We would like to thank the referee for the recheck and valuable feedbacks, which further improved the quality of the paper. We have addressed the comments point-by-point. The reviewers' comments are in black, our answers are reported in red, and the modifications we have made in the manuscript are highlighted in yellow.

The authors present in situ measurements of HO_2 reactivity, using an aerosol concentrator and filter to assess specifically the contribution of HO_2 uptake to aerosol particles. The authors use simultaneous observations of aerosol composition and surface area to derive an HO_2 reaction probability and assess drivers of the variability thereof. This is a nice experiment, and the results are well described and placed in context of previous work. I recommend publication after the authors have addressed some minor comments below.

1) Details on the VACES: The authors should more clearly describe in the main manuscript (not just the SI) the size distribution of aerosol in the reactor as determined by the VACES. Provide mean radius, geometric standard deviation, and ideally compare composition of post VACES aerosol to ambient aerosol measurements. The issue is to what extent is the VACES alterning the particle sizes and types in the reactor compared to the ambient.

We apologize for the unclear descriptions of the size distribution. We used a $PM_{2.5}$ cyclone before injecting the ambient air into the VACES system, according to the test from previous study of the VACES system, the particle concentration enrichment occurs without any coagulation, thus there is no distortion of the size distribution of the original ultrafine aerosols (Sioutas et al., 1999). However, here the size distributions of the ambient aerosols before and after VACES were measured by SMPS for particles <0.74μm, there is no measurement of the size distribution >0.74μm. We added the mean radius and geometric standard deviation (Geo. Std. Dev.) of the ambient aerosols before and after VACES during the time period of the enrichment factor measurements in Table 1. As shown on Pg 6-7, line 164-172:

"According to the test from previous study of the VACES system, there is no distortion of the size distribution of the original ultrafine aerosols as the particle concentration enrichment occurs without any coagulation (Sioutas et al., 1999), here we listed the mean radius and geometric standard deviation (Geo. Std. Dev.) of the ambient aerosols before and after VACES during the enrichment factor measurement periods, as shown in Table 1. We could see that the mean radius before and after VACES are not statistically different within the standard deviation.

Table 1: The averaged Mean radius and Geometric standard deviation before and after VACES during the time period of the enrichment factor measurements

Experimental time•	Before VACES		After VACES	
	Mean radius (nm)	Geo. Std. Dev.	Mean radius (nm)	Geo. Std. Dev.
2019.7.25	129.47±11.32	0.92±0.04	133.19±3.37	0.92±0.02

09:03 − 11:03				
2019.7.26 09:30 − 11:30	94.95±14.42	0.99±0.09	85.09±14.96	1.01±0.09
2019.7.27 10:00 − 12:00	85.09±14.96	1.01±0.09	80.40±21.01	1.01±0.07
2019.7.28 09:30 − 11:30	163.62±13.32	1.01±0.08	164.06±14.40	1.04±0.06
2019.7.29 09:10 − 11:10	128.06±6.90	0.91±0.02	125.07±7.68	0.92±0.02
2019.7.30 09:30 − 11:30	111.40±8.21	1.01±0.02	115.32±6.26	1.01±0.03

•represent the time period of the enrichment factor measurements;
±represent the standard deviation of the averaged values of mean radius and Geo. Std. Dev..”

Unfortunately, we did not measure the chemical composition after the VACES, thus we are not able to compare the chemical composition of the post VACES aerosols to ambient aerosol. However, Kim et al. (2001) performed the enrichment test using the ambient aerosol fractions including coarse and fine PM and found that the VACES system does not differentially affect the chemical composition of ambient PM during the enrichment process, thus we assume the chemical composition changing due to the enrichment process of the VACES can be neglected. We have modified the related content and discussion on Page 6, lines 147-152:

“Unfortunately, we did not measure the chemical composition after the VACES, thus we are not able to compare the chemical composition of the post VACES aerosols to ambient aerosol. However, previous test using the ambient aerosol fractions including coarse and fine PM indicated that the enrichment process of the VACES system does not differentially affect the chemical composition of ambient PM (Kim et al., 2001), thus we assume the chemical composition changing due to the enrichment process of the VACES can be neglected.”

2) Neglect of gas-phase diffusion corrections to the determination of the reaction probability seems problematic. My recollection is that limitations are significant (greater than 10%) for gamma > 0.1 and particle sizes > 0.5 micron. It is hard to know from what is provided in the main manuscript whether this issue is dealt with adequately.

We apologize for the unclear description. The mean diameter of the ambient particles ranged from 0.1-0.46 µm, with the median value of 0.25 µm. We detected an error in previous conclusion and calculated the gas-phase diffusion again using the method described in SI. The results show the gas-phase diffusion can increase γ for ~ 6.6% (on average), the absolute increase of γ due to the gas-phase diffusion is 0.03 on average, which is much smaller than the γ uncertainty (~0.21 on average), therefore, we neglected the gas-phase diffusion corrections to the determination of the reaction probability. The related description is added now on Pg11, line 281-285:

"The mean diameter of ambient particles ranged from 0.1 to 0.46 μm (with the median value of 0.25 μm), the gas-phase diffusion effects on γ were estimated to be ~ 6.6 % (further details are given in the SI). The absolute increase of γ due to the gas-phase diffusion is 0.03 on average, which is negligible compared to γ uncertainty (~0.21 on average), therefore, we ignored the gas-phase diffusion effects to γ."

3) I appreciate the authors providing the 25th and 75th percentile gamma values, but then state the gamma was 0.33 "on average". Was this the mean, or the median? I would suggest given the variability that the median be reported instead of the mean.

Thank you for the appropriate suggestion at this instance. Judging from the large variation of the mean value, we agree that it is more appropriate to use the median value instead of the mean value of γ, meanwhile, in order to compare the γ value obtained here with previous studies (where used average values instead of median values), we also added the average value as a reference. We have changed the related sentence in the manuscript on Page 11, lines 279-280:

"The corresponding γ, calculated from Eq. 2, ranged from 0.05 (25th percentile) to 0.33 (75th percentile), with the median value of 0.19 (with an average value of 0.23 ± 0.21)."

And Page 23, line 592:

"…with the median value of 0.19 and the average value of 0.23 ± 0.21,"

Accordingly, we also describe the median k_a value, instead of mean k_a value on Page 11, line 276:

"…with the median value of 0.005 s^{-1} and average value of 0.005 ± 0.005 s^{-1}."

4) I would like to see a deeper assessment of uncertainty at low surface areas and small particles. The derived k_a is likely a small number from the difference of two large numbers with uncertainties due to precision and systematic variability given that a filter must be used serially at a different time to determine k_a. The trend towards higher gammas with low surface area and small particles is at best more uncertain and possibly somewhat artificial if a) negative ka are excluded from the analysis, or b) a small positive k_a is divided by a smaller surface area, leading to a bigger gamma, but which isn't robust due to uncertainty (instrumental error).

As it is, the measured gamma time series is extremely noisy - noisier than the aerosol mass (surface area) and composition measured by the AMS. Some discussion of the different variability in these quantities is warranted and possibly provide shading that indicates the absolute error of each measurement.

We appreciate your suggestion. We actually used Ek_a and the

corresponding ES (represent the enriched k_a and enriched surface area of ambient aerosol, respectively) to calculate γ. The Ek_a was calculated from the significant differences between the measured HO$_2$ reactivity of the [gas phase + enriched ambient aerosols] (Ek_a+k_g) and the modeled HO$_2$ reactivity of the gas phase ($\approx k_g$), thus we first estimated the error of Ek_a from (Ek_a+k_g) and k_g, and then estimated the error of γ from the propagate error of Ek_a and ES. The uncertainty of the enriched surface area was estimated from the instrument systematic error of SMPS (~8%) and the uncertainty of the enrichment factor($\pm$2.5), as shown on Pg 8, line 205-207:

"The uncertainty of the enriched surface area was estimated from the instrument systematic error of SMPS (~ 8%) and the uncertainty of the enrichment factor ($\pm$2.5), which are shown in Fig.1b (see SI)."

More details of the related discussion of the different variability in these quantities can be found in on Pg 11, line 276-281:

"The error for Ek_a was estimated as ~ 0.05 s^{-1}, calculated as the propagated errors from k_g+Ek_a (i.e., the systematic error of the instrument, ~0.05 s^{-1}) and the modeled k_g in mode (b) (~ 0.001 s^{-1}). Accordingly, the errors for k_a was estimated as ~ 0.004 s^{-1} (from the obtained error of Ek_a by dividing by the enrichment factor E). The corresponding γ, calculated from Eq. 2, ranged from 0.05 (25th percentile) to 0.33 (75th percentile), with the median value of 0.19 (with an average value of 0.23 $\pm$ 0.21)."

We didn't exclude the negative k_a from the analysis, there are super small negative Ek_a exists. We add now the absolute errors of (Ek_a+k_g), modeled k_g, Ek_a and ES in Fig. 1 (gray shading areas). We detect an error in calculating the uncertainty of γ, which is now corrected in Fig. 1b. We modified the figure caption of Fig. 1 accordingly:

"Figure 1: Temporal variation of parameters under different experimental conditions. (a) Without aerosol phase: 1st panel: measured NO$_2$ concentrations (ppb); 2nd panel: measured (red line) and modeled (black line) k_g; 3rd panel: fitting residues of modeled k_g values, ranging from −0.04 (25 percentile) to 0.05 (75 percentile), therefore we consider the systematic error of the LFP–LIF instrument to be ~0.05 s^{-1}. (b) Gas + aerosol phase: 1st panel: measured total HO$_2$ reactivity (k_g+Ek_a) and modeled k_g; 2nd panel: Ek_a, calculated from the difference between the measured and modeled values from the 1st panel, the gray shadow area represents the uncertainty of Ek_a (ΔEk_a), propagated from the error of (k_g+Ek_a) and modeled k_g; 3rd panel: the upper limit surface area of the enriched ambient aerosols (ES), the gray shadow area represents the uncertainty of ES (ΔES), propagated from the systematic errors of the SMPS instrument (~8%), and the uncertainty of the enrichment factor; 4th panel: γ calculated from Ek_a and ES according to Eq. 2. The errors for γ were propagated from ΔEk_a and ΔES, $\Delta\gamma = \gamma \times \sqrt{\frac{\Delta Eka^2}{Eka} + \frac{\Delta ES^2}{ES}}$. The blue shaded area represents the air masses from group i (from coast), the remainder is from group ii (from mainland)."

5) Given the lack of size information given in the main paper, it was difficult to assess the role of particle composition, particular the role of sea spray as contributors to surface area, but not measured mass composition (the AMS

will not measure sea salt). Thus, this could bias gamma's high if sea salt is unmeasured, or the SMPS do not scan high enough, etc.

We apologize for the unclear descriptions of the size distribution. The VACES system enriches particles with diameter < 2.5 µm, the AMS and SMPS measures particles with diameter < 1 µm and < 0.74 µm, respectively. We modified the related description in the modified manuscript on Pg5, line 126-128:

"…the ambient air sample was drawn into a tank (containing ultra-pure water heated up to ~32 ºC) of VACES through a PM$_{2.5}$ cyclone at a flow rate of over ~ 100 L min^{-1},…"

As SMPS only measures the surface area of ambient particles with diameter < 0.74 µm (as shown in Sect. 2.2), there is no size distribution measurement for ambient particles with diameter > 0.74 µm. By assuming the surface area are increased in proportional to the mass concentration, the enriched surface area of PM$_{2.5}$ were estimated by multiplying the ratio of the mass between the PM$_{2.5}$ and the PM$_{0.74}$ (~1.1) by the enriched surface area of PM$_{0.75}$. However, since the larger particles (here referred to particles ranged from 0.74 to 2.5 µm) tend to have lower surface area than the smaller particles (here referred to particles ranged from 0 to 0.74 µm), we consider the calculated enriched surface area of PM$_{2.5}$ as the upper limit value. We modified the related description in the modified manuscript on pg7, line 173-179:

"The enriched surface area of ambient aerosols with aerodynamic diameter < 0.74 µm (PM$_{0.74}$) was calculated from the surface area of ambient aerosol measured by SMPS$_1$ and the enrichment factor. The enriched surface area of PM$_{2.5}$ was then calculated by multiplying the enriched surface area of PM$_{0.74}$ by the mass ratio between PM$_{2.5}$ and PM$_{0.75}$ (~1.1), where we assume the surface area are increased in proportional to the mass concentration. However, as the larger particles (here referred to particles ranged from 0.74 to 2.5 µm) tend to have lower surface area than the smaller particles, we consider the obtained enriched surface area of PM$_{2.5}$ as the upper limit value. More details can be found in SI."

According to SMPS data, most "fine-mode" particles have diameters less than 0.74 µm, with the mean diameter ranged from 0.09 µm to 0.47 µm (with the median value of 0.25 µm), therefore, we assume that particles with diameter ranged between 1 µm and 2.5 µm are negligible. As coarse mode particle generally has size of > 2.5 µm, we believe the discussions about the role of different chemical components with diameter < 1 µm (measured by AMS) played in the HO$_2$ uptake kinetics (with aerosol diameter < 2.5 µm) are reasonable. We add the related discussion on Pg15, line 383-389:

"Here we note that the different chemical components were measured using HR–ToF–AMS for ambient aerosols with aerodynamic diameters < 1 µm, while k_a and γ were measured using VACES–LFP–LIF system for ambient aerosols with aerodynamic diameters < 2.5 µm, but due to most "fine-mode" aerosols have the mean diameter ranged from 0.09 µm to 0.47 µm (with the median value of 0.25 µm, measured by SMPS), we assume the chemical components of ambient aerosols with the aerodynamic diameter ranged between 1 µm and 2.5 µm have negligible impact on Pearson correlation matrix result."

Due to VACES measured particles < 2.5 μm, and AMS measured particles < 1 μm, present results do not include the effects of coarse particles to the HO₂ uptake kinetics, we partially missed sea spray (with diameters ranged from ~ 0.05 to 10 μm) effects to the HO₂ uptake kinetics, which are described now on Pg 15, line 389-391:

"However, present results do not include the effects of coarse particles (with aerodynamic diameters > 2.5 μm) to the HO₂ uptake kinetics, and we may partially miss measuring sea spray (with diameters ranged from ~ 0.05 to 10 μm) effects."

However, we do see a relatively higher chloride concentration in group i from coast (vs. group ii from mainland), and a weak correlation between chloride concentration and γ (~0.04) in current analysis, which may be relate to the sea salt reaction, as described on Pg 16, 415-418:

"The very weak correlation of γ with f_{Cl^-} (0.04) may be related to Cl^- chemistry, for example, $HO_2(g)$ can react with $NaCl(g)$, produce $NaOH$ and $Cl_2(g)$, thus cause a decrease in the HO_2 concentration and indirectly effects γ (Remorov et al., 2002)."

When Cl^- measured by AMS increased, coarse particles may exist and our results may not represent the real ambient conditions. Consequently, we consider our results as the lower limit of the HO₂ uptake kinetics onto real ambient aerosols. The effects of coarse particle and sea salt to the HO₂ uptake kinetics will be the subject of our future study. The related discussion are now add on Pg15, line391-394:

"When Cl^- measured by AMS increased, coarse particles may exist and our results may not represent the real ambient conditions. Consequently, we consider our results as the lower limit of the HO₂ uptake kinetics onto real ambient aerosols. "

We also modified the related description in abstract:

"We developed an online approach to precisely investigate the lower limit values of (i) the HO_2 reactivities of ambient gases and aerosols and (ii) HO_2 uptake coefficients onto ambient aerosols (γ) during 2019 air quality study (AQUAS) in Yokohama,…"

and in the conclusion on Pg 23-24, line 594-596:

"However, the k_a and γ values obtained here are considered as the lower limit values for real ambient aerosols, as the coarse particles were not measured in this study."

and Pg 24-25, line 621-623:

"In summary, the chemical components and physical properties of ambient aerosols may dominate γ variation during field campaign; to yield more accurate γ value, total suspended particles in ambient air should be measured,…"