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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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Response to Reviewer 3

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

(Q1) General Comments: This article investigates the role of peroxyacetic acid (PAA) in radical chemistry based on measurements of PAA and other species carried out at both urban and rural sites of China during five campaigns. The paper presents interesting results for the implications of PAA kinetics on radical chemistry and it is based on original measurements of PAA, a species on which few measurements exist

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worldwide. I think that such measurements should be shown up on a peer-review journal. I suggest publication of the article after taking into account a number of specific comments written below.

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

Specific comments:

(Q2) Page 22588: The authors use ppbv for presenting the PAA concentrations even though in most cases the values are in tens of pptv. Why not using pptv?

(A2) Yes, we have replaced ppbv by pptv for presenting the PAA concentrations in the revised manuscript. Figure 2, 4, 5, and 8 were redrawn. For the clear comparison of PAA with other species, such as H₂O₂, MHP and PAN, we still use ppbv for presenting PAA concentrations in Figure 3, 6, 9, and 10.

(Q3) Page 22589, lines 18-21: The authors state that throughout the night there seemed to be no transportation from the residual layer. Is this a speculation or it is based on evidences from measurements? Please specify.

(A3) It is a speculation. On calm sunny nights in summer, the temperature inversion layer usually forms by the rapid cooling of the earth's surface after the sunset. So the convective transport will not be significant. Since we did not observe the elevated level of peroxides in the night of 2 Aug 2008, Beijing, we suggest that "there seemed to be no obvious transportation from the residual layer."

(Q4) Page 22590, lines 4-5: It would be helpful if the authors justify why Factor 1 is associated with photochemical aged air-masses in connection with Table1. Furthermore I think that the link between Fig.4 and Factor 1 must be discussed in a more clear way.

(A4) Factor 1 has a strong positive loading from ozone, which is a typical secondary pollutant, and has a negative loading from primary pollutants, namely, NO, NO₂, CO, and SO₂. It has been found that air masses during ozone episodes belong to the more

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aged category (Tseng et al., 2009). So we assigned Factor 1 to be associated with the photochemical aged air-masses. According to the reviewer's suggestion, we have added some discussions about the link between Fig. 4 and Factor 1 in the revised manuscript, as follows:

“Factor 1, which has a strong positive loading from secondary pollutants, ozone and PAA, while a negative loading from primary pollutants, NO, NO₂, CO and SO₂, 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 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 (HO₂) and CH₃C(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).”

References:

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.

(Q5) Page 22590, line 8-9: The authors write that a delay between the maximum solar radiation and PAA was observed. I would suggest the authors to add in Fig.4 the solar radiation in order to make more clear their statement.

(A5) Yes, we have redrawn Figure 4, adding UV-B data.

(Q6) Page 22590, lines 22-26: The authors when discussing Factor 3 they link PAA

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with photolysis under an intense radiation and dry deposition under a shallow inversion and at low wind speed. This statement sounds speculative or it is not clear to me. Please discuss in a more clear way this link based on Table1.

(A6) Factor 3 has a positive loading from WS, TI, and P, while a negative loading from PAA. The anti-correlation between PAA and WS, TI, and P indicates that under some specific wind speed, total irradiation, and pressure conditions, PAA level will correspondingly decrease. Accordingly, WS, TI, and P can be regarded some sink channels of PAA.

Based on the photolysis parameter of PAA (Jenkin et al., 1996), the photolysis rate constant of PAA at 12:00 LT of 24 July at Backgarden was estimated to be $k = 3.5 \times 10^{-6} \text{ s}^{-1}$. Take the day 24 July at Backgarden as an example, the concentration of PAA at 12:00 LT were measured as 0.05 ppbv. Then the loss rate of PAA by photolysis was estimated to be $1.7 \times 10^{-7} \text{ ppb s}^{-1}$. We suppose that photolysis of PAA could be one of its important sinks, resulting in the decrease of its concentration in the atmosphere, when the concentrations of radicals were low. As for the dry deposition, although we did not have direct observational evidence, several previous studies have reported that the deposition rate of peroxide over trees will increase significantly (Walcek et al., 1987; Wesley et al., 1989). Besides, a recent measurement of H_2O_2 over coniferous forest suggests that surface absorption and destruction processes are very efficient (Valverde-Canossa et al., 2006). The daytime dry deposition velocity for total organic peroxides (ROOH) was observed to be lower than that of H_2O_2 (Hall and Claiborn, 1997) due to smaller solubility and reactivity. As far as we know, there is no published dry deposition velocity for PAA. But it should be higher than that of MHP because PAA was more soluble than MHP ($H_{PAA} = 8.4 \times 10^2 \text{ M atm}^{-1}$ at 298 K, $H_{MHP} = 3.1 \times 10^2 \text{ M atm}^{-1}$ at 298 K, O'Sullivan et al., 1996). Considering Backgarden site is a place where natural plants are luxuriant, it is possible that dry deposition on the surface might act as an important removal pathway of PAA.

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Hall, B. D. and Claiborn, C. S.: Measurements of the dry deposition of peroxides to a Canadian boreal forest, *J. Geophys. Res.*, 102(D24), 29343 - 29353, 1997.

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.

O'Sullivan, D. W., Lee, M., Noone, B. C., and Heikes, B. G.: Henry's law constant determinations for hydrogen peroxide, methyl hydroperoxide, hydroxymethyl hydroperoxide, ethyl hydroperoxide, and peroxyacetic acid, *J. Phys. Chem.*, 100, 3241 - 3247, 1996.

Valverde-Canossa, J., Ganzeveld, L., Rappenglueck, B., Steinbrecher, R., Klemm, O., Schuster, G., Moortgat, G. K.: First measurements of H₂O₂ and organic peroxides surface fluxes by the relaxed eddy-accumulation technique, *Atmos. Environ.*, 40, S55 - S67, 2006

Walcek, C. J.: A theoretical estimated of O₃ and H₂O₂ dry deposition over Northeastern United States, *Atmos. Environ.*, 21, 2649 - 2659, 1987.

Wesley, M. L.: Parameterization of surface resistances to gaseous dry deposition in regional scale numerical models, *Atmos. Environ.*, 23, 1293 - 1304, 1989.

(Q7) Page 22591, lines 1-5: Similarly, I think that Factor 4 needs clarification with respect to Table1. What I see from Table1 1 is a strong loading from NO but the PAA loading is rather small. Please clarify why PAA levels are sensitive to NO background. This would help the reader.

(A7) Factor 4 has a strong positive loading from NO, indicating the suppression of NO on PAA formation. Temporal variation of NO and peroxides shown in the following Fig. 1 can prove this. In the early morning of 24 July, there was a spike of NO, resulting in that concentrations of all the three peroxides were nearly zero. However, in the early morning of 28 July, when the NO level was low (only several ppbv), concentrations of all the peroxides were higher than those in the early morning of 24 July. In addition, in the

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late afternoon of 28 July, the negative correlation (noted by green square) between NO and all the peroxides also prove the suppression of NO on the peroxides formation. We have added a new figure, Fig. 6 in the revised manuscript, to explain this phenomenon.

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

(Q8) Page 22595, the discussion of PAA formation and the feedback on the thermal decomposition of PAN for the different NO/NO₂ regimes needs some clarifications. What was the physical reason of using the ratio NO/NO₂ to disaggregate between low and high NO/NO₂ regimes. Is it used to reflect fresh versus aged pollution conditions or also high (more polluted) versus low NO_x regimes (less polluted)?

(A8) First, the PAN loss rate depends on temperature, NO and NO₂ concentration because high NO concentration will enhance indirectly the thermal degradation of PAN via reacting with CH₃C(O)OO, while high NO₂ concentration will be favorable to the PAN formation. Second, the following PAN loss rate equation can be simplified as:

$$-\ln[\text{PAN}]/dt = (k_{10}k_{11}[\text{NO}] + k_8k_{11}[\text{HO}_2]) / (k_8[\text{HO}_2] + k_9[\text{NO}_2] + k_{10}[\text{NO}])$$

$$= (k_{10}k_{11}[\text{NO}]/[\text{NO}_2] + k_8k_{11}[\text{HO}_2]/[\text{NO}_2]) / (k_8[\text{HO}_2]/[\text{NO}_2] + k_9 + k_{10}[\text{NO}]/[\text{NO}_2])$$

Considering that the concentrations of HO₂ are much lower than NO₂ in polluted atmosphere, $k_8k_{11}[\text{HO}_2]/[\text{NO}_2]$ and $k_8[\text{HO}_2]/[\text{NO}_2]$ can be approximated to zero. Therefore, the key factor determining the loss rate of PAN will be the ratio of NO/NO₂. Third, the NO/NO₂ ratios chosen in our manuscript, namely, 0, 0.05, and 0.2, are statistical values based on the calculated PAA formation rate and PAN loss rate. For example, when NO/NO₂ ≤ 0.05 and [HO₂] > 20 pptv, the loss rate of PAN was nearly ten times higher than the formation rate of PAA.

(Q9) Page 22596, lines 18-21: The authors anticipate that due to high SO₂ levels it is possible that a large portion of H₂O₂ was consumed in the oxidation of S(IV) to S(VI) in aqueous phase. However according to their kinetic calculations this loss rate is very small to match with the lower H₂O₂ observed values. Have the authors considered

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the possibility of different transport pathways and hence sampling of air masses with different characteristics? It can be anticipated, for example, that higher SO₂ values correspond to more polluted air masses reaching the site. As it is well known in more polluted air masses (in terms of NO_x) the radical chemistry favors a decrease in H₂O₂ levels and an increase in HNO₃ levels. Have the authors checked this possibility to attribute the measured low H₂O₂ levels?

(A9) Thanks for the reviewer's suggestion. We have checked data of other pollutants on 6 July, as shown in the following Figure 2. It is clear that at around 12:00, an air-mass transported to the sampling inlet, resulting in the increase of SO₂ and NO_x, and the decrease of ozone and all the peroxides (the left gray shade). However, from 17:00 to 19:00, only SO₂ and the three peroxides exhibited strong anti-correlation. The NO_x level throughout the daytime was low, so its influence on H₂O₂ level can be ignored.

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

(Q10) In Figure 2, I would suggest the authors to consider the possibility of using the same scale in the plots.

(A10) We are afraid that the same scale will cause the variation of PAA in Beijing 2006 and 2008 to be obscure. Thus we keep the previous scales in our revised manuscript.

Technical corrections:

(Q11) Abstract, 1 line: “. . .is one of important . . .” I would suggest “is among the most important” or “is one of the most important”

(A11) Yes, we have changed this sentence into “. . .is one of the most important. . .”

(Q12) Introduction, Page 22683, line 16: “Besides A” should be “Besides a”

(A12) Yes, we have revised this.

(Q13) Page 22588 line 15: “ at several-decade pptv” should be “ in the order of several tens of pptv”

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(A13) Yes, we have changed “at several-decade pptv” into “in the order of several tens of pptv” according to the reviewer’s suggestion.

(Q14) Page 22593, line 12: “. . . of PAA is associated . . .” I would suggest “. . . of PAA to be associated . . .”

(A14) Yes, we have revised this.

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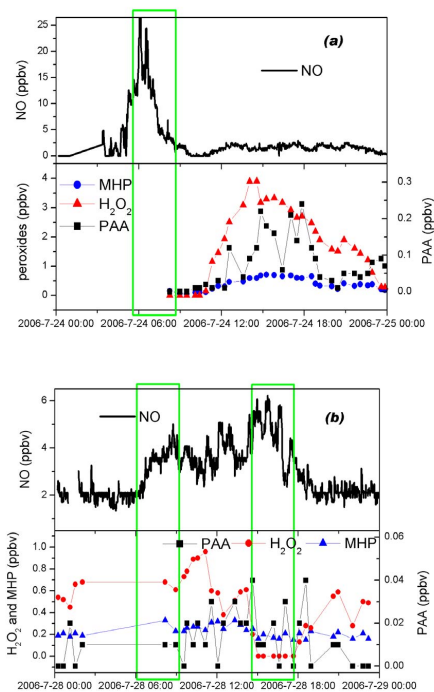


Fig. 1. Temporal profile of NO, H₂O₂, MHP and PAA on July 24 and 28 at Backgarden.

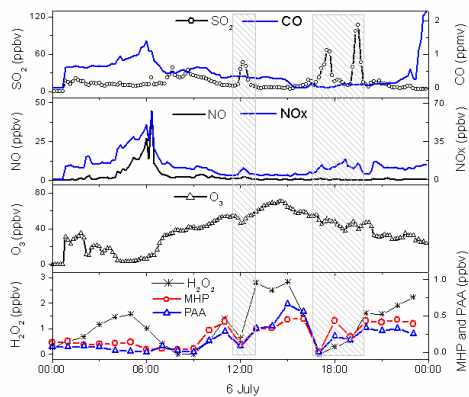
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Fig. 2. Temporal profile of peroxides, SO₂, CO, NO, NO_x, and O₃.

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