Response to Reviewer #2

We gratefully thank you for your constructive comments and thorough review. Our point-by-point responses can be found below.

(Q=Question, A=Answer, C=Change in the revised manuscript)

Q1: This manuscript by Xuan et al describes a detailed study of the partitioning of H_2O_2 in the atmosphere through field measurements. The authors quantified H_2O_2 in the gas phase, aerosol, and rainwater (as a surrogate for cloud water). By comparing the measured and theoretical Henry's law constant, as well as the measured and theoretical partitioning coefficient, the authors conclude that the measured values for both are higher than the theoretical values. An in-depth assessment is conducted to evaluate the influence of raindrop falling on the quantified H_2O_2 concentration, as well, a discussion on the source and sink of H_2O_2 in aerosol is provided. H_2O_2 plays an important role in the atmosphere, and understanding its partitioning in different atmospheric phases is of great importance for the atmospheric chemistry community. The manuscript is within the scope of ACP. The data analysis and calculation were performed with caution. I recommend publication on ACP after addressing the following comments.

A1: We highly appreciate your comments and suggestions. The questions you mentioned are specifically answered as follows.

Major comment:

Q2. In section 3.2.4, the authors present the evolution of H_2O_2 as a function of time in the aerosol abstract, and a detailed discussion on the potential source of H_2O_2. This result highlights the challenges in making off-line H_2O_2 measurement from filter samples. Especially, when the sampling time is as long as 11.5 h (Line 100), it is very likely that the organic peroxides present in the aerosol sample is continuously decomposing on the filter. The authors categorize the H_2O_2 evolution into three types and postulate the relevant source of H_2O_2 for each type. However, in my opinion, this appears too speculative. The decomposition of H_2O_2 on filter is difficult to control, and the quantified H_2O_2 could be merely a snapshot of an ongoing decomposition process. The authors must justify whether it is valid at all to establish gas-aerosol partitioning of H_2O_2 based on the current technique.

A2: Thanks for your suggestion. We have deleted the relevant source of H_2O_2 in each type in Table 4 in the revised manuscript. Because organic peroxides are unstable and can easily decompose, off-line

measurement of the aerosol-phase H_2O_2 could only obtain a snapshot of the decomposition process. Although there may be uncertainties regarding the aerosol-phase H_2O_2 measurement and the calculation of gas-aerosol partitioning coefficient of H_2O_2, this paper provides new insights into understanding the gas-aerosol partitioning of H_2O_2, as well as the sources and sinks of aerosol-phase H_2O_2, which may contribute to the future studies related.

Provided that the influence of Teflon filters on the reactions of aerosol particles is so little as to be unnoticeable, the decomposition/hydrolysis rates of organic peroxides in aerosol particles on the filters are same as that in the atmosphere. It is well known that the decomposition/hydrolysis rates of organic peroxides are often positively related to the levels of organic peroxides. Due to the low aerosol water content of particles, the concentrations of aerosol-phase organic peroxides were ~ 5 orders of magnitude higher than that in the extracted solution, which were estimated based on a comparison between the amount of the extracted solution and aerosol water content. The actual decomposition/hydrolysis rates in aerosol particles may be higher than that in the extracted solution. However, we cannot know how much the difference between them due to the limitations of the available measurement technique. Based on above analysis, to a large extent, the effective gas-aerosol partitioning coefficient estimated in this paper can represent the actual gas-aerosol partitioning of H_2O_2.

Furthermore, it took around 40 min to extract and transport the sample to the observation site for H_2O_2 measurement. Organic peroxides in the extracted solution may decompose into H_2O_2 during the process, leading to overestimation of the effective gas-aerosol partitioning coefficient of H_2O_2. Provided that the maximum decomposition/hydrolysis rate of organic peroxides was 0.10 ng μg^{-1} h^{-1} (line 355 in the revised manuscript), the corrected gas-aerosol partitioning coefficient averaged 6.9×10^{-4} m^3 μg^{-1}, which was the lowest value due to the assumed maximum value of the decomposition/hydrolysis rate of organic peroxides. Because the corrected value of the effective gas-aerosol partitioning coefficient was still much higher than K_P^t, we did not correct the data. The above analysis has been added in the Supplement (lines 158−168).

In addition, the level of gas-phase H_2O_2 during BJ-2018Winter was very low, only tens of pptv. Lengthening sampling time will increase the aerosol-phase H_2O_2 concentration and ensure accurate quantitative detection of H_2O_2, but it will also introduce some unknown errors. Therefore, we will comprehensively consider to determine an optimal sampling time in the future study of the gas-aerosol partitioning of H_2O_2.

Minor comments:

Q3. Literature-reported Henry's law constants of H_2O_2 varies across a certain range. The authors should justify why they used 8.4×10^4 M/atm. Is this the recommended value by the JPL publication?

A3: Thanks for your suggestion. Henry's law constant of H_2O_2 (8.4×10^4 M atm^{-1}) used in this paper was quoted from Sander et al. (2011), which was published in JPL Publication 10-6. In addition, Sander (2015) sorted Henry's law constants of H_2O_2 based on the data reliability, and 8.4×10^4 M atm^{-1} ranked higher. In addition, the latest recommended value was 8.7×10^4 M atm^{-1} at 298 K (Burkholder et al., 2015), which was close to 8.4×10^4 M atm^{-1} used in this paper.

Q4. Line 139 – Is the $PM_{2.5}$ concentration a good indicator for C_{om} in a polluted environment like Beijing?

A4: Thanks for your suggestion. In previous studies, they used TSP in calculating the field-derived gas-aerosol partitioning coefficient and assumed that the weight fraction of the organic matter phase in TSP was 1 (Pankow et al., 1994; Odum et al., 1996; Shen et al., 2018; Qian et al., 2019). We have replaced "C_{om}" with "TSP" in Eq. (4) in the revised manuscript, and used the $PM_{2.5}$ mass concentration since TSP concentration was not available.

Q5. Line 150 – The authors state that when H_A^m was less than H_A^t, the samples followed Henry's law. Why? Shouldn't they agree (neither higher nor lower)?

A5: Thanks for your suggestion. The previous expression was inappropriate and we have redefined whether rain samples followed Henry's law in the revised manuscript.

C5: Lines 168−171 in Sec. 3.1.1:

"We divided 52 rain samples into three types based on the comparison of the measured and predicted levels of H_2O_2. When the difference between levels of the measured and predicted liquid-phase H_2O_2 fell within ± 20 %, we suggested that these samples (Type B) followed Henry's law, and the remaining samples (Type A and C) did not agree with Henry's law. The percentages of samples in Type A, B and C were 69 %, 19 %, and 12 %, respectively."

Q6. Line 275 – The authors report here that heterogeneous uptake can count for 86% of aerosol phase H_2O_2. Later in Line 346, the author report 0.5%. Please clarify.

A6: Thanks for your suggestion. The two percentages are calculated in different methods. 86 % refers to the ratio of the amount of heterogeneous uptake of H_2O_2 to the measured aerosol-phase H_2O_2 level, while 0.5 % refers to the ratio of the amount of heterogeneous uptake of H_2O_2 to the consumption amount of aerosol-phase H_2O_2. In addition, we have revaluated the contribution of the heterogeneous uptake to the aerosol-phase H_2O_2 based on the formation and consumption rates according to the reviewers' suggestions, and the heterogeneous uptake could account for 2 % of the consumption rate of the aerosol-phase H_2O_2. To avoid confusion, we have removed 86 % in Sec. 3.2.3 and 0.5 % in Sec. 3.3.

Q7. Line 370 – correct me if I am wrong. "additional source of liquid-phase H_2O_2 gradually increased" – should this be the sink of H_2O_2 due to droplet-to-gas transfer is gradually reduced?

A7: Yes, you are right. We have rewritten the description in the revised manuscript.

C7: Lines 450−451 in Sec. 4:

"In addition, the sink of H_2O_2 due to droplet-to-gas transfer was reduced with an increase in raindrop diameter, thus the liquid-phase H_2O_2 level also increased."

Q8. Figure 5, and Line 263 – the authors interpret the inversely related H_2O_2 concentration and $PM_{2.5}$/sulfate concentrations as results of a H_2O_2 sink by SO_2 oxidation. However, could the inversed relation be just due to dilution of H_2O_2 when aerosol loading is high?

A8: Thanks for your suggestion. We did not consider the dilution of H_2O_2 due to an increase in aerosol loading, and we have added it in the revised manuscript. To avoid the effects of outliers, we chose 10th and 90th percentiles of the levels of aerosol-phase H_2O_2, SO_4^{2-} and $PM_{2.5}$ to explain the inverse relationship between H_2O_2 and SO_4^{2-}/$PM_{2.5}$. The extent of the concentration variations of H_2O_2, SO_4^{2-} and $PM_{2.5}$ were 22, 6 and 5, respectively. Because the level of H_2O_2 changed more than that of SO_4^{2-} and $PM_{2.5}$, the inverse relationship still existed when we eliminated the interference of the dilution effect due to the high aerosol loading. In addition, the ratios of the extent of the concentration variations between H_2O_2 and SO_4^{2-}/$PM_{2.5}$ were equal to 4, indicating that a H_2O_2 sink by SO_2 oxidation was more important than the dilution effect and the dilution effect could be neglected.

C8: Lines 303−306 in Sec. 3.2.2:

"The extent of the concentration variations of H_2O_2, SO_4^{2-} and $PM_{2.5}$ at 10th and 90th percentiles were 22, 6 and 5, respectively, suggesting that the inverse relationship still existed when we eliminated the

interference of the dilution effect due to a high aerosol loading. The dilution effect was unimportant and could be neglected."

Technical comments:

Q9. Line 59 – "easily to absorbed" to "easily absorbed".

A9: Yes, we have revised it in line 65.

Q10. Line 144 – "statistically counted" appears awkward. Should probably remove.

A10: Yes, we have removed it in line 160.

Q11. Line 146 – "with" 25.20 μM – is 25.20 μM the theoretical value? "with" makes the sentence unclear.

A11: Yes, we have replaced "with" with "is" in line 162.

Q12. Line 171 – "almost" less than 2000 m – should this be "always" less than 2000 m?

A12: Yes, we have changed "almost" into "always" in line 194.

References

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Table 4: Comparison of the H_2O_2 evolution parameters in the extracted solution among the three types.

Parameters	First type	Second type	Third type
Peak time (h)	5	40	–
Decomposition rate of organic peroxides to H_2O_2 (ng μg^{-1} h^{-1})	0.01	0.10	–
C_{max}/C_0 of H_2O_2 (μM/μM)	1.52	39.22	1.00
TPOs/H_2O_2 (μM/μM)	5.25	40.06	47.59
Ratio of decomposable organic peroxides (%)	29	98	0