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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.

Anonymous Referee #3

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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 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.

Specific comments

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?

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.

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.

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.

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

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.

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 NOx regimes (less polluted)?

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

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small to match with the lower H2O2 observed values. Have the authors considered 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 NOx) 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?

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

Technical corrections

Abstract, 1 line: "...is one of important ..." I would suggest "is among the most important" or "is one of the most important"

Introduction, Page 22683, line 16: "Besides A" should be "Besides a"

Page 22588 line 15: " at several-decade pptv" should be " in the order of several tens of pptv"

Page 22593, line 12: "... of PAA is associated ..." I would suggest "... of PAA to be associated ..."

Interactive comment on Atmos. Chem. Phys. Discuss., 9, 22581, 2009.