

Interactive comment on “Understanding atmospheric peroxyformic acid chemistry: observation, modeling and implication” by H. Liang et al.

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Received and published: 2 June 2015

This paper by Liang et al. entitled ‘Understanding atmospheric peroxyformic acid chemistry: observation, modeling and implication’ discusses formation mechanism of peroxyformic acid (PFA) based on field observation data and a box model. I have several comments on the manuscript.

Thanks for your constructive and thoughtful comments. We have revised our manuscript, according to your comments. Below is our response, as shown in answer (A), to your comments.

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P2059 L24 ‘The relative position of PFA peak coincides with that reported in Kok et al. (1995).’ It seems that this is the only one reason why the authors have identified the peak as that originated from PFA. However, I am not sure if the systems used by Kok et al. and this study are exactly the same or not. In addition, no information is provided about the calibration. How the authors did quantify the concentration of PFA? These points need to be clarified.

(A): You are right. The paper Huang et al. (2013) cited in the manuscript was a previous study carried out by our group, in which we synthesized a series of organic peroxides including alkyl hydroperoxides, hydroxyalkyl hydroperoxides, and peroxy acids to examine the retention time of different peroxides. In that study, we confirmed that the peak of PFA appeared at 8.6 min. The instruments we used to measure peroxides in the current study were the same with those used in Huang et al. (2013). In the current study, authentic samples of PFA were prepared by the acid catalyzed reaction of HC(O)OH with H₂O₂. An acidic potassium permanganate titration method was used to determine the concentration of PFA samples. Using these samples, a multipoint calibration of PFA was done, showing that the PFA resented a good linear response in a wide concentration range relative to the atmosphere. Standard solution of PFA was unstable to reserve, making it difficult to do a direct calibration during the field measurement. Instead, we used a standard solution of H₂O₂ to do single point calibrations for PFA twice a day since response factors for PFA and H₂O₂ were proved to be almost the same in our HPLC analyzing system. We have added the above statements in our manuscript. We have clarified the manuscript as follows: “In our previous study (Huang et al., 2013), we synthesized a series of organic peroxides including alkyl hydroperoxides, hydroxyalkyl hydroperoxides, and peroxy acids to examine the retention time of these peroxides. In that study, we confirmed that the retention time for PFA chromatographic peak in our analyzing system is 8.6 min (Huang et al., 2013), between the peaks of hydroxymethyl hydroperoxide (HMHP, 7.1 min) and Bis-hydroxymethyl peroxide (BHMP, 8.8 min). The relative position of PFA peak coincides with that reported in Kok et al. (1995). Authentic samples of PFA were prepared by the acid catalyzed

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reaction of HC(O)OH with H₂O₂. An acidic potassium permanganate titration method was used to determine the concentration of PFA samples. Using these samples, a multipoint calibration of PFA was done, showing that the PFA presented a good linear response in a wide concentration range relative to the atmosphere. Standard solution of PFA was unstable to reserve, making it difficult to do a direct calibration during the field measurement. Instead, we used a standard solution of H₂O₂ to do single point calibrations for PFA twice a day since response factors for PFA and H₂O₂ were proved to be almost the same in our HPLC analyzing system.”

P2060 L19 ‘The rates of these reactions were assumed to be the same with the corresponding reactions of PAA and peroxyacetyl radical.’ It would be valuable to discuss (1) how much these reaction rates of organic peroxyacids could vary, and (2) how the uncertainty could affect the interpretation of the results. PFA is the smallest peroxyacid molecule; the reactivity of this compound might be quite different from other peroxyacids. This point needs to be investigated more carefully.

(A): Thanks for the suggestion. Unfortunately, there was no literature being helpful to discuss the reaction rate variation of PFA. PFA participate only three reactions in our model mechanism, i.e., photolysis ($\text{HC(O)OOH} + h\nu (+ \text{O}_2) = \text{OH} + \text{HO}_2 + \text{CO}_2$), OH-reaction ($\text{HC(O)OOH} + \text{OH} = \text{HC(O)OO} + \text{H}_2\text{O}$) and PFA decomposition ($\text{HC(O)OOH} = \text{HC(O)OH} + 0.5\text{O}_2$). We proposed that PFA decomposition was the most important sink for PFA and the corresponding rate for PFA decomposition used in the model was a best-guess value based on previous experiments. Therefore, the variation of reaction rates of PFA will not significantly affect the interpretation of the results.

P2062 L13 ‘Here, we provide an estimation of the Henry’s law constant of PFA on the basis of the PFA observation data in both gas phase and rainwater.’ It would be important to discuss if this method is sufficiently accurate, and what kinds of artifacts could exist. I am not sure how fast the chemical composition of rain droplets equilibrate with the surrounding air. Rain droplets fall down from the upper atmosphere, where both temperature and concentration of PFA could be different from the surface level.

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(A): Thanks for your question. In our previous study (Liang et al., 2013), we found that peroxyacetic acid (PAA) was not in equilibrium between the gas and aqueous phases. In the current study, we found that PFA and PAA have a similar variation trend in both gas and aqueous phases. Based on this phenomenon, we supposed that PFA and PAA deviated from the Henry’s law constant to the same extent. The method was not sufficiently accurate, due to the lack of sufficient observation data under different conditions. Yet we found an estimation of the Henry’s law constant of PFA in the Hazardous Substances Data Bank (<http://toxnet.nlm.nih.gov/cgi-bin/sis/search2/f?./temp/6Zu9c3:1> last access: March 21, 2015) using a fragment constant estimation method reported by Meylan and Howard (1991). The estimated value was $1.9 \times 10^{-6} \text{ atm m}^3/\text{mol}$ at 298 K, equivalent to 526 M atm^{-1} , which was comparable with the value we estimated in the current study (210 M atm^{-1}).

P2063 L18 ‘The most important factor seems to be the solar radiation. As is shown in Fig. 1, observed PFA/PAA in June (BJ-2012S) was about 0.10 on average whereas the ratio in August and September (BJ-2012F) was about 0.33 on average. ‘A detailed comparison with solar radiation data is needed to derive this conclusion. Other meteorological parameters such as temperature and relative humidity could also be different for these two different time periods.

(A): Yes, you are right. We did not get the solar radiation data during the observational periods. We have revised the statements in the manuscript as follows: “PFA/PAA ratio seems to be very different in different seasons. As is shown in Fig. 1, observed PFA/PAA in June (BJ-2012S) was about 0.10 on average whereas the ratio in August and September (BJ-2012F) was about 0.33 on average. This may be because that meteorological parameters including solar radiation, temperature and relative humidity lead to different photochemical processes of PAA and PFA.”

P2067 L14 ‘In a foggy day, the production rate of PFA in this pathway could be 2 or 3 orders of magnitude higher than the clear day value, owing to the greatly enhanced liquid water content compared to clear days.’ Was the observation conducted only

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during clear days? If the observation periods include both clear and foggy days, this difference should also be discussed.

(A): Our observations were conducted only during clear days. The statement was just indicating the potential importance of aqueous decomposition of methylglyoxal in the production of gaseous PFA in foggy days.

Interactive comment on Atmos. Chem. Phys. Discuss., 15, 2055, 2015.

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