Response to RC1

The manuscript presents results of a comprehensive field campaign at two different altitudes, the foot (150 m a.s.l.) and the summit (1534 m a.s.l.) of Mt. Tai (Shandong province, China). Mt. Tai locates in the middle of the NCP with a relatively high pollution level. The measured HONO diurnal profile shows a daytime peak at 12:30 local time, which is interesting since HONO diurnal profiles would typically peak during the night and early morning in more polluted regions. The topic is of interest to the scientific community and is suitable for publication in ACP after addressing the comments below.

The authors claim that OH+NO gas-phase reaction accounts for only 8% of measured HONO, and that 70-98% of the unknown HONO sources can be attributed to vertical transport from ground surfaces. However, the authors didn't show/present the OH values used to calculate the OH+NO reaction rate, and they didn't consider this reaction when calculating the net production of OH from HONO. The authors used an unjustified circular assumption that OH loss in the OH+NO reaction at the ground will be recycled back to OH at a higher altitude without any valid calculation of HONO lifetime vs transport time from the ground to the summit. The authors claim that they calculated HOx budget, although they only calculated gross HONO photolysis and O3 photolysis. (primary sources of OH only). I suggest the authors limit their discussions to HONO sources and sinks, and that they should account for NO+OH reaction in calculating HONOpss or assume several OH values around those published earlier to calculate their uncertainties. Otherwise, the manuscript is publishable after addressing these comments.

Response: Thanks for your efforts and comments, which help to improve our manuscript. Please see the point-to-point response below (**Comments in Black; Response in Blue; Changes in Red**).

Specific comments:

Page 15, Line 320: The authors didn't justify the use of OH-j(O^1D) correlation from previous publications to calculate OH in this study. Although some studies showed a good correlation, it still may not be a good proxy for OH given the large variation in the obtained slops. The authors use a circular argument that OH is not important since NO+OH is not important, to justify the uncertainty associated with their approach. At which OH levels does the NO+OH reaction accounts for 8%?

Maybe, it is safer to either simulate OH using a box model or use a range of OH levels around those reported previously by Kanaya et al. (2009) to show that it is not important, as they claim This is a major issue that the authors need to address before continuing with their calculations of unknown HONO sources.

The authors used several assumptions to calculate the contribution of different HONO sources to measured HONO levels. Most importantly is the photolysis of pNO3, for which the authors used a range of enhancement factors (EF) that ranges from 1 to ~15.6, accounting for 0.6 to 9.6%, depending on EF, leaving ~93% of HONO unknown sources unknown. I think. A major uncertainty here is related to HONOpss, which the authors didn't sufficiently address, which affects the unknown fraction HONO.

Response: We agree that the estimated OH could result in some uncertainties in calculation on unknown HONO sources and net OH production. We added OH sensitivity tests and found very small impacts on $P_{unknown}$. Figure S6 and the below texts are added in the manuscript.

The estimated OH could lead to some uncertainties. Hence, we added OH sensitivity tests to reinforce our analysis and conclusion. The used OH, the corresponding $HONO_{pss}$, P_{un} and results from the sensitivity tests were also shown in Figure S6. The estimated OH level was lower than that measured during the MTX campaign (Kanaya et al., 2013). This is mainly caused by lower $J(O^1D)$ resulting from frequent cloudy weather during the present study period. For instance, the average RH during this campaign was 96%, which is much higher than that during the MTX campaign (67%). The variation of OH levels indeed remarkably impact $HONO_{pss}$. However, $HONO_{pss}$ (5-15 pptv level) is still 1-2 orders of magnitude lower than the observed HONO (50-200 pptv level), leading to a negligible impact of variable OH and $HONO_{pss}$ levels on P_{un}.

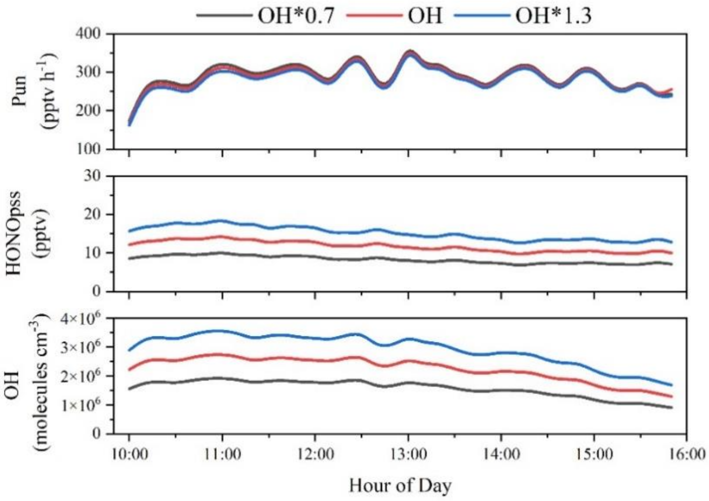

Figure S6: Estimated OH concentrations (red line) used in this study and corresponding $HONO_{pss}$ and P_{un} (red lines). Black lines represent OH level reduced by 30% and corresponding $HONO_{pss}$ and P_{un}. Blue lines represent OH level enlarged by 30% and corresponding $HONO_{pss}$ and P_{un}.

Page 18, lines 404-412: The authors' argument of OH recycling via HONO photolysis as the source of OH at higher altitude is not justified and is flawed. The authors didn't provide information about the HONO lifetime vs the transport time to this altitude. I think this whole paragraph should be just deleted.

Response: The maximum of average diurnal J(HONO) is 8.0×10^{-4} s^{-1} (Figure 9), corresponding to a minimum HONO lifetime of about 21 min against photolysis, longer than the estimated transport time of 7-17.5 min. As shown in Figure 9, the remaining proportion of HONO after a period of transport from the ground to the summit levels is about 50-80% at noontime. α could be even larger because the calculation only considers HONO loss, whereas HONO production during the transport along the mountain slope was not taken into consideration. Then whether the transport of HONO could constitute an OH transport path depends on the amount of OH consumption to produce HONO through NO+OH at the foot station.

At the foot station, NO+OH contributed 15% of daytime HONO formation and photo-enhanced NO_2 uptake on the ground surface dominated the rest as reported in the companion ACP paper (Xue et al., 2021). Besides, hydrogen peroxide (H_2O_2), an important OH reservoir, could also be transported from the ground to the summit levels as reported in our recent study (Ye et al., 2021). At the ground level, H_2O_2 was mainly produced by HO_2+HO_2 (Ye et al., 2021). Hence, it could be preliminarily inferred that radicals (i.e., OH and HO_2) could be transported through their precursors/reservoirs (like HONO and H_2O_2) with lifetimes longer than themselves.

We improved the texts as:

Radicals, including OH and HO_2, are not expected to be transported far due to their short enough lifetimes (<1 s). However, 15% of daytime HONO was formed at the ground level through NO + OH as reported in the companion ACP paper (Xue et al., 2021), and part of OH consumed at the ground level would be released at the summit level through HONO photolysis. This could be supported by our recent finding that hydrogen peroxide (H_2O_2), an important OH reservoir, could be transported from the ground to the summit levels (Ye et al., 2021). At the ground level, H_2O_2 was mainly produced by HO_2+HO_2 (Ye et al., 2021). Hence, it could be preliminarily inferred that radicals (i.e., OH and HO_2) could be transported through their precursors/reservoirs (like HONO and H_2O_2) with lifetimes longer than themselves. Furthermore, the enhanced vertical air mass exchange could also lead to fast transport of other pollutants ($PM_{2.5}$, O_3, CO, SO_2, etc.) from the ground to the summit levels, which will significantly impact the atmospheric composition as well as its chemistry in the upper boundary layer or the residual layer. The discussion and implications in this study are instructive for further laboratory or model studies.

Page 18, line 414: provide a reference…

Response: A reference was added.

(Jiang et al., 2020)

Page 19, lines 418-420: This long sentence is not clear at all….either provide all relevant information or leave it for the accompanying paper. Otherwise, HONO net photolysis should be used to calculate HONO relative contribution to OH primary sources.

Page 19, lines 428-438: Again, this is all irrelevant if HONO net contribution is not calculated.

Response to both comments: The whole of Section 3.6 was improved as we replaced gross OH production from HONO photolysis with its net OH production (Figure 11). We also calculated the contribution $P(OH)_{HONO\_net}$ to $P(OH)_{sum}$ (Figure S8).

The improved figures and Section 3.6 are as follows:

3.6 Role of HONO in the Oxidizing Capacity of the Lower and the Upper Boundary Layer

O_3 was typically the major OH source at high altitude regions, including the upper boundary layer. Then we compared the OH production rates from O_3 and HONO photolysis to investigate whether HONO could play a significant role in the oxidizing capacity of the atmosphere at this high-altitude site. Photolysis of HONO and O_3 with their net OH production is shown in R-2 and R-5 to R-7, respectively. OH loss through HONO + OH and NO + OH was subtracted from $P(HO_x)_{HONO}$ to obtain $P(HO_x)_{HONO\_net}$.

$$O_3 + h\nu \rightarrow O_2 + O(^1D), \qquad J(O(^1D)) \tag{R-5}$$

$$O(^1D) + H_2O \rightarrow 2OH, \qquad k_3 \tag{R-6}$$

$$O(^1D) + M\ (N_2\ or\ O_2) \rightarrow O(^3P) + M\ (N_2\ or\ O_2), \qquad k_4 \tag{R-7}$$

$$P(HO_x)_{HONO\_net} = [HONO] * J(HONO) - k_1 * [NO] - k_2 * [HONO], \tag{Eq-8}$$

$$P(HO_x)_{O_3} = [O_3] * J(O(^1D)) * \phi, \tag{Eq-9}$$

where the reaction constants were taken from the IUPAC kinetic database (https://iupac-aeris.ipsl.fr).

The atmospheric RH and temperature largely influenced the branching ratio of R-6 toR-7. The average OH yield (ϕ) during the campaign of 20% was used for calculating OH production from O_3 photolysis.

Additionally, in the companion paper in which HONO was reported to be the most important primary OH source at the foot station (Xue et al., 2021). A comparison between the role of HONO at the foot and the summit stations could provide more insights into the importance of HONO throughout the boundary layer. Moreover, as reported in the companion paper, HONO observed at the foot station was mainly produced through NO_2 heterogeneous reactions and NO+OH. Therefore, the comparison could also shed light on the link between the atmospheric oxidizing capacity in the lower and the upper boundary layer, although measurements at two stations were conducted during two consecutive periods rather than the same one in summer 2018.

Figure 11 displays the diurnal profiles of net OH production rates from HONO and O_3 photolysis at the foot and the summit stations. It is apparent that both $P(OH)_{HONO\_net}$ and $P(OH)_{O_3}$ showed higher levels at the foot station compared to the summit station. For instance, average $P(OH)_{HONO\_net}$ and $P(OH)_{O_3}$ at the foot station are 0.9 and 0.5 ppbv h^{-1}, respectively, both of which are significantly higher than those (0.06 and 0.28 ppbv h^{-1}) at the summit station. This is caused by relatively lower HONO and O_3 concentrations and lower solar photolysis frequencies as a result of frequent cloud formation observed at the summit station.

In particular, after night-time accumulation, HONO photolysis is found to initialize daytime photochemistry in the early morning at the ground level (Alicke et al., 2002; Kleffmann, 2007; Platt et al., 1980). This was also observed at the foot station. As shown in Figure S8, at the foot station, the contribution of $P(OH)_{HONO\_net}$ to $P(OH)_{sum}$ was almost 100% at sunrise around 5:00. It showed a declining trend but still played the dominant role in $P(OH)_{sum}$, with a contribution larger than 90% in the early morning (5:00-7:00). At the summit station, at 5:00, solar radiation was very weak, for instance, $J(NO_2)$ was only 3.6×10^{-4} s^{-1}. At this time, $P(OH)_{HONO\_net}$ was slightly negative (-7×10^{-3} ppbv h^{-1}) due to OH loss through HONO + OH and NO + OH. O_3 photolysis was initialized at the same time, but $P(OH)_{O_3}$ was nearly zero (7×10^{-4} ppbv h^{-1}). From 6:00 to 7:00, a considerable amount of net OH was produced through HONO photolysis (0.04-0.09 ppbv h^{-1}), with its contribution to $P(OH)_{sum}$ decreasing from 64% to 39% (Figure S8). Hence, it could be inferred that daytime atmospheric photochemistry at the summit level is also initialized by HONO photolysis.

On average, the contribution of $P(OH)_{HONO\_net}$ to $P(OH)_{sum}$ was 64% at the foot station, higher than that (18%) at the summit station (Figure 11), indicating the essential role of HONO in the atmospheric oxidizing capacity at both the ground (lower boundary layer) and the summit (upper boundary layer) levels in mountainous regions. As discussed before, the transport from the ground to the summit levels contributed to the majority of HONO observed at the summit level. This points to a new insight that ground-derived HONO played an important role in the oxidizing capacity, not only at the ground level but also in the upper boundary layer (~1500 m) in mountainous regions. Yet this vertical exchange might be only valid in the mountainous areas, and the follow-up regional impact still needs to be quantified by further model studies.

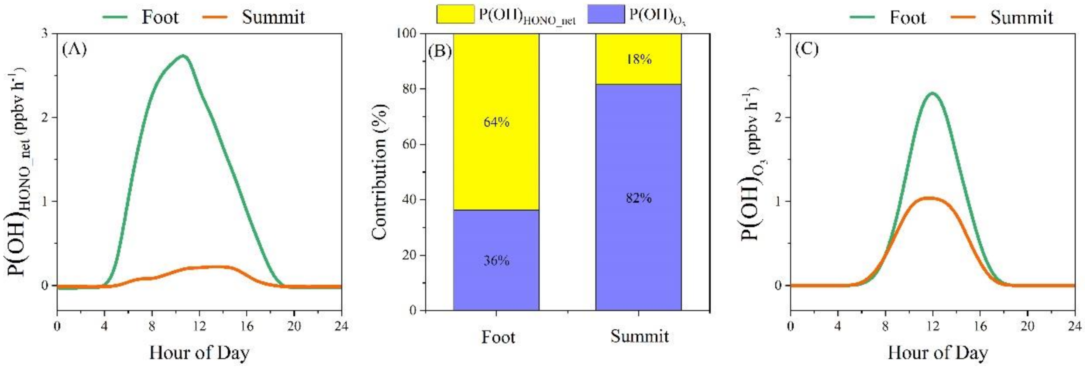

Figure 11: OH production from photolysis of HONO ($P(OH)_{HONO\_net}$) and O_3 ($P(OH)_{O_3}$) at the foot and the summit of Mt. Tai. (A): $P(OH)_{HONO\_net}$, (B): relative contributions, and (C): $P(OH)_{O_3}$.

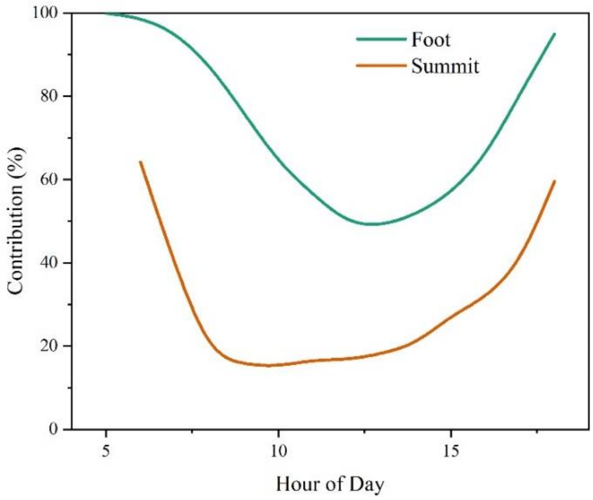

Figure S8: Relative contribution of $P(OH)_{HONO\_net}$ to $P(OH)_{sum}$ at the foot and the summit stations.

Page 19, lines 425-445: replace HOx with OH since you HONO and O3 photolysis are sources of OH only, not HO2.

Response: Done.

Reference

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