Dear Editor,

We appreciate the careful consideration of our manuscript by the reviewer and you. We have carefully responded to all of the point-by-point comments and issues raised by the reviewers and have revised the manuscript accordingly. We also have edited the language. These revisions are described in detail below.

Reviewer 2#

A main problem with this paper is that the authors make use of many qualitative arguments based on previously published papers instead of using their observation data to quantitatively support their speculations. Despite my strong objections to these speculations in the first-round review, the long-winded response mostly re-stated what was in the original paper. Reviewing the original paper and reading the responses are painful exercises because the authors' arguments are mostly based on some "beliefs" seemingly garnered from incorrectly reading other papers. Their observations were often either ignored or misused. My concerns are not properly addressed and I cannot find good reasons to change my original recommendation. (1) In response to my first comment, they cited several previously published papers and corrected a mistake I pointed out in the first-round review. A larger primary radical source from HONO photolysis does not mean that OH increases in the same proportion as the primary source increase. The question, which they did not answer in the response, is how much OH increase can be sustained by the photolysis of HONO. The response ran around in circles of this question.

Response: Thank you for your patience to review the response file. We hope to well reply each point of your comments. So, the response file was somewhat long.

We agree with you that it is better to quantitatively discuss the contribution of HONO to OH concentration if it is possible. However, it is impossible to get the quantitative information at the present time. This will be done using an air quality model in the future. In the revised manuscript (lines 720-722), we have pointed out it as

"Finally, it is necessary to quantify the contribution of traffic-related source of HONO on OH production and secondary aerosol formation based on modelling studies in the future". And in lines 372-374, we pointed it as "Overall, this work qualitatively supported the recent modelling results that HONO could promote the aerosol production in winter (Zhang et al., 2019a;Zhang et al., 2019b;Xing et al., 2019;An et al., 2013) from the point of view of observation".

The logic of this work is: 1) HONO could promote wintertime OA formation based on qualitative analysis; 2) traffic related emission should be an important contributor to ambient HONO in Beijing. We think the significance of this work is to provide a new perspective to Haze Beijing although more quantitative work is required in the future.

The newly added statement, "These results mean that the photolysis of HONO should play an important role in the initiation of the daytime HOx and ROx chemistry on polluted days in winter, while photolysis of O_3 becomes more important from April to June.", did not answer the question on the quantitative effect of HONO photolysis on OH. The statement itself is meaningless. What does "more important" mean? Is "more" for comparison between April-June and winter or between HONO and O3 photolysis? The understanding of chemistry is also flawed. The primary radical source from O3 photolysis is not JO1D*CO3. It is much smaller because most O1D reacts with N2 and O2. JO1D*CO3 cannot be compared to the photolysis rate of HONO directly (which was done in this paper).

Response: Thank you. As for the contribution of HONO photolysis on OH concentration or production, we have replied in the first question. The quantitative analysis will be carried out using air quality model in the future.

$J_{O1D}*c_{O3}$ reflects the production rate of O1D instead of OH production rate. The production rate of OH from photolysis of O_3 is directly proportional to $J_{O1D}*c_{O3}$. However, the increase of $J_{O1D}*c_{O3}$/JHONO in summer indicates the enhanced role of O_3 in OH production compared with that in winter. In the revised manuscript in lines 298-301, we pointed it as "We simply compared the OH production via photolysis of

HONO ($P_{OH\text{-}HONO}=J_{HONO}\times c_{HONO}$) and O1D production rate from O_3 ($P_{O1D}=J_{O1D}\times c_{O3}$) in Fig. 2 when the $PM_{2.5}$ concentration was larger than 50 μg m^{-3} and the RH was less than 90 % to understand the chemistry in pollution events". In lines 315-319, we revised the sentence as "Because the production of OH from photolysis of O_3 should be directly proportion to P_{O1D}, these results imply that the relative importance of the photolysis of HONO compared with that of O_3 for initiating the daytime HO_x and RO_x chemistry on polluted days should be more important in winter than that from April to June".

The response did not address my comment of "There are many reasons that HONO/CO correlates with OA/CO. For example, CO is primary in winter in Beijing. If HONO and OA variations are from secondary sources, there will be high correlations as shown."

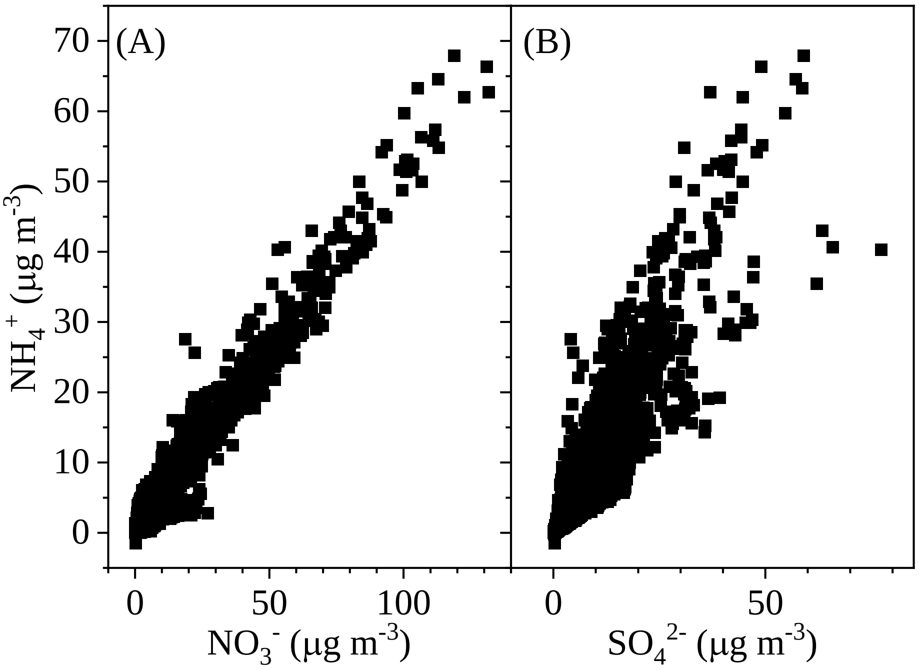
Response: Thank you. If two pollutants are from secondary sources and driven by a third factor, their concentration or normalized concentration to CO will be highly correlated. However, the absolute value of HONO/CO was actually anti-correlated with OA/CO in the selected pollution events although secondary reaction was the important contributor to both OA and HONO. In this work, we correlated the increased value of OA/CO from the early morning to noon with the corresponding consumed HONO/CO in different pollution events. Because HONO is a well-recognized precursor of OH in the morning and SOA formation is greatly affected by oxidants, we proposed that HONO should promote SOA formation. We think the correlation is reasonable based on the well-known knowledge. In the revised manuscript (lines 324-330), we made it clearer as "Oxidation of trace gas pollutants, in particular VOCs, by OH is their main removal pathway in the troposphere (Atkinson and Arey, 2003), subsequently contribute to secondary aerosol formation (Kroll and Seinfeld, 2008). A very recent work has found that oxidation of VOCs from local traffic emission is still efficient even under pollution conditions (Guo et al., 2020). This means high HONO concentration might promote SOA formation after sunrise because HONO is an important primary OH source in the early morning".

The statement, “It should be noted that the daytime lifetime of HONO is very short due to photolysis. This means regional transport should has little influence on local HONO concentration.”, is also incorrect. The lifetime of HONO at night is long and transport affects HONO concentrations. In daytime, if a substantial fraction of HONO is from NO_2, transport certainly affects NOx and therefore HONO. In the statement, “As the meteorological condition was stagnant during these cases as indicated by the low wind speed (< 1.0 m s-1, Fig. S5D), it was reasonable to mainly ascribe the increase of OA concentration to local secondary formation initiated by OH radical from HONO photolysis”, how could the authors know that the increase of OA is from “local secondary formation initiated by OH radical from HONO photolysis”?

Response: Thank you. To make our statement stricter, we revised the statement “As the meteorological condition was stagnant during these cases as indicated by the low wind speed (< 1.0 m s^{-1}, Fig. S5D), it was reasonable to ascribe the increase of OA concentration to local secondary formation initiated by OH radical and photolysis of HONO should play an important role in initiation the HOx and ROx chemistry” to “The dataset under stagnant meteorological conditions as indicated by the low wind speed (< 1.0 m s^{-1}, Fig. S5D) was analyzed to decrease the contribution of transport to the observed HONO and OA” in lines 331-333.

The new statement, “We explained the increased ammonium as the result of enhanced neutralization of HNO_3 by NH_3 (Wang et al., 2018;Wen et al., 2018;Sun et al., 2018) because NH_4^+ was adequate to neutralize both sulfate and nitrate as shown in Fig.S8” is incorrect. In Beijing winter, higher HNO_3 does not necessarily convert more NH_3 to ammonia. The authors appear to have a limited understanding of aerosol chemistry.

Response: Thank you for your comment. Ammonium is a secondary pollutant. Thus, the increase of particulate ammonium should be correlated to the conversion from ammonia to ammonium. As shown in Figure R1, the concentration of particulate ammonium linearly correlated with that of nitrate and sulfate. In particular, the correlation between nitrate and ammonium is stronger that that between sulfate and ammonium. Therefore, the daytime increase of ammonium should be highly related to neutralization of sulfate and nitrate by ammonia. We revised the statement (lines 358-360) as "We explained the increased ammonium as the result of enhanced neutralization of sulfate and nitrate by NH_3 (Wang et al., 2018; Wen et al., 2018; Sun et al., 2018) because NH_4^+ was adequate to neutralize both sulfate and nitrate as shown in Fig. S8".



(2) In response to my comments on the HONO budget, Table S3 is useful. However, looking at Fig. S9, could some of the HONO measured with ~100 ppb NOx be a result of inlet conversion of NO_2 to HONO? Some dirty vehicles may have high HONO/NO_2 emission ratios, but I find it puzzling why no measurements seem to have HONO/NO_2 ratio < 1% for the selected "fresh emission" data points.

Response: Thank you for your comment. For HONO measurement, the interference from the sampling inlet is inevitable for any kind of instrument. To decrease the interference, we sampled ambient air from the window and used a sample line as short as possible (~1.0 m). In addition, we did the control experiment by sampling 100 ppb of NO_2 balanced with zero air at 50% RH into the instrument. The measured HONO was 0.4 ppb, while the ambient HONO concentration was 5.98±1.00 ppb when the NO_2 concentration was higher than 80 ppb on pollution days. This means sampling interference would overestimate ~6.7 % of HONO concentration on pollution days. If the conversion ratio of NO_2 to HONO in the sampling line is constant, the emission ratio of HONO to NOx should be decrease from 1.17 % to 1.09 %. In the revised manuscript, we updated the related data. In the revised manuscript (lines 397-401), we added a paragraph "It should be pointed out that the interference from the sampling inlet overestimated 6.7 % of HONO concentration based on control experiments. Thus, the ratio of ΔHONO/ΔNOx should be 1.09±0.05% when the interference from the sampling inlet was taken into consideration". The data in Figs.3 and 4 and in the text have been updated correspondingly.

The response did not answer my comment "No discussion was given on what volume was used and how it varied in a day." The response states "The hourly NOx emission inventory from vehicles in Beijing, with an annual emission rate of 109.9 Gg yr-1 (Yang et al., 2019), was used when calculating the E_{vehicle} in this work." The authors need to state what area is used for Beijing. The Beijing metropolitan area is very large. Vehicle emission rates can be extremely low in the rural regions of Beijing, the area of which is much larger than the urban core. A further statement "…the PBL height as described in Section 2.2. Thus, the calculated emission rate reflected the diurnal variation of both the emission inventory and the PBL height" does not provide useful information. I cannot find where they got the PBL data and their calculation on the effects of diurnally varying PBL on the budget of HONO. For example, the nighttime PBLH is usually 10-50 times less than the daytime. Therefore, the nighttime vehicle HONO source is 10 times or more than daytime (after accounting for lower emissions at night). The diurnal variation for the vehicle source in Figure 3 is too small.

Response: Thank you. In the first-round of response and in Section 2.2, we pointed out that "The emission rate (E_{HONO}, ppbv h^{-1}) was calculated based on the emission flux (F_{HONO}, g m^{-2} s^{-1}) and PBL height (H, m) according to the following equation,

$$E_{HONO} = \frac{\alpha \cdot F_{HONO}}{H} \quad (2)$$

where, α is the conversion factor ($\alpha = \frac{1\times10^{9}\cdot3600\cdot R\cdot T}{M\cdot P} = \frac{2.99\times10^{13}\cdot T}{M\cdot P}$), M is the molecular weight (g mol^{-1}), T is the temperature (K) and P is the atmospheric pressure (Pa)". Here, F_{HONO} is the emission intensity of HONO over a unit area.

When calculating the F_{HONO} according to $F_{HONO}=EI_{HONO}/A$, the core urban area of Beijing was used (with 20 km of diameter based on google map and the distribution of annual-average vehicular NOx concentration in Beijing (Yang et al., 2019). This was added in the revised manuscript (lines 173-174) as "where, EI_{HONO}, is the emission inventory of HONO (g s^{-1}), A is the core urban area of Beijing (m^2, with diameter of 20 km),…"

After divided by the PBL height, the emission rate means the emission intensity of HONO in a column. Therefore, the variation of E_{HONO} depends on both the F_{HONO} (or the emission inventory of NOx) and the PBL height. Fig. R2 shows the diurnal variation of the PBL height and the emission inventory of NOx from vehicles in Beijing (Yang et al., 2019). Because both the emission of NOx from vehicles and the PBL height were significantly higher in the day than that in the night, the difference in the daytime and nighttime E_{HONO} in Fig. 3 should be smaller than that of PBL height because the PBL height is the denominator in Eq. (2).

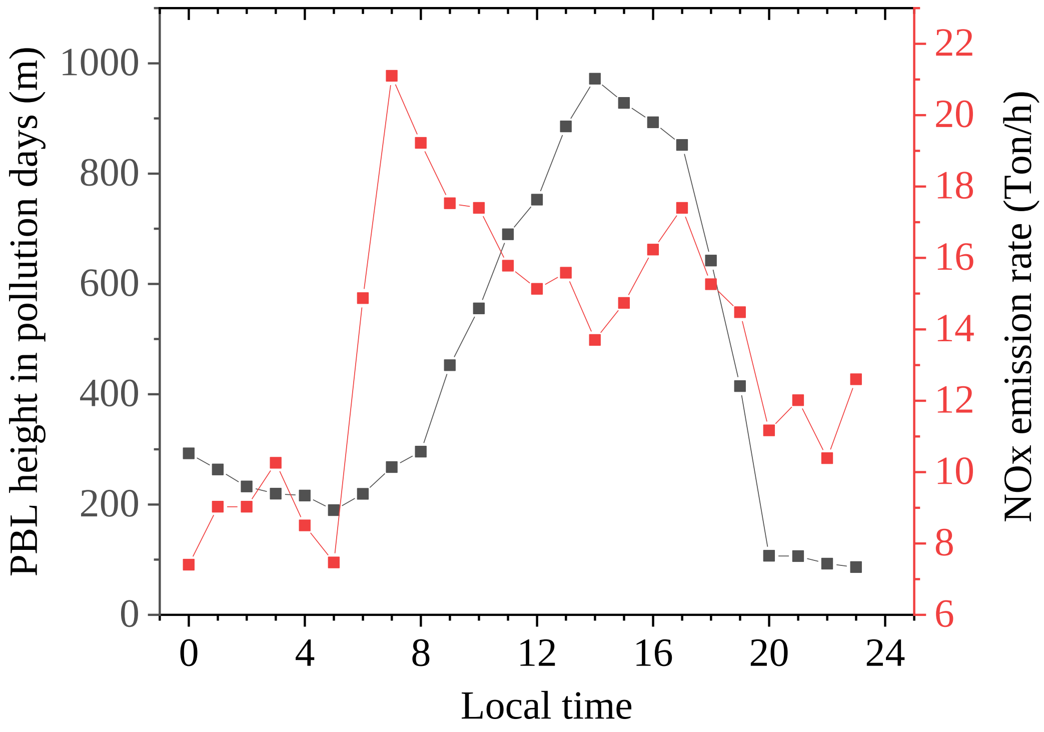


Figure R2. Diurnal curve of PBL height in pollution days and the hourly emission inventory of NOx from vehicles in Beijing (Yang et al., 2019)

As for the PBL height, we measured it using a ceilometer. In lines 146-158, we pointed it "Visibility and planetary boundary layer (PBL) height were measured using a visibility sensor (PWD22, Vaisala) and a ceilometer (CL51,Vaisala), respectively". In addition, the time series of PBL height was shown in Fig. 1F.

The only information of PBLH data used in this study I can find is Fig. S4A. The figure shows that PBLH varies from 20 to 3500 m. The distribution does not seem to show that PBLH increases from winter to summer. It provides no useful information on answering my question of diurnal HONO budget variation.

Response: Thank you for your comment. We showed the time series of the PBL height in Fig.1F and Fig. R3. It increased from winter to summer as you pointed out.

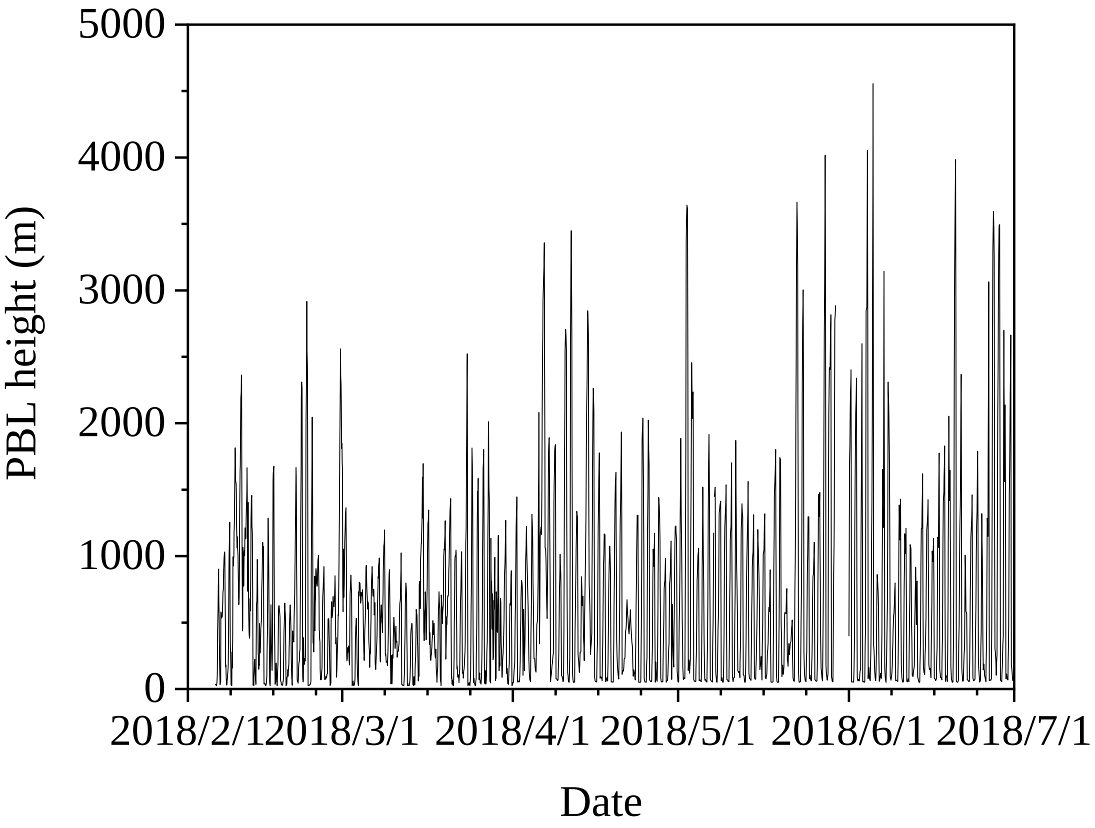


Fig. R3. The time series of the PBL height.

The newly added statement, “In the daytime, we assume a zero concentration gradient”, is wrong. If the PBLH is 3 km, how can HONO be constant from the surface to 3 km? At night, PBLH is usually low. Vertical mixing is not even a sink of HONO for a budget analysis that extends from the surface to the PBL top. (Eqs. (12) and (13) cannot even be used to estimate the vertical loss of HONO when the vehicle emission source is estimated as emission rate/PBLH).

Response: Thank you for your comment. The measurement on the vertical distribution of HONO was scarce at the present time. According to a recent field measurement, the concentration of HONO showed nearly flat profiles from ground level to 240 m in pollution events after sunset, while negative profiles of HONO were observed in pollution events during night (Meng et al., 2019). Unfortunately, they did not measure the vertical profiles in the daytime. In the revised manuscript (lines 571-573), we revised this sentence as “Because the daytime vertical gradient of HONO concentration is unavailable in Beijing, we do not calculate the daytime vertical transport".

The maximal PBL height was around 3 km in clean days. However, we calculated the HONO budget in pollution days. The mean PBL height was 487±460 m in pollution days. As pointed in the manuscript, we calculated the nighttime T_{vertical} using the reported concentration gradient but not the PBL height. We agree with you that the height of the vertical mixing layer might be lower than the PBL height. This will underestimate the emission rates from vehicle, soil and heterogeneous reaction on ground surface using the PBL height. Actually, this is a common problem for HONO budget calculation even for modelling studies. In the revised manuscript, we added a sentence to discuss the uncertainty in lines 710-713 as "In addition, the exact height of vertical mixing of HONO was assumed to be the same as the PBL height, this might underestimate the contribution of vehicle, soil and heterogeneous reaction on ground surface".

The statement "In the night, 79 % of the wind speed was lower than 1.0 m s-1 in winter" is likely based on surface wind measurements at a site where wind is blocked by buildings in the city. Looking at any meteorological data, wind speed is stronger in winter than summer in Beijing and the average wind speed in Beijing in winter is much higher than 1 m/s.

Response: Thank you for your comment. The wind speed was measured on the ground surface (18 m above the ground surface). This was pointed out in Section 2.1. The wind speed is usually stronger in winter than summer in Beijing. However, it varied monthly as shown in Fig. S4. The mean wind speed in Beijing in winter is much higher than 1 m s^{-1}. Here, we meant that 79 % of the wind speed was lower than 1.0 m s^{-1} on polluted days when the $PM_{2.5}$ concentration was larger than 50 μg m^{-3} and the RH was less than 90 %. In the revised manuscript (lines 580-584), we corrected it as "In the night, 79 % of the surface wind speed was lower than 1.0 m s^{-1} on pollution days when the $PM_{2.5}$ concentration was larger than 50 μg m^{-3} and the RH was less than 90 % in winter, thus the air masses from suburban areas should have influence on the sources and sinks of

HONO in Beijing”.

The authors assume that ground level gamma values are the same as dust aerosols and calculated a low surface HONO source. What is the justification? The assumption is arbitrary.

Response: At the present time, the uptake coefficient of NO_2 on ground surface was usually assumed to be the same as that on particle surface in modelling studies (Zhang et al., 2016;Aumont et al., 2003). In the revised manuscript (line 511), the references have been added. The urban ground surfaces include plant leaves, building surface, and rock and soil surfaces and so on. To our best knowledge, the uptake coefficient of NO_2 on ground surfaces is unavailable at the present time. For example, there is no publication on reaction kinetics of NO_2 on plant leaves and rocks. In our previous work, we measured the kinetics of NO_2 uptake and HONO formation on kaolinite, which is an important kind of soil. The uptake coefficient of NO_2 is on 10^{-8} order of magnitude. It is close to that on aerosols recommended by Crowley et al. (2010).

I do not follow the reasoning from “If both the $\gamma_{NO2,BET}$ ($1x10^{-6}$) and surface roughness are increased to the values used in modelling studies, the nighttime production rate of HONO via heterogeneous reaction of NO_2 on ground surface will be 2.9 ppb h^{-1}. This means a large sink missed if this number is reasonable” to the conclusion statement “These results mean that heterogeneous reaction might not be a major HONO source. This is consistent with a recent work that found heterogeneous reaction being unimportant when compared with traffic emission during haze events in winter in Beijing (Zhang et al., 2019c)”. The authors found that the surface source can be much larger (a factor of 10) than the vehicle source. However, because they or previous publications believe that the vehicle HONO source is most important, the authors concluded that the vehicle HONO source is the most important in their dataset too. The argument is circular and meaningless.

Response: Thank you for your comment. In the first-round of response file, you pointed out that we got a too small ground source of HONO, but a large source from vehicle. We calculated the ground source according to these parameters used in previous modelling studies and obtained a very large HONO source from ground surface (2.9 ppb h^{-1}). Even if the contribution of other sources is omitted, the nighttime HONO source is much higher than these reported values. On the other hand, according to the reported kinetics of NO_2 on different aerosols, we don't think these parameters are reasonable. Thus, we chose a small $\gamma_{NO2,BET}$. This value was recommended by Crowley et al. (2010) and was close to that measured in our laboratory. That is the reason why we get a small ground source compared with vehicular emission. As discussed in the first-round of response file, heterogenous reactions on ground surface and aerosol cannot explain the decrease of HONO concentration during the Chinese New Year, 2020 because the concentrations of both $PM_{2.5}$ and NO_2 did not decrease obviously, while HONO concentration decrease obviously due to reduction of vehicle emissions compared with that before Chinese New Year. These results will be discussed in a separate work. This further supported our conclusion that vehicular emission should be more important for HONO source in Beijing when compared with heterogeneous reaction. In the revised manuscript (lines 718-720), we added a sentence "The importance of vehicle emission to HONO source also needs to be further confirmed during special periods such as Chinese New Year when vehicle emission reduces obviously in the future".

The HONO budget analysis is flawed for several reasons. The methodology has errors. There is no closure on the (hourly) budget. Each source and sink terms have very large uncertainties and some arbitrary decisions were made on the parameter values to justify that vehicle emissions are the largest HONO source. The analysis results in this paper are not scientifically credible.

Response: Thank you for your comment. Actually, the method for HONO budget calculation is a simple model in this work. Some methods such as emission sources from vehicle and soil, homogeneous reaction between OH and NO, were also reported in literatures. Because each source was calculated based on several parameters, the uncertainties was inevitable like other modelling studies. The uncertainties of each source have been discussed in the manuscript. Although the sources and sinks are still not closed as shown in Fig. 4, the unknown source has been taken into consideration when we discuss the relative contribution of these sources. Therefore, we think the importance of vehicle emission in HONO source in Beijing should be credible and has been well confirmed by the vehicle emission reduction in Chinese New Year, 2020 as replied in the first-round response file. We think the results of this work will help for understanding the complex cause of haze in Beijing. In addition, this work provided the details about the parameterization for HONO budget calculation. Some parameters are more reasonable compared with previous modelling studies. For example, the surface to volume ratio of ground was calculated based on a surface roughness calculated based on the building surface and PBL height in this work rather than a fixed value of 0.3 m^{-1} (Zhang et al., 2016;Aumont et al., 2003); the uptake coefficients of NO_2 on aerosol was chosen based on laboratory results; the emission ratio of HONO/NOx was calculated based on measured data and the newest emission inventory of traffic NOx was used in this work.

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