

Response to Reviewer #1

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)

General comments:

Q1: Xuan et al. performed field measurements of the gas-, liquid- and aerosol-phase H_2O_2 in the urban atmosphere of Beijing to understand the partitioning of H_2O_2 between gas- and liquid-phase or aerosol-phase. They show that the partitioning of H_2O_2 in the gas-liquid phase can be explained by Henry's law and the residual H_2O_2 in the raindrops while the aerosol-phase H_2O_2 level is significantly higher than that predicted value based on Pankow's absorptive partitioning theory. This paper has important implications for understanding the H_2O_2 chemistry and sulfate formation in the atmosphere, so it is well within the scope of ACP. This paper is of great interest to the atmospheric community although some clarifications regarding the data analysis are required. I recommend this paper to be published after addressing the specific comments below.

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

Specific comments:

Q2. Estimation of effective partitioning coefficients: The authors determined the gas-aerosol partitioning coefficient instead of the effective Henry's law constant for the gas-aerosol phase. Is this due to that aerosol water content cannot be accurately estimated for low RH? The effective Henry's law constant should be estimated for the high RH condition, e.g. heavy haze episodes from 2 Jan to 3 Jan 2019 and compared with the theoretical value.

A2: Yes, you are right. After considering your suggestion, we have calculated the effective Henry's law constant for the gas-aerosol phase during a heavy haze episode from 2 Jan to 3 Jan 2019 and compared it with the theoretical value in the revised manuscript.

C2: Lines 267–272 in Sec. 3.2.1:

“Because aerosol water content (AWC) cannot be correctly evaluated at low RH, the effective field-derived Henry's law constant (H_p^m) of H_2O_2 was estimated for high RH condition, e.g. a heavy haze

episode from 2 January to 3 January 2019 (RH, 30 %). Details regarding the estimation of AWC was shown in the Supplement. It was calculated that AWC, C_p^m and C_g^m levels averaged $3.20 \mu\text{g m}^{-3}$, $6.63 \times 10^3 \mu\text{M}$, and $1.90 \times 10^{-11} \text{ atm}$. Based on Eq. (5), the average H_p^m on 2–3 January 2019 was calculated to be $2.7 \times 10^8 \pm 1.8 \times 10^8 \text{ M atm}^{-1}$. However, the theoretical Henry's law constant (H_p^t) at 270 K was $1.1 \times 10^6 \text{ M atm}^{-1}$ (Sander et al., 2011), which was lower than H_p^m by two orders of magnitude.”

Q3. The authors estimated that heterogeneous uptake of H_2O_2 could account for 86% of the measured H_2O_2 in the aerosol phase in Sec 3.2.3 while stated that the heterogeneous uptake of H_2O_2 on aerosols contributed less than 0.5% of the aerosol-phase H_2O_2 in Sec 3.3. Please clarify.

A3: Thanks for your advice. 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 reevaluated 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.

Q4. The authors stated that the rates of the decomposition/hydrolysis of organic peroxides in the first and second types were $0.14 \text{ ng } \mu\text{g}^{-1}$ and $3.65 \text{ ng } \mu\text{g}^{-1}$ (lines 296–297) and further estimated the contribution of decomposition/hydrolysis of organic peroxides to aerosol H_2O_2 to be 32% (lines 343–346). However, these numbers seem to be the steady-state or maximum amount of H_2O_2 , not formation rates. The estimation should be based on the formation and consumption rate of H_2O_2 .

A4: Thanks for your suggestion. We have recalculated the estimation considering the formation and consumption rates of H_2O_2 and removed the calculation based on the steady-state or maximum amount of H_2O_2 in the revised manuscript. Furthermore, we have changed the relevant data in Table 3 and 4.

C4: Lines 417–430 in Sec. 3.3:

“We estimated the contribution of different sources to the aerosol-phase H_2O_2 based on the formation and consumption rates. According to the previous estimation of the theoretical sulfate formation rate from January 2 to January 3 2019 ($0.29 \mu\text{g m}^{-3} \text{ h}^{-1}$) and the average mass concentration of $\text{PM}_{2.5}$ (106.19

$\mu\text{g m}^{-3}$), the consumption rate of H_2O_2 should be $0.97 \text{ ng } \mu\text{g}^{-1} \text{ h}^{-1}$. With respect to the sources of the aerosol-phase H_2O_2 , the decomposition/hydrolysis of organic peroxides was firstly considered, with average rates of the rising stage for the first and second types (Fig. 6), $0.01 \text{ ng } \mu\text{g}^{-1} \text{ h}^{-1}$ and $0.10 \text{ ng } \mu\text{g}^{-1} \text{ h}^{-1}$, respectively. Because the extracted solution was stored under 255 K, lower than the actual atmospheric temperature (270 K), the decomposition/hydrolysis rates of organic peroxides were underestimated and an adjusting factor should be multiplied. The factors for the three typical labile organic peroxides (HMHP, PFA, and PAA) were 13, 3, and 2, respectively, as shown in the Supplement. Assuming the factor was in the range of 2–13, the average decomposition/hydrolysis rate of organic peroxides for the first and second types ($0.055 \text{ ng } \mu\text{g}^{-1} \text{ h}^{-1}$) was used to calculate the formation rate. The formation rate of the aerosol-phase H_2O_2 from the decomposition/hydrolysis of organic peroxides could account for 11–74 % of the consumption rate by sulfate formation. Moreover, the heterogenous uptake of HO_2 and H_2O_2 were also likely to improve the aerosol-phase H_2O_2 level at the rates of $0.22 \text{ ng } \mu\text{g}^{-1} \text{ h}^{-1}$ and $0.02 \text{ ng } \mu\text{g}^{-1} \text{ h}^{-1}$, respectively, which can offset 22 % and 2 % of the consumption rate of H_2O_2 , respectively.”

Q5. Though the heterogeneous uptake of HO_2 on aerosols is not well understood, it is possible to estimate its contribution to aerosol H_2O_2 using the reactive uptake coefficient of HO_2 to aerosol from literature and assuming the product to be H_2O_2 (Li et al., 2019). It is recommended to perform such calculations to provide more insights.

A5: Thanks for your advice. We have added the calculation of the heterogeneous uptake of HO_2 on aerosols in the revised manuscript.

C5: Lines 325–331 in Sec. 3.2.3:

“As HO_2 radical is a precursor of H_2O_2 , the heterogeneous uptake of HO_2 onto aerosols may also contribute to the formation of the aerosol-phase H_2O_2 . We assumed that the reactive uptake coefficient of HO_2 to aerosol particles was 0.2, and the product of HO_2 was H_2O_2 (Li et al., 2019). At the same observation site in winter of 2017, HO_2 concentration for noontime averaged $(0.4 \pm 0.2) \times 10^8 \text{ cm}^{-3}$ and $(0.3 \pm 0.2) \times 10^8 \text{ cm}^{-3}$ on clean and polluted days, respectively (Ma et al., 2019). Since HO_2 level data in 2018 was not available, we used the level of HO_2 on clean days in winter of 2017 for calculations, and the average was about $0.2 \times 10^8 \text{ cm}^{-3}$ at day-time. The heterogenous uptake rate of HO_2 on aerosols was calculated the same way as H_2O_2 , and the formation rate of the aerosol-phase H_2O_2 by reactive uptake of

HO₂ averaged 0.22 ng μg⁻¹ h⁻¹ at all day.”

Q6. The authors should discuss the “salting in” effect of high ionic strength of aerosol particles on gas-aerosol partitioning of H₂O₂ though it may only have a minor contribution to the enhanced aerosol H₂O₂ concentrations.

A6: Thanks for your suggestion. We have discussed the “salting-in” effect of high ionic strength of aerosol particles on the gas-aerosol partitioning of H₂O₂ in the revised manuscript.

C6: Lines 272–278 in Sec. 3.2.1:

“In Chung’s study (2005), “salting-in” effect can improve the level of H₂O₂ by a factor of two when the concentrations in salt solutions were up to 10 M, and the most obvious “salting-in” effect of salt solutions was ammonium sulfate. In this paper, the levels of aerosol-phase NH₄⁺ and SO₄²⁻ on 2–3 January 2019 were 94 M and 21 M, respectively, and the level of (NH₄)₂SO₄ was assumed to be 21 M. The increasement of H_p^m by the “salting-in” effect of (NH₄)₂SO₄ was about 3.2×10^6 M atm⁻¹ at 286 K based on equations in Chung et al. (2005). Even though aerosol particles were collected at 270 ± 4 K and the increasement may be greater, the “salting-in” effect could not fully explain the difference between H_p^m and H_p^f . Other sources need to be found later.”

Q7. Line 82: Are the organic peroxide concentrations corrected for the collection efficiency?

A7: Thanks for your suggestion. Because the measured concentrations of organic peroxides were near the detection limit of the HPLC method in BJ-2018 Winter measurement, the levels of organic peroxides were not discussed in this paper. Alternatively, we used the concept of total peroxides as a measure to estimate the sources of the aerosol-phase H₂O₂ in Sec. 3.2. The level of total peroxides was measured using the iodometric spectrophotometric method with an extraction efficiency close to ~ 98 % (Li et al., 2016), so we did not correct the total peroxides level.

Q8. Lines 149–150: Please explain how 88% is derived.

A8: Thanks for your suggestion and we have explained it in line 166 in the revised manuscript. The percentage was calculated as the average ratio of the predicted level to measured level of H₂O₂ in each rain sample. The value indicated that 88 % of the liquid-phase H₂O₂ in all the rain samples collected was from gas-phase partitioning. Since the measured H₂O₂ level in some rain samples was lower than the

predicted value, gas-phase partitioning accounted for a high proportion in all samples based on statistics on averages.

Q9. Line 181: What is the gas-phase H_2O_2 concentration used to estimate the liquid-phase H_2O_2 ?

A9: The gas-phase H_2O_2 concentration used to estimate the liquid-phase H_2O_2 was 0.30 ± 0.26 ppbv, and we have added it in lines 203–204 in the revised manuscript. We assumed that the gas-phase H_2O_2 concentration was homogeneous, and the gas-phase H_2O_2 in the cloud atmosphere was equal to the gas-phase H_2O_2 near the ground (line 191).

Q10. Section 3.2.4: The experimental details on the decomposition of organic peroxides should be provided. Is the extracted solution exposed to light at room temperature? Are these experiments conducted at atmospheric relevant conditions so that the derived rates of decomposition can be applied to ambient?

A10: Thanks for your suggestion. The extracted solution was away from light at 255 K. The experimental conditions were chosen based on certain considerations, which have been added in the revised manuscript and Supplement. The influence of experimental conditions on the derived rates has also been discussed in the revised manuscript and Supplement. We think that the derived rates of decomposition can be applied to the ambient atmosphere.

C10: Lines 111–115 in Sec. 2.2.3:

“The remaining extracted solution was stored at 255 K away from light for subsequent measurement of H_2O_2 concentration variation with time, and details of the experimental conditions of the extracted solution are shown in the Supplement. Photochemical reactions of aerosols may produce aerosol-phase H_2O_2 (Zhou et al., 2008), and the effect of the photochemical reactions on the level of H_2O_2 in the extracted solution was discussed in the Supplement.”

Lines 1–48 in the Supplement:

“The extracted solution was stored under refrigeration at 255 K, away from light. The first reason to choose 255 K was that the temperature during BJ-2018 Winter measurement averaged 270 K, less than 273 K. The second reason was that under 255 K, the decomposition rate of H_2O_2 should be reduced, which contributed to a more accurate estimation of the decomposition rates of organic peroxides to H_2O_2 . Li et al. (2016) studied the stability of H_2O_2 in SOA stored on-filter at 255 K and 298 K. It was found

that the level of H_2O_2 remained stable for 6 days at 255 K but decreased gradually at 298 K. The third reason was that the H_2O_2 level in the extracted solution was very low at time=0, which could easily decompose at 277 K, therefore, the extracted solution should be stored at 255 K.

Due to the positive correlation between temperature and decomposition rates, the derived rates of decomposition in this paper were lower than the actual rates of decomposition. To discuss the influence of the storage temperature on the decomposition rates of organic peroxides, hydroxymethyl hydroperoxide (HMHP), peroxyformic acid (PFA), and peroxyacetic acid (PAA) were chosen as representatives. According to the Arrhenius equation, the reaction rate usually increases exponentially as temperature increases. The ratios of the decomposition/hydrolysis rates of HMHP, PFA, and PAA at 270 K to 255 K were 13, 3, and 2, respectively (Zhou and Lee, 1992; Dul'neva and Moskvina, 2005; Sun et al., 2011). We have considered the influence of temperature on the decomposition rates of organic peroxides when calculating the aerosol-phase H_2O_2 formation rate from the decomposition/hydrolysis of organic peroxides, as shown in Sec. 3.3.

The extracted solution was away from light in this paper, which was different from atmospheric relevant conditions (i.e., exposure to sunlight in the ambient atmosphere), and may affect the data applicability in this study. We chose this experimental condition because if the extracted solution was exposed to sunlight, the photochemical reactions of organic matters and the decomposition/hydrolysis of organic peroxides will coexist, and we cannot distinguish the effects of these two processes. By doing so, the specific contribution of the decomposition/hydrolysis of organic peroxides to the aerosol-phase H_2O_2 was estimated. With respect to the photochemical reactions of organic matters, Zhou et al. (2008) have discussed that as the exposure time of the extracted solution to sunlight increased, the production of peroxides in nascent marine aerosols first increased rapidly and then slowly. The change trend in Zhou's study was the same as that of the aerosol-phase H_2O_2 level in this paper (Fig. 6). The estimated 24-h-average rate of H_2O_2 photochemical production in Alert particles was about 9 mM h^{-1} at 248 K (Anastasio and Jordan, 2004). We assumed that the photoformation rate of H_2O_2 in Beijing particles was also 9 mM h^{-1} . And the concentrations of AWC and $\text{PM}_{2.5}$ from 2 January to 3 January 2019 were $3.20 \text{ } \mu\text{g m}^{-3}$ and $90.36 \text{ } \mu\text{g m}^{-3}$, respectively. The formation rate of the aerosol-phase H_2O_2 from photochemical reactions was estimated to be $0.011 \text{ ng } \mu\text{g}^{-1} \text{ h}^{-1}$ at 248 K. In addition, the activation energy of H_2O_2 photoformation was 9 kJ mol^{-1} (Anastasio et al., 1994), and the rate of H_2O_2 photoformation at 270 K should be 1.4 times higher than the value at 248 K. Compared with the aerosol-phase H_2O_2 formation rates from the

decomposition/hydrolysis of organic peroxides and the heterogeneous uptake of HO₂, the H₂O₂ photoformation could be neglected.

Based on the above analysis, we believe that the derived rates of decomposition under the experimental conditions in this paper can be applied to the ambient atmosphere.”

Technical corrections:

Q11. Lines 59–60: References are missing.

A11: Thanks for your reminder. We have added related references in line 65.

Q12. Equation 4: TSP or PM_{2.5} should be used instead of C_{om}.

A12: Yes, we have changed “C_{om}” into “TSP” in Eq. (4) in the revised manuscript, and used the PM_{2.5} mass concentration as an indicator because the PM_{2.5} concentration was available based on our measurements.

Q13. Line 331: “measured” should be “was measured to be”.

A13: Thanks for your advice. We have revised it in line 391.

References

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Table 3: Calculating the theoretical heterogeneous uptake rate of H₂O₂ on aerosols ($d[X]_p^{t,h}/dt$)^a.

Parameters	T_W (K)	RH (%)	γ — ^b	S_{aw} (cm ²) ^c	$[X]_g$ (molecules m ⁻³) ^d	$d[X]_p^{t,h}/dt$ (ng μg^{-1} h ⁻¹)
Averages	270	17.89	1.54×10^{-4}	46	6.54×10^{14}	0.02

^a These parameters are calculated based on Wu et al. (2015).

^b γ is the heterogeneous uptake coefficient, dimensionless.

^c S_{aw} is the surface area of aerosols, quoted from Kuang et al. (2019).

^d $[X]_g$ is the concentration of gas-phase H₂O₂.

Table 4: Comparison of the H₂O₂ 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 ₂ O ₂ (ng μg ⁻¹ h ⁻¹)	0.01	0.10	–
C_{max}/C_0 of H ₂ O ₂ (μM/μM)	1.52	39.22	1.00
TPOs/H ₂ O ₂ (μM/μM)	5.25	40.06	47.59
Ratio of decomposable organic peroxides (%)	29	98	0