Response to RC2

This paper presents comprehensive field campaign which was performed in summer at the foot (150 m a.s.l) and the summit (1534 m a.s.l) of Mt. Tai (Shandong province, China). The author performed the analysis of HONO budget and found strong unknown HONO sources. Constraints on the kinetics of aerosol-derived HONO sources were discussed and their contribution to HONO formation were negligible. The vertical transport form the ground to the summit levels and heterogeneous conversion of NO_2 was proposed to support the remaining majority of unknown HONO sources. The subject is suitable for publication in ACP and I would recommend the paper is accepted after the author have addressed the following concerns.

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:

Instrumentation: Low levels of HONO were measured by LOPAP technique with detection limit of 1.5 pptv at the summit of Mt. Tai in summer 2018. The QA and/or QC for LOPAP instrument should be stated to guarantee data quality.

Response: In Section 2.2 we added more information about the operation of the LOPAP instrument. At the summit station, a temperature-controlled measurement container was used to house all the instruments. The external sampling unit of LOPAP was installed on the top of the container, about 2.5 m above the ground surface. Zero air (ultrapure N_2) measurements were conducted 2 or 3 times per day. Liquid calibration with diluted standard nitrite solution (Sigma-Aldrich) was conducted every week. Both zero air measurements and liquid calibration were conducted after changing any solution, cleaning the instrument, or replacing any component of the instrument (the air pump was broken on 21st July and replaced by a new one on 25th July). The precision of the instrument determined from 2σ noise of the calibration was 1%. An accuracy of 7% was determined by error propagation including all known uncertainties, i.e., the concentration of the calibration standard (±3-4%) and the liquid (±1%) and gas flow (±2%) rates. Known artificial HONO formation on inlet surfaces (e.g., Zhou et al., 2002) were minimized by using the external sampling unit, with only a 3 cm sunlight-shielded glass inlet to the ambient atmosphere. Other interferences were considered of minor importance, as they were corrected for by the two-channel concept of the instrument. In addition, excellent agreement between LOPAP and DOAS techniques was observed under complex conditions in a smog chamber and in the ambient atmosphere (Kleffmann et al., 2006).

Anthropogenic emissions: The author stated that low NO_x/NO_y of 0.43 ± 0.28 indicated aged air masses and small impact of anthropogenic emissions. However, NO and NO_x were measured simultaneously at the summit station. Why did not the author utilize NO/NO_x to evaluate the influence of nearby anthropogenic emissions. Moreover, the rapid increase in pollutants (HONO, NO, NO_2, NOy, CO, $PM_{2.5}$) was observed on 29 July. Low NO concentrations (1-2 ppbv) were observed at high O_3 levels (~50 ppbv), which should originate from local emissions. However, the author stated the high HONO levels could come from the heterogeneous conversion. The author should reexamine the data and explore the sources of increased pollutants.

Response: As demonstrated in Section 2.1, potential anthropogenic emissions could happen around the Southern Heavenly Gate, the Bixia Temple, and the Jade Emperor Peak. All of the three places

are within 1 km west of our station. If emissions originated from those regions, sharp peaks would be observed and the NO/NO_x ratio should be near to that of fresh plumes.

However, this event lasted about 1.5 hours (5:20-6:50), much longer than the duration of the fresh plumes observed at the foot station. Besides, during this event, air mass originated from the south (Figure 2), the polluted urban region rather than the direction of the potential sources at the summit level. Furthermore, the NO/NO_x ratio in this plume is 0.21, lower than fresh combustion plume with a NO/NO_x ratio of ~0.9 or even higher (Carslaw and Beevers, 2005; He et al., 2020; Kurtenbach et al., 2012; Wild et al., 2017). This is also lower than the fresh plumes observed at the foot station with an average NO/NO_x ratio of 0.46±0.19 at high O_3 levels (Xue et al., 2021).

Therefore, we could conclude that the observed plume should originate from transport from the foot urban region rather than nearby emissions at the summit.

We then improved related texts as:

During this event, air mass originated from the south (Figure 2), the polluted urban region (Figure S1E) rather than the direction of the potential sources at the summit level. This event lasted about 1.5 hours (5:20-6:50), much longer than the duration of the typical fresh plumes observed at the foot station. Furthermore, the NO/NO_x ratio of this plume was 0.21, lower than the direct NO/NO_x emission ratio of ~0.9 (Carslaw and Beevers, 2005; He et al., 2020; Kurtenbach et al., 2012; Wild et al., 2017). This is also lower than that of the fresh plumes observed at the high-O_3 foot station with an average NO/NO_x ratio of 0.46±0.19 (Xue et al., 2021). Therefore, we could conclude that the observed plume should originate from the foot urban region rather than nearby emissions at the summit. The $\Delta HONO/\Delta NO_x$ within this plume was 8%, much larger than that inferred from direct emissions (typically inferred as less than 1%). The ratio could be enhanced by: 1) night-time NO_2-to-HONO conversion at the ground level where the air mass was already aged before being transported to the summit level, 2) in-plume NO_2-to-HONO conversion along the mountain slope (rock and vegetation surfaces, etc.), and 3) in-plume NO_2-to-HONO conversion on particle surfaces as both the boundary layer height (BLH) elevation and the valley breeze are initialized after sunrise.

Figure 5: The data of HONO and $J(NO_2)$ for summit and foot station were measured at different periods. Whether it is appropriate to exhibit the data at different periods together in the figure? The measured data at different periods were different. Is such comparison meaningful?

Response: Measurements at the foot and the summit stations represent typical average diurnal variations for ground surface or summit measurements, respectively. Similar pattern of variations have also been reported by many previous studies including ground surface measurements (Alicke et al., 2002, 2003; Gu et al., 2020; Hendrick et al., 2014; Kleffmann et al., 2005; Platt et al., 1980; Su et al., 2008) and summit measurements (Jiang et al., 2020; Kleffmann et al., 2002; Kleffmann and Wiesen, 2008). Besides, our measurements at the two stations were conducted during two consecutive periods in summer 2018. To confirm our argument, we also compared pollutants at the ground and summit stations during the same period, such as $PM_{2.5}$, CO, O_3, and SO_2 (Figure 7 in the manuscript) discussed in Section 3.2.2.3 of our manuscript.

Hence, the comparison could allow potential insights into the link between atmospheric chemistry at the ground surface and summit levels.

Page 13, line 285-290: The author stated that south wind could enhance the upslope valley breeze wind because higher wind speeds (>5 m s^{-1}) were observed at the summit station than at the foot of

the mountain (> 2 m s^{-1}). However, the wind speeds are generally higher at the summit station, which requires detailed explanation by the author.

Response: The fact that the south wind could enhance the upslope valley breeze wind is not because of higher wind speed at the summit level. It's because the urban site (150 m a.s.l.) is south of the summit station (1534 m a.s.l.).

The reported upslope valley breeze wind speed was about 2-5 m s^{-1}. With consideration of south wind at the ground level (>2 m s^{-1}), the integrated wind speed along the mountain slope could be 4-7 m s^{-1}. Alternatively, with consideration of south wind at the ground level (>5 m s^{-1}), the integrated wind speed along the mountain slope could be 7-10 m s^{-1}. Therefore, we used the wind speed range of 4-10 m s^{-1} to consider all the possible situations.

Related texts are improved as:

The upslope valley breeze wind could transport polluted air mass from the foot to the summit levels. This process could be accelerated by the dominant south wind (Figure 8) as the urban site (150 m a.s.l.) is south of the summit station (1534 m a.s.l.). The mean south winds measured at the ground and summit stations are >2 and >5 m s^{-1}, respectively. Then the integrated wind speed along the mountain slope should be 4 – 10 m s^{-1}, and the calculated $t_{transport}$ will be reduced to 7 – 17.5 min.

Page 16, line 347-348: "Note that the uncertainty of …". I don't quite understand this sentence. Section 3.6 stated the contribution of photolysis of HONO and O_3 to OH. Please give the explanation.

Response: We cited Figure 10 and added the below discussion on the contribution (3%) of $P(HONO)_a$ to HONO formation. It has been revised as:

Note that the uncertainty of S_a is not expected to cause a significant uncertainty on HONO budget analysis as $P(HONO)_a$ was not the dominant source (Figure 10 and see the below discussion on $P(HONO)_a$ contribution).

The author calculated the enhanced uptake coefficient of NO_2 on the aerosol surfaces. The dark uptake of NO_2 on the aerosol surface could be considered to evaluate the influence of heterogeneous reaction on the aerosol surfaces since the dark uptake coefficient of NO_2 were mostly investigated.

Response: From the correlation analysis (Table 4), we found poor correlations (r = 0.17 or 0.64) between P_{un} and NO_2*S_a or $NO_2*S_a*J(NO_2)$, suggesting minor roles of dark and photo-enhanced NO_2 uptake on the aerosol surface in the HONO formation.

Besides, with $\gamma_a = 2\times10^{-5}$, photo-enhanced $P(HONO)_a$ could only explain 3% of P_{un}. For dark NO_2 uptake, γ_{a_dark} is generally at a level of 10^{-6} (George et al., 2005; Han et al., 2017; Stemmler et al., 2006, 2007), implying that $P(HONO)_{a\_dark}$ is much lower than $P(HONO)_a$. Therefore, we didn't consider dark NO_2 uptake on the aerosol surface.

The following sentence was added in Section 3.4:

Note that dark NO_2 uptake on the aerosol surface was not considered due to a much lower uptake coefficient generally at a level of 10^{-6} (George et al., 2005; Han et al., 2017; Stemmler et al., 2006, 2007).

Page 19, Section 3.6: The author only calculated the contribution of the photolysis of HONO and O_3 to OH and not HO_x. The HO_x should be replaced by OH.

Response: Done.

Page 21, line 470: What dose λ_a stand for? It is γ_a?

Response: It has been changed to γ_a.

Reference

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