General comments:

HONO and related parameters were measured at the foot of Mt. Tai in the summer 2018. 0-D box model coupled with the MCM were used to explore the budget of HONO, OH, ROx and NO3 radical chemistry. The homogeneous reaction of NO and OH has been adopted as the default HONO source in the box model and account for 12%-15%. The family constraint was used in this Model scenario to correct for interferences of NO2 measurements. Large amount of unknown source of HONO appeared especially on the noontime. Then many sources of HONO were discussed and added in the models. Corrected NO2, direct emission, heterogeneous reactions of NO2, and photolysis reactions were considered in the model. Another part of the manuscript studied the Radical chemistry. The authors gave very detailed consideration on the sources of HONO, and some corrected methods were suggested. These results is meaningful for the development of HONO investigation.

Response: Thanks for your great efforts and valuable comments, which helps to improve our manuscript. Please see the point-to-point response below.

(Comments in Black, Response in Blue, Changes in the manuscript in Red)

There also existed some problems the authors need to improve the manuscript. The manuscript had two parts, one was about the sources of HONO, the other was about the radical chemistry. The connection between these two parts was not very tightly. The first part, more focused on the sources of HONO which had some relationship with OH radical, but how about NO3? I suggested the authors gave some descriptions on the connection between these two parts. For example, the significant of first part was that model was corrected more accuracy and could give more accurate results of radicals, such as ROx, NO3? Some relationship of HONO in NO3 chemistry?

Response: We added two sentences in Section 3.3 to strengthen the connection between these two parts: "Comprehensive field measurements in comparison to model studies allow studying the role of HONO in the radical chemistry of the atmosphere. HONO is expected to strongly impact OH levels in the lower atmosphere due to strong daytime HONO sources and due to its fast photolysis. In addition, considering high O_3 levels at the present field site, NO_3 chemistry could also be important particularly during night-time, which will also be discussed in this section."

Specific comments:

The logical of Introduction was not very well. The authors should give more discussions between the relationship of the investigation of HONO sources and radical (ROx + NO3) chemistry.

Response: See the above explanation about the connection between these two parts.

More detailed information of foot site should be presented especially the real environment around the site, which were very useful for the analysis of HONO sources.

Response: Locations of the foot and the summit sites could be found in Figure 1 in the companion paper. Besides, we add additional information about this site: "Tai'an is located nearly in the middle between Beijing and Shanghai. The city has a population of about 5.6 million and is about 60 km south of Jinan city (the capital city of Shandong province, population: ~8.7 million). Measurements were conducted both at the ground level (the foot of Mt. Tai, 150 m a.s.l.) and the summit level (the summit of Mt. Tai, 1534 m a.s.l., 36.23°N, 117.11°E). The foot station was inside Shandong College of Electric Power (36.18°N, 117.11°E) in the Taishan district of Tai'an city. There are no industrial

activities around this site, which is surrounded by the campus, residential area, and a business district. The 801st province road is in the northeast of this typical urban site."

In 3.1.2. Since the NO2 concentration is not credible by using thermo 42i, how did authors prove that the model results of NO2 correction were reliable. Additionally, the interference could be as high as +75% after adding HNO3 in model simulation, which corrected NO2 was used, consider HNO3 or not? If not, please give the explanation on why not considered HNO3 interference? By the model results, PAN had most impact on the NO2 concentration, how accuracy about the model results of PAN, have compared with observation PAN?

Response: HNO_3 was not considered. HNO_3 is highly sticky so that it is expected to be absorbed on the wall of sampling tubes (about 2 m) or on the filter before reaching inside of the instrument. Nevertheless, we included HNO_3 in an additional scenario for uncertainty analysis.

Regarding model results of PAN, we only have 10 days of PAN measurement in this model period. During these 10 days, diurnal profiles of the measured NO_2, modeled PAN, and the measured PAN were shown in the following figure. The model could well reproduce PAN in the daytime but there is underestimation during the night-time. Therefore, using the modeled PAN to correct NO_2 could improve the accuracy of daytime NO_2. Since night-time NO_2 was more than one order of magnitude higher than PAN, the underestimation of PAN during the night-time would not cause significant error in NO_2.

In summary, we have to admit that this method still has uncertainties but indeed reduced the overestimation in NO_2 measured by the chemiluminescence technique.
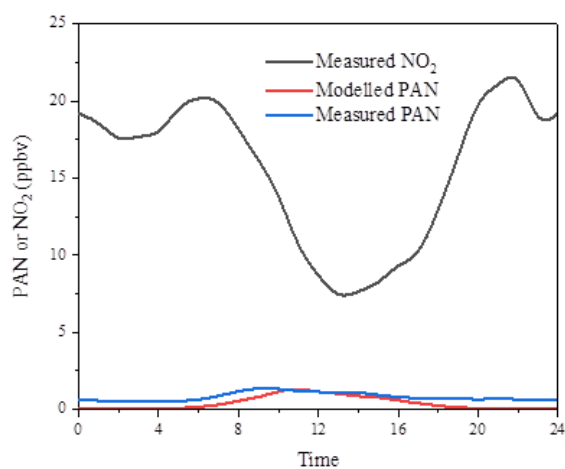

Figure: Diurnal profiles of the measured NO_2, modeled PAN, and the measured PAN.

What's the meaning of Fig S3? NOz*??? Line 223, also NOz*?

Response: There is a spelling mistake. NO_z^* should be NO_2^* defined as $NO_2^* = NO_2 + HNO_4 + 2N_2O_5 + NO_3 + PANs + $ organic nitrates* (see Section 3.1.2). We did the correction in the manuscript and the supporting information.

In 3.2.2.1. What was the correlation between $\Delta HONO/\Delta NOx$ data in table 4 and $HONO/NOx$ data in Fig 5. In Fig 5, the phenomenon of "the observed $HONO/NOx$ is convergentas $NO/NO2$ increases" was unclear, this was not convincing for the further correction on $\Delta HONO/\Delta$ NOx. There were definitely different meanings for $\Delta HONO/\Delta NOx$ and $HONO/NOx$, why authors choose NOx

concentrations?

Response: "HONO/NO$_x$" appeared in Line 269 in this section was a spelling mistake. It should also be "ΔHONO/ΔNO$_x$" which represents the emission ratio from vehicle exhaust.

We chose NO$_x$ (NO+NO$_2$) as many previous studies did because 1) a rapid NO increase indicates a fresh plume emitted by vehicles and 2) NO-to-NO$_2$ conversion is fast but NO$_x$ doesn't change.

Give the explanation of why HONO from direct emission (HONOemi) is likely significantly overestimated with a constant ΔHONO/ΔNOx because of different lifetimes of HONO (τ(HONO)) and NOx (τ(NOx)) in the daytime. Please give the more reasonable explanation of the modified factor of $\frac{\tau(HONO)}{\tau(NO_x)}$ in equation 3, and detail information on the calculation of $\frac{\tau(HONO)}{\tau(NO_x)}$.

Response: In the daytime, NO$_x$ and HONO have distinctly different lifetimes as shown in Figure S7. For instance, at noon, the lifetime of NO$_x$ is about 4.4 h, which means the measured NO$_x$ at noon represents an accumulation of NO$_x$ emission during >4.4 h. However, the lifetime of HONO at noon is about 0.2 h, which means HONO has much less accumulation. Therefore, if we want to calculate HONO emission from vehicle exhaust, the accumulation time (i.e., lifetime) of HONO and NO$_x$ should be taken into consideration.

τ(HONO), could be obtained from HONO concentration divided by its total loss rates (HONO+hν and HONO+OH), which could be directly achieved from the F0AM model (Wolfe et al., 2016).

τ(NO$_x$) depends on the lifetime of NO$_2$ (τ(NO$_2$)) and NO/NO$_2$ ratio regarding the net loss of NO$_x$ is mainly in the form of HNO$_3$ produced through OH or NO$_3$ induced reactions. Similar to τ(HONO), we can calculate τ(NO$_2$) through NO$_2$ concentration divided by its net loss rate (NO$_2$ + OH → HNO$_3$, NO$_3$ + VOCs → HNO$_3$, and NO$_3$ + NO$_2$ + wet surface → HNO$_3$). Then we can get τ(NO$_x$) through the following equation (Seinfeld and Pandis, 2016):

$$\tau(NO_x) = \tau(NO_2) * (1 + \frac{NO}{NO_2})$$

Related texts were presented in Section 1 in the supporting information.

The observation site is special, how to choose NO2 uptake coefficient on aerosol surfaces and ground surfaces? what's the reasonable? Why the γa was larger than γa_dark? As shown in Eq-5, photo-enhanced effects had been considered. Similar question also appeared on the γg and γg_dark. Please give the explanation for the higher value of γa and γg.

Response: γ$_{a\_dark}$ and γ$_{g\_dark}$ represent NO$_2$ uptake coefficients on the aerosol surface and ground surface, respectively. γ$_{a\_dark}$ and γ$_{g\_dark}$ were found to be low, generally less than few 10^{-6} (George et al., 2005; Han et al., 2016; Kurtenbach et al., 2001; Ndour et al., 2008; Stemmler et al., 2006, 2007). NO$_2$ uptake could be enhanced by radiation, so photo-enhanced NO$_2$ uptake coefficients on the aerosol surface and ground surface (γ$_a$ and γ$_g$) are much higher than γ$_{a\_dark}$ and γ$_{g\_dark}$, which could be obtained from laboratory studies and widely used in field/model studies (George et al., 2005; Han et al., 2016; Stemmler et al., 2006, 2007).

MLH values have great impact on the simulation results, so the reasonable MLH value was very important. Why 50 m was good? please combined the real environment and give the reasonable discussions.

Response: Near-ground HONO measurements are typically more weighted by ground-derived

sources (Vandenboer et al., 2013; Vogel et al., 2003; Wong et al., 2011, 2013). As shown in a recent vertical HONO measurement in southwest China (Xing et al., 2021), HONO levels rapidly decreased from 4.8 ppbv at the ground level (~4 m above the ground surface) to 1.6, 0.7, 0.3, 0.2, and 0.1 ppbv averaged in height ranges of 0 – 100, 100 – 200, 200 – 300, 300 – 400, and 400 – 500 m above the ground level, respectively. This indicates that the near-ground HONO was remarkably affected by ground-derived sources and hence MLH should be much less than 100 m in box model studies constrained by near-ground surface measurement data. A similar phenomenon could also be found in Brown et al. (2013) and Vandenboer et al. (2013) in which they used a tower-based platform to measure the vertical profile of HONO. Therefore, we chose 50 m as the MLH.

To reduce the uncertainties caused by the assumed MLH, we also conducted a) several sensitivity tests with different MLH (35, 50, and 100 m, see Figure 6B and Section 3.2.2.4) and b) enlarged aerosol-derived sources to see whether the aerosol-derived sources could explain the observations if ground-derived sources were reduced. Results showed a significant discrepancy between the modeled HONO and the observations assuming aerosol-derived sources dominated HONO formation (Figures S8 and S9), which reinforced our main conclusion about the HONO budget.

Hence, the MLH used in this study may have uncertainties (honestly, this is still an open question for near-ground HONO studies), but does not change the main conclusions about the HONO budget. Additionally, we also addressed the necessity of the vertical measurement based on tower-, balloon-, or aircraft-based platforms and the coupling with 1-D model simulations (See Section 3.2.2.4).

Line 380: how HONOemi was included in the model? The HONOemi was not the production rate data by Eq-2 and Eq-3.

Response: $HONO_{emi}$ was calculated based on Eq-2 for nighttime and Eq-3 for night-time with consideration of different lifetimes of HONO and NO_x during daytime. Details can be found in the above response.

In Figure 7, to include direct emission in the mode result, we added $HONO_{emi}$ (concentration in ppbv) to the modeled HONO (concentration in ppbv) to compare with the observations and then calculate its contribution.

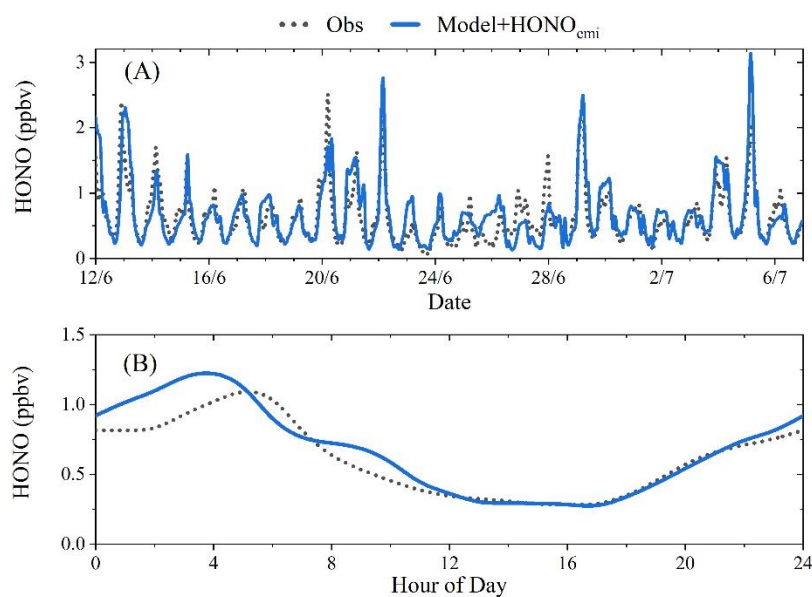To make it clear, we improved the captions in the figure as follows:

Figure 7: Modeled HONO mixing ratios (Model, in blue) in comparison with observations (Obs, in black). (A): time series; (B): diurnal variations. Model+HONO$_{emi}$ represents the sum of the modeled HONO and HONO$_{emi}$.

Line 534: what's the percentage of HONO contribution to OH radical not considering only HONO and O3 photolysis? From Fig 10, there were many sources in production of OH, and HONO not the most important sources.

Response: In Figure 10, all the OH sources (initiation and propagation) are included. Some of them are not primary OH sources but radical propagation sources (such as HO$_2$→OH, etc.). However, atmospheric chemistry is initialized by primary OH from initiation sources. Hence, we need to compare the relative contributions of primary OH sources, which leads to Section 3.3.4 and Figure 13.

I can't understand why put the foot and summit of Mt. Tai together in the title, through the two part manuscripts, the Part I was the results on the summit of Mt. Tai, while Part II was the results on the foot of Mt. Tai. the comparation of these two sites was only given some discussions in this manuscript 3.3.5, but these discussions had no new sights and meaning. Furthermore, the analysis methods were different in these two parts. I suggested the authors revised the title, this manuscript was "Atmospheric Measurements at Mt. Tai-Part II: HONO Budget and Radical (ROx + NO3) Chemistry in the Lower Boundary Layer".

Response: After careful consideration of the comments on the two papers, we decided to move Section 3.3.5 (Role of HONO in OH Production at the Foot and the Summit Stations) to the summit paper because the most important of this section is to highlight the important role of HONO in the summit level.

Besides, the titles of these two papers are modified as suggested.

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