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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 #1

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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.

Page 22583, line 16, "A small . . ." should be "a small. . ." Page 22584, line 2, the "ïĄő" in equation R4 should be "hïĄő" 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." Page 22585, line 12-13, I think the information about No.4 subway is useless. Page 22587, line 3, "China" should be "Chinese". 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. 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. 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". 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. 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? 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. 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. 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. 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 CH3(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. 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. 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." 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 to PAA formation. Page 22593, line 10, the "precursors" should be "precursor" Page 22594, 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. Page 22595, line 1, "mea-

sured" 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. Page 22596, section 3.3.3, the diurnal variations of the measured peroxides 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 H2O2 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 H2O from the upper atmosphere. Page 22599, line 6-7, this sentence isn't proper, because large amount of VOCs without acety group can generate CH3C(O)OO. Page 22600, line 7-8, the listed compounds aren't acetyl-containing compounds.

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