to zero. However, the level of NO was low in the early morning of Jul 28. As a result, we observed higher concentrations of peroxides compared to those in the early morning of 24 July, see Fig. 1 (a,b). In addition, in the late afternoon of 28 July, the negative correlation (noted by the right green square) between NO and all the peroxides also prove the suppression of NO on the peroxides formation.

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We have added a new figure, Fig. 6. in the revised manuscript, to explain this point.

Fig. 1 (a,b). Temporal profile of NO, H_2O_2, MHP and PAA on July 24 and 28 at Backgarden.

We think the combination of R6, R7, and R10 in the revised manuscript can better explain the suppression of NO on peroxides formation.

(Q17) Page 22591, line 11-12, the sentence was suggested to be changed as “PAA is produced from the photochemical oxidation of some volatile organic compounds (VOCs) via CH3C(O)OO formation.”

(A17) Yes, we have revised this.

(Q18) Page 22593, line 7-8, this statement is not precise, because peroxide radicals will preferably react with NO under high NO concentration. The sentence is better change as “any reaction leading to CH3CO or CH3C(O)OO will probably contribute o PAA formation.

(A18) Yes, we have revised this.

(Q19) Page 22593, line 10, the “precursors” should be “precursor”

(A19) Yes, we have revised this.

(Q20) Page 2594, line 14-16, the steady-state equation for acetyl peroxy radical is not suitable to the actual atmosphere, because the large amount of acetyl peroxy radical from VOCs oxidation was not considered. The steady-state concentration of acetyl peroxy radical must be extremely underestimated based on their simplification, and then, resulted in higher loss rate for PAN and lower formation rate for PAA.

(A20) It is a very good question and we agree with the reviewer that we overestimated the loss rate of PAN and underestimated the higher loss rate of PAA.

Actually, a previous study has calculated the fraction of PAN undergoing the thermal

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decomposition using the steady-state equation for acetyl peroxy radical (Grosjean et al., 2002). In their study, three reactions, including PAN, NO, and NO_2, were considered. So here we would like to employ this method to make a preliminary discussion of the relationship of PAN and PAA.

We would like to keep the previous discussions in order to give readers a relative complete description about the quantitative relationship between PAA and PAN. However, to answer the reviewer's question, we have added an explanation for the uncertainty of the steady-state approximation in our revised manuscript as follows: "It should be noted that the amount $CH_3C(O)OO$ 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."

Reference:

Grosjean, E., Grosjean, D., Woodhouse, L. F., and Yang, Y. J.: Peroxyacetyl nitrate and peroxypropionyl nitrate in Porto Alegre, Brazil, Atmos. Environ., 36, 2405 - 2419, 2002.

(Q21) Page 22595, line 1, "measured" is suggested to be deleted; line 7, "its" should be "CH3C(O)OO"; all discussions about PAN loss rates and PAA formation rates should be suspected as mentioned in above question; are the data of PAN shown in Fig.7 measured? If so, the method for measuring PAN should be briefly introduced in the experimental section.

(A21) We have revised these grammar mistakes as the reviewer suggested.

Yes, data of PAN in Fig. 7 are measured value, and we have added the method of PAN measurement in the experimental section, together with methods for other pollutants mentioned in the manuscript.

(Q22) Page 22596, section 3.3.3, the diurnal variations of the measured peroxides

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in Fig. 9 indeed exhibited good anti-correlations with SO2, but the difference in detail should be mentioned, e.g. the concentration of SO2 and the humidity were much higher at 19:00 than during 07:00-11:00 and 17:00-18:00, but the concentrations of the measured peroxides didn't drop to low values as those during 07:00-11:00 and 17:00-18:00. Therefore, the complex meteorological condition may have important influence on atmospheric peroxides in addition to the impact of SO2 and humidity. The reviewer think the average diurnal variation may be more convincing for explaining the influence of SO2 and humidity on the measured peroxides. Although the correlation between H_2O_2 and PAA (MHP) for the whole data is not significant, it cannot conclude that the sinks of H2O2 were potentially different from those of MHP and PAA at Mazhuang site. As shown in Fig. 9, strong correlation between H2O2 and PAA (MHP) existed during daytime (6:00-20:00), the different variation trends for them on happened during nighttime, which is attributed to "extra H2O2 formation via the ozonolysis of alkenes by the authors". Therefore, the less correlation between H2O2 and PAA (MHP) for the whole data was probably due to abnormal formation of H2O2 during night. I also wonder the abnormal high concentration of H2O2 during night being ascribed to the ozonolysis of alkenes, because the ozone concentration is commonly low in the polluted site during night, the contribution from ozonlysis must be much less than during daytime. The most probably reason for the high concentration during night was the diffusion of H2O2 from the upper atmosphere.

(A22) Thanks for your suggestion. It is very possible that the "complex meteorological condition may have important influence on atmospheric peroxides". We have checked data of other pollutants on 6 July, as shown in Figure 2. It is clear that at around 12:00, an air-mass transported to the sampling inlet, resulting in the increase of SO_2 and NO_x, and the decrease of ozone and all the peroxides (the left gray shade). However, from 17:00 to 19:00, only SO_2 and the three peroxides exhibited strong anti-correlation.

Fig. 2. Temporal profile of peroxides, SO_2, CO, NO, NO_x, and O_3.

As far as we know, there are three H_2O_2 production pathways at night: (1) the ozonol-

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ysis of alkenes in the presence of water vapor (Becker et al., 1993; Sauer et al., 1999; Anglada et al., 2002; Hasson et al., 2003); (2) the nighttime reactions of NO_3 with aldehydes and alkanes, which could produce RO_x and HO_x radicals (Wayne et al., 1991; Atkinson 1991), thus contributing to the night production of H_2O_2 and organic peroxides; and (3) the subsidence of H_2O_2 from aloft where chemical production occurs (Takami et al., 2003; Ganzeveld, et al., 2006). Since we did not observe elevated NO_x at night, the high concentrations of peroxides during night of 6 July can be attributed to the local night production and the transport from the upper atmosphere.

We have rewritten Section 3.3.3 in the revised manuscript.

References:

Atkinson, R.: Kinetics and mechanisms of the gas-phase reactions of the NO_3 radical with organic compounds, J. Phys. Chem. Ref. Data, 20(3), 459-507, 1991.

Becker, K. -H., Brockmann, K. J., and Bechara, J.: Production of hydrogen peroxide in forest air by reaction of ozone with terpenes, Nature, 346, 256 - 258, 1990.

Ganzeveld, L., Valverde-Canossa, J., Moortgat, G. K., and Steinbrecher, R.: Evaluation of peroxide exchanges over a coniferous forest in a single-column chemistry-climate model, Atmos. Environ. 40, S68 - S80, 2006.

Möller, D.: Atmospheric hydrogen peroxide: evidence for aqueous-phase formation from an historic perspective and a one-year measurement campaign, Atmos. Environ., 43, 5923 - 5936, 2009.

Sauer, F., Schäfer, C., Neeb, P., Horie, O., and Moortgat, G. K.: Formation of hydrogen peroxides in the ozonolysis if isoprene and simple alkenes under humid conditions, Atmos. Environ., 33(2), 229 - 241, 1999.

Takami, A., Shiratori, N., Yonekura, H., and Hatakeyama, S.: Measurement of hydroperoxides and ozone in Oku-Nikko area, Atmos. Envrion., 37, 3861 - 3872, 2003.

Wayne, R. P., Barnes, I., Biggs, P., Burrows, J. P., Canosa-Mas, C. E., Hjorth, J., Le Bras, G., Moortgat, G. K., Pertner, D., Poulet, G., Restelli, G., and Sidebottom, H.: The nitrate radical: physics, chemistry, and the atmosphere, Atoms. Environ., 25A(1), 1 - 203, 1991.

(Q23) Page 22599, line 6-7, this sentence isn't proper, because large amount of VOCs without acetyl group can generate CH3C(O)OO. Page 22600, line 7-8, the listed compounds aren't acetyl-containing compounds.

(A23) Yes, some compounds, like dialkylbenzenes, do not contain acetyl group. But their oxidation products can lead to $CH_3C(O)OO$ via undergoing further photo-chemical reaction. Thanks for the reviewer's correction and we have rewritten this sentence.

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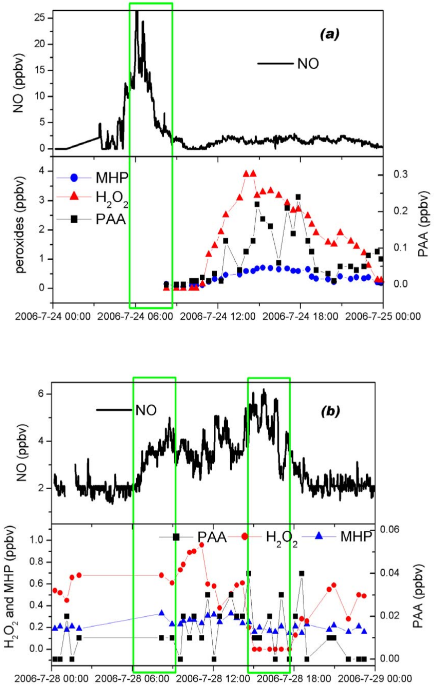

Fig. 1. Temporal profile of NO, H2O2, MHP and PAA on July 24 and 28 at Backgarden.

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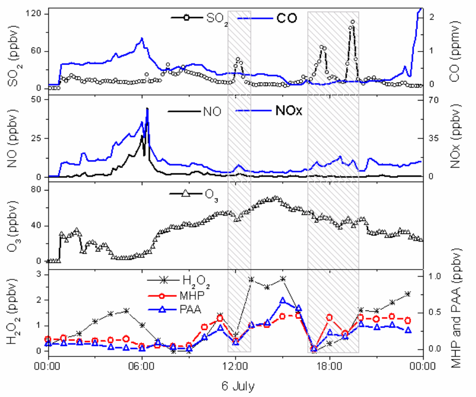

Fig. 2. Temporal profile of peroxides, SO2, CO, NO, NOx, and O3.

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