Dear Editor,

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

Reviewer 1#

The work by Liu et al present field measurements of HONO, a key source of radicals in the boundary layer, along with supplementary gas and particle-phase measurements in over a 5-month period in Beijing. The authors used this dataset to probe the sources and their contributions to ambient HONO, with a focus on pollution events. Using a steady state approach, the authors calculated the contributions of different sources to the HONO budget and concluded that traffic emission (via direct emission and conversion of NO by homogenous reactions) was the key source of HONO during winter pollution events. Liu et al present a comprehensive and interesting long-term dataset that enables the authors to perform a budget analysis to investigate the main sources of HONO. The main sources of HONO in Beijing and urban area in general is an open research topic, and consequently this work would be of interest to the community, particularly their HONO budget analysis of the haze events.

Response: Thank you so much for your positive comments.

There are, however, a few issues that in my opinion should be addressed prior to publication. While the manuscript is mostly well written, it is long. For example, Section 3.1 and 3.2 could be much shorter. In my opinion much of the text in these sections is unnecessary and could be reduced, without losing the key points.

Response: Thank you so much for your instructive suggestions. We have revised the redundant descriptions in Section 3.1 and 3.2.

In Section 3.1, the paragraph "In particular, the frequency of severe polluted episodes in March was obviously higher than that in the rest months (Fig. 1 and S3), resulting in the highest monthly mean concentration of $PM_{2.5}$ (88.5±60.0 μg m^{-3}) and NR-$PM_{2.5}$ (67.0±56.8 μg m^{-3}). This can be explained by both intensive emission during the heating season, which is supported

by the high concentration of primary pollutants including CO, SO_2 and BC (Table S1), and the stagnant meteorological conditions that physically and chemically promote the accumulation of pollutants. For example, the low wind speed (<2 m s^{-1}) mainly from south-based directions accompanied with the low planetary boundary layer (PBL) height frequently occurred in March compared with other months (Fig. S4A)." has been shortened as "Both the frequency of severe polluted episodes and the mean mass concentration of $PM_{2.5}$ and NR-$PM_{2.5}$ were obviously higher in March than that in the rest months (Fig. 1 and S3). This can be explained by both the intensive emission during the heating season as evidenced by the high concentration of primary pollutants including CO, SO_2 and BC (Table S1) and the stagnant meteorological conditions supported by the low wind speed (<2 m s^{-1}) and the low planetary boundary layer (PBL) height in March (Fig. S4A)" from lines 249 to 255 in the revised manuscript. In addition, we also deleted the sentences "It should be noted that the median mass concentrations of nitrate and OA also were higher in March than that in other months (Fig. S4C). The median mass concentrations of nitrate were 1.42, 8.76, 6.30, 3.15, and 3.23 μg m^{-3} from February to June, respectively. And the corresponding OA concentrations were 4.78, 14.04, 11.64, 13.89, and 14.08 μg m^{-3}. Secondary formation is the major source of OA and nitrate in the atmosphere" from line 232 to 237 in the original version of the manuscript.

In Section 3.2, we deleted the following sentences "The hourly averaged $P_{OH\text{-}HONO}/P_{OH\text{-}O3}$ ratio varied in the range of 1-25.4 during the daytime, while it varied from 0.3 to 2.8 from April to June" (lines 284-288, in the original manuscript), "Although the high loading of fine particles in polluted days could reduce the surface solar radiation (Li et al., 2017), subsequently, the OH concentration, the noon-time OH radical concentrations observed in polluted wintertime of Beijing were 2.4×10^6 cm^{-3} compared with 3.6×10^6 cm^{-3} in clean days (Tan et al., 2018). It was around 2 times compared to places such as Tokyo (Kanaya et al., 2007) and New York City (Ren et al., 2006)" (lines 295-300, in the original manuscript), and " This implies that oxidation of atmospheric trace gases by OH may still be highly effective even in wintertime, thereby facilitating the vigorous formation of secondary pollutants in Beijing" (lines 301-304, in the original manuscript).

The most interesting work is presented in Section 3.3, where a detailed and comprehensive budget analysis is presented. However, throughout section 3.3 some of the calculations and equations need more explanation, as it was not always clear from section 2.2 how they were performed. Some examples are given below in the minor comments. It would also help the reader if the equation used to calculate the rates of emission for each source (I.e. the eqn numbers) were referenced throughout section 3.3.

Response: Thank you for your good suggestions. We have referenced all the equation numbers throughout the revised manuscript. For example, in line 389 in the revised manuscript, "The $E_{vehicle}$ was calculated according to Eq. (2) using the relative emission rate of HONO to NO_x and the emission inventory of NO_x from vehicles"; In lines 446-448 in the revised manuscript, "The lower limit, the middle value and the upper limit of the E_{soil} are 0.0032±0.0027-0.013±0.014, 0.0046±0.0039-0.020±0.20 and 0.0057±0.0047-0.025±0.024 ppbv h^{-1}, respectively, calculated according to Eq. (2)"; In lines 473-475 in the revised manuscript, "Thus, the lower limit, the middle value and the upper limit of P_{NO-OH} were 0.007±0.019-0.43±0.26, 0.026±0.053-0.99±0.79 and 0.028±0.053-2.14±1.71 ppbv h^{-1}, respectively, calculated according to Eqs. (3) and (4)"; In lines 495-498 in the revised manuscript, "Therefore, the corresponding daytime lower limit, the middle value and the upper limit of HONO from photolysis of nitrate were 0.0011±0.0021-0.096±0.092, 0.0072±0.0021-0.66±0.092 and 0.042±0.082-3.86±0.008 ppbv h^{-1}, respectively, calculated in the light of Eqs. (3) and (8)"; And in lines 499-501 in the revised manuscript, "The production of HONO from heterogeneous reactions of NO_2 on aerosol surface was calculated according to Eqs. (3) and (5)".

We also added the more details about budget calculations. For example, we added the following paragraphs "Oswald et al. (2013) measured the emission flux of HONO from 17 soil samples, including eucalyptus forest, tropical rain forest, coniferous forest, pasture, woody savannah, grassland, stone desert, maize field, wheat field, jujube field an cotton field etc. Tropical rain forest, coniferous forest and grassland are the typical plants in downtown Beijing (Huang et al., 2017a). At the same time, their emission fluxes of HONO are comparable (Oswald et al., 2013). Thus, we used the emission flux from grassland to calculate the emission rate of HONO from soil in Beijing because the temperature and water holding content dependent emission flux of HONO was available for grassland soil" lines 433-441; "The

method for the photolysis rates calculation were shown in the SI and the time series of the photolysis rates were shown in Fig. S7" in lines 458-460; "The time series of the measured nitrate concentration and the middle value of $J_{nitrate}$ were shown in Fig. 1 and Fig. S7, respectively" in lines 493-495; "The A_s of aerosols varied from 1×10^{-4} to 4.8×10^{-3} m^{-1} with a mean value of $1.4\pm0.5\times10^{-3}$ m^{-1} during pollution events. This value is comparable with that used in modeling studies (Zhang et al., 2016;Aumont et al., 2003). The A_s of ground surface which was calculated according to Eq. (6) and (7) varied from 1.5×10^{-3} to 3.85×10^{-2} m^{-1} with a mean value of $1.3\pm0.9\times10^{-2}$ m^{-1} during pollution events. The surface roughness was 3.85 calculated according to Eq. (7). The Y_{HONO} was set to 0.5 because of the hydrolysis reaction of NO_2 (Liu et al., 2015), while it was 0.8 for light enhanced reaction (Liu et al., 2019;Ndour et al., 2008) and on BC (Han et al., 2013)" in lines 523-530 in the revised manuscript.

My major comment is from Section 3.3, the way the OH concentration was estimated is problematic in my opinion. As the authors rightly point out, to measure OH is difficult and requires highly specialized kit and therefore as they did not have access to these instruments, OH concentration needs to be estimated for this study. I am not sure about the way the OH concentration was calculated, as the equations they use (e.g. 13), use the levels of ozone and NO_2. The problem is that during winter, the main source of OH in Beijing is HONO photolysis, as the authors themselves state earlier in the manuscript (Section 3.2, line 288, with references), and is in facto one of their conclusions from Fig 2. Therefore, without considering OH produced from HONO photolysis, how can they be sure that their estimated OH concentration is reasonable, especially in winter? I think that for an atmosphere as chemically complex as Beijing, to estimate the OH concentration requires a box-model approach. It is important as the estimated OH concentration will affect the budget analysis, both sources and loss terms, and therefore the conclusions drawn from it. If this is not possible, then the uncertainties with their approach to estimating OH concentrations should at least be discussed/quantified.

Response: Thank you for your instructive suggestion. We agree with you that OH concentration is an important parameter when calculating the HONO source from homogenous reaction between NO and OH. Some uncertainties of OH concentration should be resulted from the estimation approaches used in this work. In strictly speaking, it is better to directly measure

OH concentration using a LIF or a CIMS. However, these instruments are unavailable at the present time. A box-model simulation is an other choice as you suggested because both the source and sink terms can be considered. A comprehensive sheet of VOCs including different isomers is required when doing box-model simulation because the reactivity varies greatly among different isomers even with the same mass to charge ratio (m/z). Unfortunately, the VOCs concentration was measured using a SPI-MS in this work. Similar to a PTR-MS, this instrument cannot separate the isomers with the same m/z. Therefore, we did not simulate OH concentration using a box-model. If we had the measured or modeled OH concentration, we could parameterize the J_{HONO} and c_{HONO} into the Eq. (15).

We indirectly verified the estimated OH concentration by comparison with diurnal curves of OH concentration in this work and that reported in literatures (Tan et al., 2019). Overall, the estimated OH concentration was comparable with that measured in the literature (Fig. S10). In addition, we further compared it with the OH concentration derived from the measured H_2SO_4 concentration using a nitrate-CIMS from December 2019 to February 2020. In a box model, we considered the daytime source of H_2SO_4 from oxidation of SO_2 by OH and the sinks of H_2SO_4 using the measured concentration of the monomer and the dimer of H_2SO_4, the condensation sink (CS, from 1 nm to 10 μm of aerosol) and the meteorological parameters. Then, OH concentration was calculated using a steady state method. As shown in Fig. R1, the predicted OH concentrations was generally comparable between these two different methods. This means the estimated OH concentration in this work is overall credible.

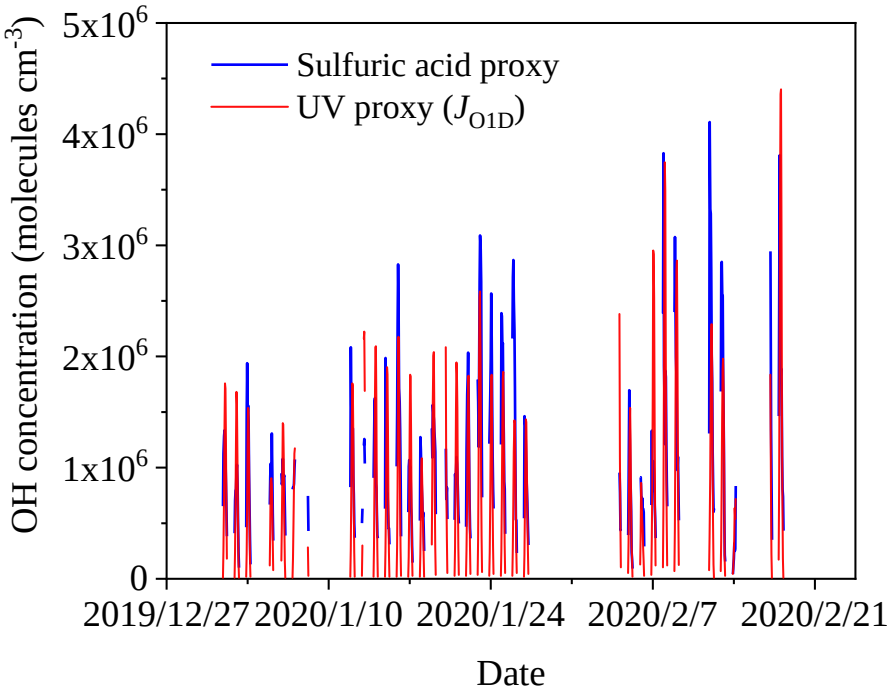

Fig. R1. Comparison of OH concentration between UV proxy method and H_2SO_4 proxy method.

In the revised manuscript (lines 482-488), we added the discussion about the uncertainties from OH concentration estimation as you suggested. "It should be noted that OH concentration was estimated based on J_{O1D} (Tan et al., 2019;Tan et al., 2018) or J_{O1D} and J_{NO2} (Li et al., 2018). As discussed in Section 3.2, HONO was an important primary OH source in the daytime. Unfortunately, it could not be parameterized for calculating OH concentration because the measured or modelled OH concentration was unavailable in this work. This might underestimate the early daytime OH concentration, subsequently, the contribution of homogeneous reaction of NO with OH to HONO source. This need to be further investigated in the future".

Minor comments Line 82: I assume you mean nitrous acid not nitric acid?

Response: Thank you. It is nitrous aid. We have corrected this error in line 81 in the revised manuscript..

Line 112: it would be good to specify that your ACSM was configured for $PM_{2.5}$, as many of these instruments measure PM_1

Response: Thank you. It has been pointed out in the revived manuscript in lines 136-137 as "Then a Time-of-Flight Aerosol Chemical Speciation Monitor equipped a $PM_{2.5}$ aerodynamic lens (ToF-ACSM, Aerodyne)".

Line 207: Why does it matter if $PM_{2.5}$ is above 75 ug m^{-3}? I assume you are referring to the regulatory limits, but it is good to be clear on this.

Response: Thank you. Yes, it the regulatory limits. The air quality is in pollution level if the $PM_{2.5}$ concentration is above 75 ug m^{-3} according to the national air quality standards. In the revised manuscript (lines 247-249), we revised the sentences "During the observation period, 20-60% of hourly $PM_{2.5}$ concentration was higher than 75 μg m^{-3} (the criterion for pollution according to the national air quality standards) in each month (Fig. S3A)"

Line 211: I am a bit confused by your explanation for there being more pollution episodes and higher concentrations of BC, CO and $PM_{2.5}$ in March, as it was the heating season. But isn't February just as cold? So why would there more heating in March?

Response: Thank you for your comments. In Beijing, the air quality is always determined by both the emission and meteorological conditions. In both February and March are in heating season. However, in March the meteorological condition is more favorable for haze formation due to low wind speed and low PBL height. This is a long sentence in the original manuscript. We revised it as "This can be explained by both the intensive emission during the heating season as evidenced by the high concentration of primary pollutants including CO, SO_2 and BC (Table S1) and the stagnant meteorological conditions supported by the low wind speed (<2 m s^{-1}) and the low planetary boundary layer (PBL) height, in particular, in March (Fig. S4A)" in lines 251-255 in the revised manuscript.

Line 222: Are the percentages listed for nitrate, chloride and ammonium also monthly means?

Response: Yes, they are monthly means. It has been pointed out in the revised manuscript. "At the same time, the monthly mean fraction of nitrate and chloride decreased from 26.7±8.8 % to 16.7±12.8 % and from 7.7±6.1 % to 0.3±0.2 %, respectively" in lines 260-262 in the revised manuscript.

Line 226: I am bit surprised that fireworks is regionally transported from Tangshan, are there no fireworks in Beijing?

Response: Thanks. According to the regulation on fireworks of Beijing government, firework burning is totally forbidden within the fifth ring road of Beijing. Based on back trajectory analysis of air masses, we found that firework burning in Tangshan should also contribute to the high mass concentration of chloride in Beijing during Chinese New Year.

Line 232-240: As example to one of my main comments above, I found that this paragraph was repeating much of the information presented in the preceding one. Perhaps these two paragraphs could be edited and combined.

Response: Thank you for your suggestion. We deleted the paragraph "It should be noted that the median mass concentrations of nitrate and OA also were higher in March than that in other months (Fig. S4C). The median mass concentrations of nitrate were 1.42, 8.76, 6.30, 3.15, and 3.23 μg m^{-3} from February to June, respectively. And the corresponding OA concentrations were 4.78, 14.04, 11.64, 13.89, and 14.08 μg m^{-3}. Secondary formation is the major source of OA and nitrate in the atmosphere" in lines 232-237 in the original manuscript.

Line 272: why have you chosen to subset the data based on 'when the $PM_{2.5}$ concentration was larger than 50 μg m^{-3} and the RH was less than 90 %'. Furthermore, as you state 'Under these conditions, local chemistry should be more important as 75 % of the wind speed was less than 1.0 m s^{-1}'. Why not then subset the data based solely on wind speed if local sources are of interest?

Response: Thank you for your comment. Because the aim of this paper is to understand the influence of HONO on secondary aerosol formation and the possible HONO source during pollution events. The dataset based solely on wind speed less than 1.0 m^{-1} could be also meaningful to discuss local chemistry. However, there are around one third data with low wind speed (<1.0 m^{-1}) and low $PM_{2.5}$ concentration (< 50 μg m^{-3}). Therefore, the concentration of $PM_{2.5}$ was considered as one of the standards in this work. In the revised manuscript (lines 307-311), we revised it as "We simply compared the OH production via photolysis of HONO (P_{OH}-

$_{HONO}$=J_{HONO}×c_{HONO}) and O_3 (P_{OH-O3}=J_{O1D}×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".

Line 275: How where these maximal $P_{OH-HONO}$ and P_{OH-O3} values calculated? I could not find the equation in the methods or reference.

Response: Thank you for your comment. They were calculated according to $P_{OH-HONO}$=J_{HONO}*c_{HONO} and P_{OH-O3}=J_{O1D}*c_{O3}. In lines 307-311 in the revised manuscript, we defined them. "We simply compared the OH production via photolysis of HONO ($P_{OH-HONO}$=J_{HONO}×c_{HONO}) and O_3 (P_{OH-O3}=J_{O1D}×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 addition, the *J* values were also added in Fig. S7 and Fig. R2.

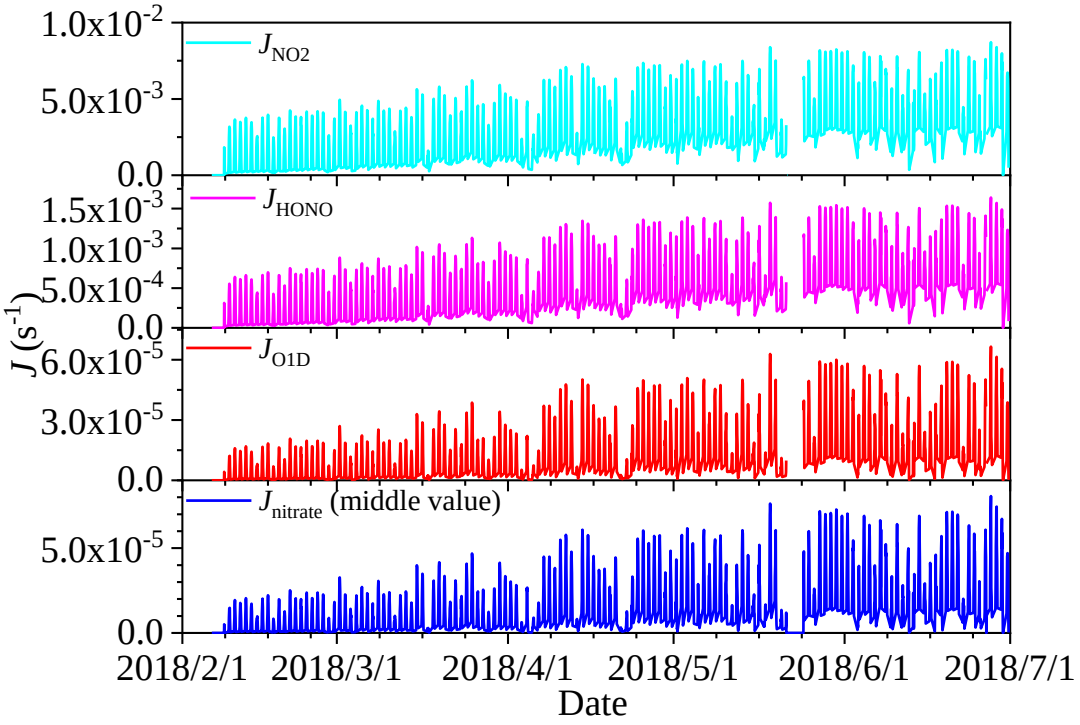

Fig. R2. The photolysis rate of NO_2, HONO, O_3 (O1D) and nitrate (middle value) from 8:00 am to 6:00 pm.

Line 304: Is it not the production of the OH that changes in winter relative to summer, rather than the rate of oxidation of VOC by OH? Please clarify

Response: Thank you. We mean OH production from photolysis of HONO will compensate the relative weak sunlight in winter. As you suggested above, we removed this redundant sentences (This implies that oxidation of atmospheric trace gases by OH may still be highly effective even in winter, thereby facilitating the vigorous formation of secondary pollutants in Beijing) in lines 301-304 in the original manuscript.

Line 318-20 and Fig 2: I am not so sure that is 'reasonable to mainly ascribe the increase of OA concentration to local secondary formation initiated by OH radical from HONO photolysis'. This is because if only OH from HONO photolysis was driving secondary formation, then shouldn't the OA/CO peak earlier, as the ambient HONO is essentially run out by 10am?

Response: Thank you for your instructive comment. During pollution events in winter in Beijing, the absolution HONO concentration was still above 0.6 ppb at noon (Fig. R3). The instrument automatically carried out zero point calibration twice per day during our observation. The measured HONO concentration at noon was much higher than the detection limit (10 ppt). Therefore, it reflected the real HONO concentration. Thus, it means that a photochemical steady state should be achieved between the daytime HONO sources and sinks and OH from photolysis of HONO should play an important role in initiation the HO_x and RO_x chemistry even after 10:00 am. In lines 350-353 in the revised manuscript, we revised this sentence to "…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 HO_x and RO_x chemistry".

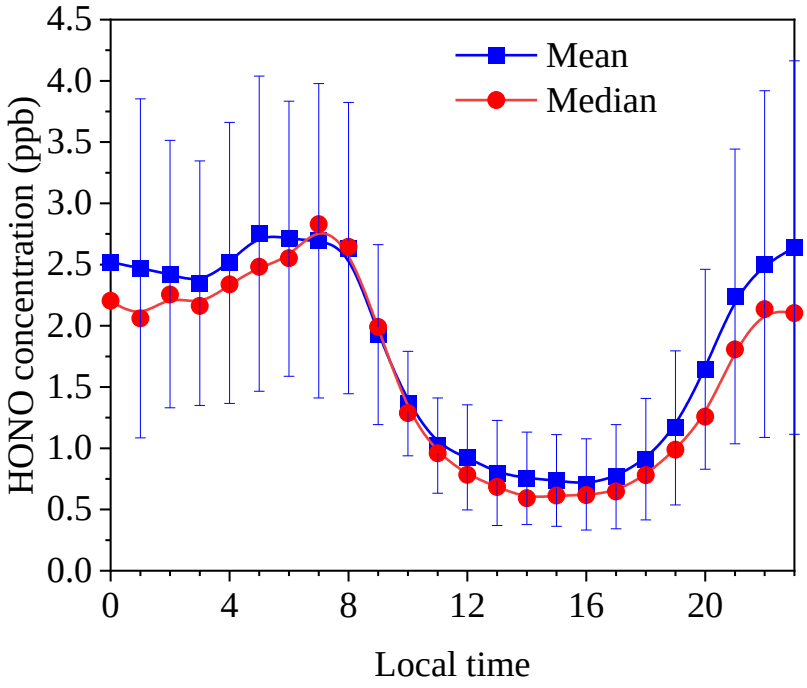

Fig. R3. The diurnal curve of HONO concentration during pollution events in winter.

Line 324: But can't there also be anthropogenic sources of alkenes? For example, isoprene can also be from vehicle emissions (See e.g. Zou et al 2019).

Response: Thank you. We agree with you that vehicles can also emit isoprene. In August, 2019, we measured the isoprene using a GC-FID, the mean isoprene concentration was 0.35 ppb. And the mean concentration was 0.5±0.3 ppb at noon and 0.11±0.11 ppb in night, respectively. The nighttime isoprene concentration was comparable with that in winter (0.13 ppb) in Guangzhou (Zou et al., 2019). If we assume the isoprene concentration in winter being equivalent to the nighttime concentration in August, the SOA formation potential of isoprene is 0.015±0.015 μg m^{-3}. This contributes less than 0.5 % to the typical increase of OA concentration observed in this work. Therefore, we think the contribution of isoprene to the observed increase of OA concentration should be unimportant. In lines 358-360 in the revised manuscript, we added a sentence as "Although vehicles can emit isoprene (Zou et al., 2019), the contribution of isoprene to the observed increase of OA concentration should be unimportant due to the low concentration of isoprene in winter (Zou et al., 2019)".

Line 379: at the start of the sentence, you state that hourly NOx EI were available, yet than go

to give a yearly emission factor? Why wasn't hourly EI used, and did you consider your measured NOx concentrations, as the diurnal variation in NOx would be important? Please clarify in more detail how the Vehicle was calculated Especially as emission inventories can have significant bias (See for example very recent work for Beijing by Squires et al, 2020).

Response: Thank you for your good suggestion. In this work, we used the hourly emission inventory of NO_x (Fig. R4A) (Yang et al., 2019) to calculate the emission rate of HONO from vehicles. When calculating the emission rate of HONO, we converted the the hourly emission inventory (*EI*) to hourly emission flux ($F=EI/A$, where A is the area of Beijing). Then, the emission flux was normalized to the hourly mean PBL height according to Eq. (2). This resulted into the diurnal variation of NO_x. If the annual emission inventory was used to calculate the emission rate of HONO, the daily emission inventory was required to normalize to the measured NO_x concentration to catch the diurnal variation. As shown in Fig. R4B, the emission rate of HONO using these two methods are overall comparable, but the daytime emission rate of HONO based on the hourly emission inventory is higher than that calculated using the annual emission inventory. We used the hourly emission inventory because it contained the traffic details on road such as emission factor of NO_x for vehicle category, speed, traffic volume and congestion map and so on (Yang et al., 2019).

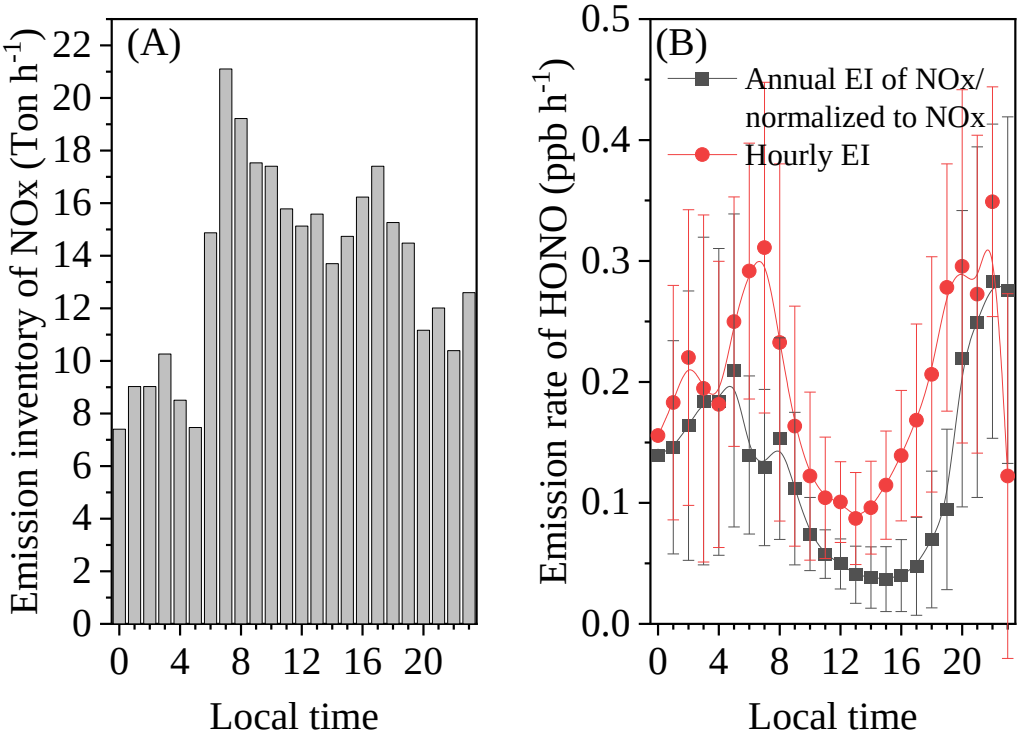

Fig. R4. (A) Hourly emission inventory of NOx from vehicles in Beijing (Yang et al., 2019) and calculated emission rate of HONO from vehicles using different methods.

To make it clearer, in lines 180-185 the revised manuscript, we added more details as "The emission rate (E_{HONO}, ppbv h^{-1}) was calculated based on the emission flux (F_{HONO}=EI_{HONO}/A, 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, EI_{HONO}, is the emission inventory of HONO (g s^{-1}), A is the urban area of Beijing (m^2), 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)".

In lines 421- 423 in the revised manuscript, we revised the sentence "The $E_{vehicle}$ was calculated using the hourly NO_x emission inventory from vehicles in Beijing (Yang et al., 2019) after converted to emission flux of HONO (F_{HONO}=F_{NOx}× HONO/NO_x) and the PBL height as described in Section 2.2"

We agree with you that a bias should exist for the emission inventory. According to the most recent work, the MEIC 2013 emissions inventory might significantly overestimate the emission of NO_x in Beijing (Squires et al., 2020). In this work, we used the newest emission inventory (Yang et al., 2019) but not the MEIC 2013. We compared the wintertime emission flux of NO_x calculated using the emission inventory from Yang et al. (2019) with the emission flux reported by Squires et al. (2020) (Fig. R5). The former emission flux is as 2.4±0.5 times as the later one. This will introduce an additional uncertainty to our estimation. In lines 712-716 in the revised manuscript, we added a paragraph "The source of HONO from vehicles was calculated based on the emission inventories, which should have a significant bias (Squires et al., 2020). For example, the emission flux of NO_x calculated using the emission inventory from Yang et al. (2019) is as 2.4±0.5 times as the reported emission flux reported by Squires et al. (2020).".

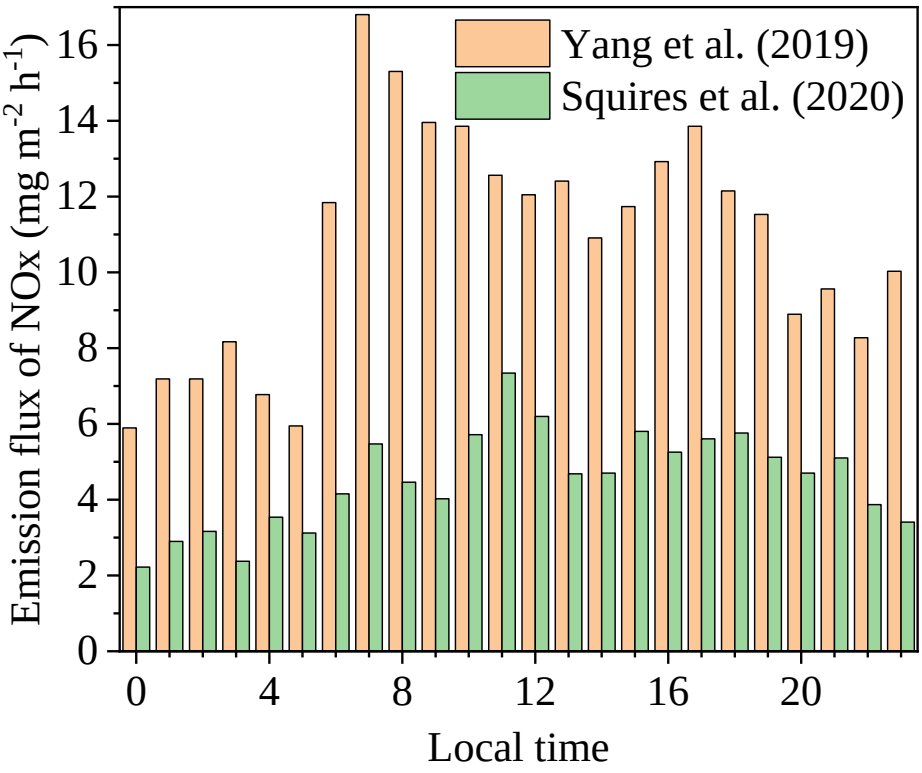

Fig. R5. Comparison of the wintertime emission flux of NO_x based on different emission inventory.

Line 381: This may be related to the above comment, but how did you report a range for calculated middle value of vehicle, when the NOx EI rate is constant and the HONO/NOx is constant? Furthermore, what does the middle value refer to? Daily avg? hourly avg? please specify. This applies throughout this section

Response: Thank you. As discussed above, the hourly emission of NOx reflected the diurnal variation vehicle emission. In addiction, the variation of PBL height was considered when we calculating the emission rate. Although the HONO/NOx was constant, the emission rate should show a diurnal variation. Three different emission rates of HONO were calculated because we chose three levels of HONO/NOx, i.e., the lower limit is 0.18% measured using a Chassis dynamometer test (Liu et al., 2017), 1.17% calculated using the low limit correlation of field data and 1.8 % using the empirical analysis of field data in this work. We called "middle value" for the emission rate calculated using HONO/NOx=1.17%. In lines 423-425 in the revised manuscript, we added a sentence "Thus the calculated emission rate reflected the diurnal

variation of both the emission inventory and the PBL height". In lines 425-427 in the revised manuscript, the sentence was revised "The calculated hourly middle value of $E_{vehicle}$ using the HONO/NO_x of 1.17% was from 0.085±0.038 to 0.34±0.15 ppbv h^{-1}, which was slightly higher than the daytime emission rate of HONO in Xi'an (Huang et al., 2017b)".

Line 386: the reported range for the upper limit is the same as reported for the lower limit, I'm guessing a typo?

Response: Thank you. From line 428 to 431 in the revised manuscript, "The lower limit of $E_{vehicle}$ was 0.013±0.006-0.053±0.023 ppbv h^{-1}, which was close to the estimated emission rate of HONO in Jinan (Li et al., 2018). The upper limit was in the range of 0.13±0.06-0.53±0.23 ppbv h^{-1}". The upper limit is one order of magnitude higher than the lower limit because the corresponding HONO/NOx is 0.18 % and 1.8%.

Line 389: Please give the reference for the emission flux you used, the value and also why grassland was the most appropriate.

Response: Thank you. Oswald et al. measured the emission flux of HONO from 17 soil samples, including eucalyptus forest, tropical rain forest, coniferous forest, pasture, woody savannah, grassland, stone desert, maize field, wheat field, jujube field an cotton field etc. (Oswald et al., 2013). Tropical rain forest, coniferous forest and grassland are the typical plants in downtown Beijing (Huang et al., 2017a). At the same time, their emission fluxes of HONO are comparable (Oswald et al., 2013). Thus, we used the emission flux from grassland to calculate the emission rate of HONO from soil in Beijing because the temperature and water holding content dependent emission flux of grassland was available (Fig. R6). We added this paragraph "Oswald et al. (2013) measured the emission flux of HONO from 17 soil samples, including eucalyptus forest, tropical rain forest, coniferous forest, pasture, woody savannah, grassland, stone desert, maize field, wheat field, jujube field an cotton field etc. Tropical rain forest, coniferous forest and grassland are the typical plants in downtown Beijing (Huang et al., 2017a). At the same time, their emission fluxes of HONO are comparable (Oswald et al., 2013). Thus, we used the emission flux from grassland to calculate the emission rate of HONO from soil in Beijing because the temperature and water holding content dependent emission flux of

HONO from grassland soil was available" in lines 433-441 in the revised manuscript.

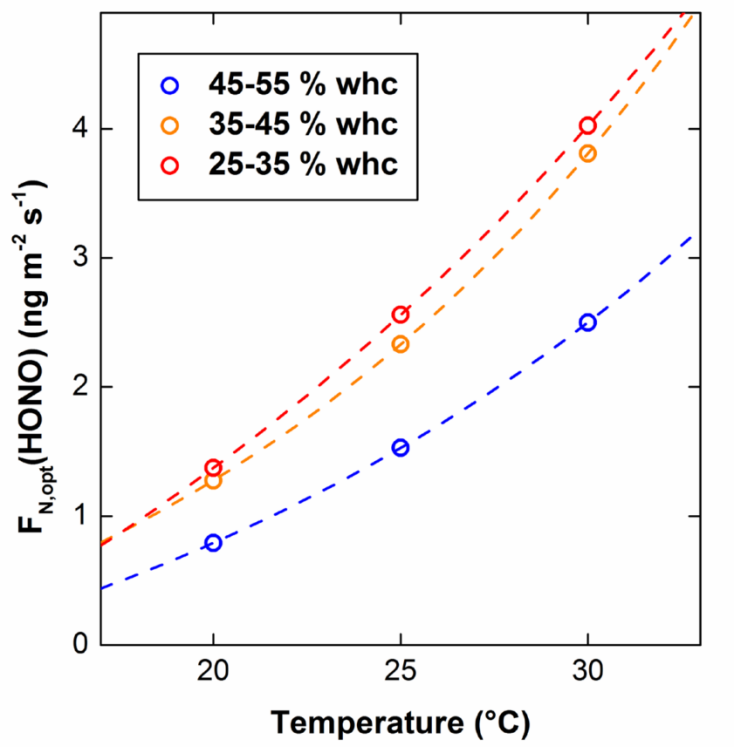

Fig. R6. The emission flux of HONO from grassland at different temperature and water holding capacity (Oswald et al., 2013).

Line 397: why does only the middle values for E_{soil} have uncertainty calculated? Also how did you estimate the uncertainty for E_{soil}? And why did you use a range of soil water content for lower, middle and upper, why not just use a single value?

Response: Thank you. We added the uncertainties of other values in lines 446-448 in the revised manuscript. "The lower limit, the middle value and the upper limit of the E_{soil} are 0.0032±0.0027-0.013±0.014, 0.0046±0.0039-0.020±0.20 and 0.0057±0.0047-0.025±0.024 ppbv h^{-1}, respectively, calculated according to Eq. (2)". The uncertainty is the standard deviation when calculating the diurnal curve. We didn't measure the water content of the soil, while it should vary with seasons. Thus, we used a range of soil water content rather than a single value. For other sources, we also added all the uncertainties in the revised manuscript.

Line 416: Please provide more information on the night time temperature dependence of OH concentration, and the equations used in this calculation.

Response: Thank you. In the night, OH concentration usually varied from 1.0×10^5 molecules cm^{-3} (Li et al., 2012;Tan et al., 2018) in winter to 5×10^5 molecules cm^{-3} in summer (Tan et al., 2017). In the original manuscript, we linearly calculated the nighttime OH from 1×10^{-5} to 4×10^{-5} molecules m^{-3} according to

$$c_{OH,night} = 1\times10^5 + 4\times10^5 \times \frac{T-T_{min,night}}{T_{max,night}-T_{min,night}} \quad \text{(R1)}.$$

In the revised manuscript, we updated the calculation method as suggested by another reviewer. Because the nighttime OH is mainly generated from reaction of O_3 with alkenes measured with the SPIMS, we changed the estimation method using

$$c_{OH,\mathrm{night}} = 1\times10^5 + 4\times10^5 \times \frac{(c_{O_3}\times c_{alkenes})_{night}-(c_{O_3}\times c_{alkenes})_{night,min}}{(c_{O_3}\times c_{alkenes})_{night,max}-(c_{O_3}\times c_{alkenes})_{night,min}} \quad \text{(R2)}.$$

In lines 468-471 in the revised manuscript, we changed it as "The nighttime OH concentration was estimated linearly correlated with the product of nighttime O_3 concentration and alkenes concentration, namely,

$$c_{OH,night} = 1\times10^5 + 4\times10^5 \times \frac{(c_{O_3}\times c_{alkenes})_{night}-(c_{O_3}\times c_{alkenes})_{night,min}}{(c_{O_3}\times c_{alkenes})_{night,max}-(c_{O_3}\times c_{alkenes})_{night,min}} \quad (16)$$"

Line 419: Please give the reported OH concentrations by Li et al (2018) and Huang et al (2017) and if they were calculated or measured OH levels.

Response: Thank you. Here we compared the production rate of HONO from homogenous reaction between NO and OH among different researches but not OH concentration. In lines 475-478 in the revised manuscript, we added the corresponding $P_{\text{NO-OH}}$ as "The calculated middle value of $P_{\text{NO-OH}}$ (with mean daytime value of 0.49±0.35 ppb h^{-1}) was comparable with these estimated values by Li et al. (2018) (0.4 ppb h^{-1}) and Huang et al. (2017b) (0.28 ppb h^{-1})".

Line 433: How was the HONO form nitrate photolysis calculated? Which equation (give number)? What do these ranges represent?

Response: Thank you. HONO formation from nitrate photolysis was calculated according to Eqs (3) and (8). Bao et al. reported the J_{nitrate} at zenith angle of 0°. We normalized the J_{nitrate} with the zenith angle at our observation station. The time series of the middle value was shown in Fig. R2 and was also added in Fig. S7. In lines 489-495 in the revised manuscript, we revised

it. "A recent work reported the photolysis rate of nitrate ($J_{nitrate}$) in ambient $PM_{2.5}$ at a solar zenith angle of 0° (Bao et al., 2018). The $J_{nitrate}$ varied from 1.22×10^{-5} to 4.84×10^{-4} s^{-1} with the mean value of 8.24×10^{-5} s^{-1}. These values were further normalized according to the zenith angle and UV light at our observation station to calculate the low limit, the upper limit and the middle $J_{nitrate}$. The time series of the measured nitrate concentration and the middle value of $J_{nitrate}$ were shown in Fig. 1 and Fig. S7, respectively". In addition, the equation numbers was pointed out in line 498 in the revised manuscript. "The corresponding daytime lower limit, the middle value and the upper limit of HONO from photolysis of nitrate were 0.0011±0.0021-0.096±0.092, 0.0072±0.0021-0.66±0.092 and 0.042±0.082-3.86±0.008 ppbv h^{-1}, respectively, calculated in the light of Eqs. (3) and (8)".

Line 447: by the end of this paragraph, it was not at all clear to me which uptake co-efficient you actually used. Please clarify.

Response: Thank you. In the dark, the low limit, middle value and upper limit of $P_{aerosol}$ were calculated using the RH dependent γ_{NO2} on kaolin ($4.47 \times 10^{39}/(1.75 \times 10^{46} + 1.93 \times 10^{45}RH)$) (Liu et al., 2015), the fixed γ_{NO2} (1.2×10^{-8}) recommended by Crowley et al. (Crowley et al., 2010) and the RH dependent γ_{NO2} on kaolin on hematite ($\gamma_{NO2}=4.46 \times 10^{39}/(6.73 \times 10^{44} + 3.48\times10^{44} RH)$) (Liu et al., 2015), respectively, along with the γ_{NO2} on black carbon (1.17×10^{-5}). In the daytime, the light enhanced uptake γ of NO_2 (1.9×10^{-6}) on mineral dust was parameterized (Ndour et al., 2008) after normalized to the solar radiation intensity in Beijing. For P_{ground}, the low limit, middle value and upper limit of P_{ground} were calculated using the same γ_{NO2} as $P_{aerosol}$ in night, while γ_{NO2} of NO_2 on urban regime ($\gamma_{NO2}=7.4\times 10^{-7}+5.5\times10^{-8}$ RH) (Liu et al., 2019) was used after normalized to the light intensity at BUCT in the daytime. In the revised manuscript, we pointed out these equations as "($\gamma_{NO2}=4.47 \times 10^{39}/(1.75 \times 10^{46} + 1.93 \times10^{45}RH)$", "($\gamma_{NO2}=4.46 \times 10^{39}/(6.73 \times 10^{44} + 3.48\times10^{44} RH)$" and "($\gamma_{NO2}=7.4\times 10^{-7}+5.5\times10^{-8}$ RH)" in lines 507-508, 509 and 521, respectively.

Line 477-9: the authors state that 'Heterogeneous reactions of NO_2 on aerosol surface and ground surfaces were unimportant compared with other sources because of the very low uptake coefficient'. What do you mean by the very low uptake coefficient, low compared to what? Is

the issue more that you used the wrong co-efficient?

Response: Thank you. For heterogeneous reaction of NO_2 on aerosol surface, the production rate is determined by the uptake coefficient according to Eqs. (3)-(5). Modelling studies have found that a given chemical process should be important in the tropospheric chemistry if the uptake coefficient of a trace gas on particles is greater than 10^{-5} (Zhang and Carmichael, 1999;Zheng et al., 2015). As discussed in this work, the typical uptake coefficient of NO_2 on aerosol is on the order of 10^{-7}-10^{-8}. It was it was recommended to be 1.2×10^{-8} (Crowley et al., 2010). Furthermore, we also performed laboratory studies about uptake of NO_2 on kaolin, hematite and soot particles. The uptake coefficient on mineral dust is on the order of 10^{-7}-10^{-8} (Liu et al., 2015). In addition, we found that the $\gamma_{NO2,\,BET}$ at steady state (or after aged in air) was one order of magnitude lower than that of fresh sample. Therefore, we chose the $\gamma_{NO2,\,BET}$ 10^{-7}-10^{-8} in this work. It was lower than that (10^{-6}) used in modeling studies (Zhang et al., 2016;Aumont et al., 2003).

We double checked the parameters for budget calculation. We found a bug when calculating the heterogeneous reaction of NO_2 on black carbon. A conversion factor of time from second to hour was missed. So, the contribution of heterogeneous reaction to HONO source was underestimated. Now, the $P_{aerosol}$ was 0.038±0.030-0.088±0.072. It was on the same orders as soil emission. In the revised manuscript, we updated Figs. 3-5 and the corresponding numbers in section 3.3.

In lines 544-554 the revised manuscript, we added a paragraph "It should be pointed out that HONO production from heterogeneous reaction of NO_2 on both aerosol and ground surface greatly depend on the $\gamma_{NO2,\,BET}$ and A_s. The A_s of aerosols was comparable with the modeling input. However, the small nighttime $\gamma_{NO2,\,BET}$ (10^{-8} - 10^{-7}) on dust were used in this work rather than the $\gamma_{NO2,\,BET}$ (1×10^{-6}) used in modelling studies (Zhang et al., 2016;Aumont et al., 2003;Gall et al., 2016). This leads to a lower production rate of HONO from heterogeneous reaction of NO_2 on aerosols. As for heterogeneous reaction of NO_2 on ground surface, besides the small $\gamma_{NO2,\,BET}$ used in this work, the A_s of ground surface (0.0015 to 0.0385 m^{-1}) calculated using the surface roughness and PBL height was also significantly lower than the fixed value of 0.3 m^{-1} in modeling studies that might overestimate the contribution of HONO production from heterogeneous reaction of NO_2 on ground surface". In lines 558-561 in the revised

manuscript, we revised the sentences as "These results mean that heterogeneous reaction might not be a major HONO source. This is consistent with a recent work that heterogeneous reaction should be unimportant when compared with traffic emission during haze events in winter in Beijing (Zhang et al., 2019)". And in lines 605-607 in the revised manuscript, we also revised the sentence "Heterogeneous reactions of NO_2 on aerosol surface and ground surfaces were not the major HONO source during night unlike the modelled results (Zhang et al., 2016;Aumont et al., 2003).".

Fig 2D: if you take the bottom and top points in Feb/Mar (blue), I am not sure there this a correlation. It would be good to check if you get a similar slope and r2 without these 2 points.

Response: Thank you. If we remove these two points as you suggested, the correlation coefficient will decrease from 0.74 to 0.31. A positive correlation can be still observable when the uncertainty is taken into consideration (Fig. R7). We think it is unreasonable to remove them because these data points are valid. We agree with you that it should be better if more data points are available. This will be further investigated in the future.

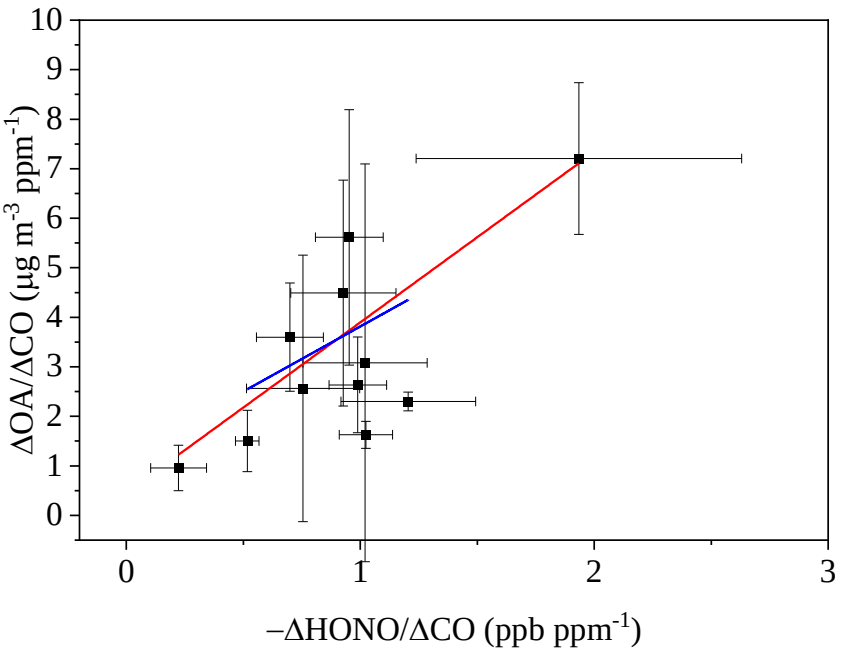

Fig. R7 Correlation of the daytime OA/CO increased and consumed HONO/CO in March.

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Reviewer 2#

This paper reports the possible promotion effect of nitrous acid (HONO) on the formation of secondary organic aerosol (SOA) and nitrate in winter based on a five-month comprehensive observation in urban Beijing. Evidence for the relationship between secondary aerosol formation and the consumed HONO was obtained from the observations. The detailed budget of ambient HONO was explored, and vehicle emission was proposed as a significant source of HONO in Beijing. Overall, the manuscript is logically organized and well written, and the measurement data are much valuable. I would like to recommend that it can be considered for publication after the following major and specific comments being properly addressed.

Response: Thank you so much for your positive comments.

Section 2.2. HONO budget calculation: the description of the budget calculation is not clear enough. Firstly, the method used in this study was the budget analysis, other than the stationary state analysis. For a thorough budget analysis, physical terms (such as vertical and horizontal transport) should be considered for equations (1) and (12). At least, the authors need to evaluate if the physical processes were negligible for the analysis presented here. Secondly, a number of parameters (e.g., F_{HONO}, c_{OH}, gamma, Y_{HONO}, $J_{nitrate}$, J_{HONO}, etc.) are required for the analysis. It is not clear how these parameters were obtained or approximated in this study. Although they were described more or less in the following Section 3.3, the authors may need clearly state the data source and uncertainties of these key parameters at their first appearance. This may help the readers better understand the overall methodology of this study.

Response: Thank you for your good suggestions. We revised the "stationary state HONO concentration" to "HONO budget" in line 171 in the revised manuscript.

The vertical and horizontal transport have been added in Eq. (1) and (12) from line 171 to 179 in the revised manuscript. "The HONO budget could be calculated by,

$$\frac{dc_{HONO}}{dt} = E_{HONO} + P_{HONO} - L_{HONO} + T_{vertical} + T_{horizontal} \quad (1)$$

where $\frac{dc_{HONO}}{dt}$ is the observed change rate of HONO mixing ratios (ppbv h^{-1}); E_{HONO} represents the emission rate of HONO from different sources (ppbv h^{-1}); P_{HONO} is the in-*situ* production

rate of HONO in the troposphere (ppbv h^{-1}); L_{HONO} is the loss rate of HONO (ppbv h^{-1}) (Li et al., 2018); $T_{vertical}$ and $T_{horizontal}$ are the vertical and horizontal transport (Soergel et al., 2011), which can mimic source or sink terms depending on the HONO mixing ratios of the advected air relative to that of the measurement site and height (Soergel et al., 2011)".

In addition, we added two paragraphs to discuss the transport in lines 222-232 "Vertical transport by advection ($T_{vertical}$), which is an important sink of HONO in the night (Gall et al., 2016;Meng et al., 2019), can be calculated according to equation (12).

$$T_{vertical} = -K_h(z,t)\frac{\partial c(z,t)}{\partial z}\frac{1}{h} \quad (12)$$

where K_h(z,t) is the eddy diffusivity of heat (m^2 s^{-1}) at height z (m) and time t, h is the height of the second layer (18 m in this study) (Gall et al., 2016). On the other hand, both the vertical and horizontal transport can be estimate according to Eq. (13),

$$T_{vertical} = k_{dilution}(c_{HONO} - c_{HONO,background}) \quad (13)$$

where $k_{dilution}$ is a dilution rate (0.23 h^{-1}, including both vertical and horizontal transport) (Dillon et al., 2002), c_{HONO} and $c_{HONO,background}$ is the HONO concentration at the observation site and background site, respectively (Dillon et al., 2002)" and lines 574-598 "As pointed in Section 2.2, vertical transport by advection is an important nocturnal sink of HONO (Gall et al., 2016). In this work, the vertical distribution of HONO concentration is unavailable. Recently, Meng et al. (2019) measured the vertical distribution of HONO in Beijing in December, 2016. 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). The nighttime concentration gradient was 0.0047±0.0025 ppb m^{-1} derived from the nighttime dataset (Meng et al., 2019). In the daytime, we assume a zero concentration gradient. On the other hand, the eddy diffusivity of heat in urban environment was measured in New Delhi, Indian (Yadav et al., 2003). Using their dataset with the wind speed lower than 2.0 m s^{-1}, we derived the relationship between the K_h and the wind speed (WS) (K_h=0.9389×WS-0.3374 m^2 s^{-1}). The nighttime $T_{vertical}$ changed from 0.15 to 0.37 ppbv h^{-1} in winter, while it was from 0.12 to 0.68 ppbv h^{-1} according to Eq. (12) from April to June. Because the wind speed was usually lower than 1.0 m s^{-1} in pollution events (Fig. S6), horizontal transport should have little influence on the daytime sources or sinks of HONO

because of the short lifetime of HONO. In the night, 79 % of the wind speed was lower than 1.0 m s^{-1} in winter, thus the air masses from suburban areas should have influence on the sources and sinks of HONO in Beijing. If the HONO concentration at background was zero, the vertical and horizontal transport rate of HONO varied from 0.17 to 0.61 ppbv h^{-1} which is calculated in the light of Eq. (13) on haze days in winter and from 0.15 to 0.74 ppbv h^{-1} in pollution events from April to June. These values were higher than that calculated according to Eq. (12). Because the background HONO concentration was unavailable, we only considered the nighttime transport calculated according to Eq. (12) in the following section". At the same time, the relative contribution of each source in Section 3.3 was updated based on the total sinks.

We added a sentence "The $E_{vehicle}$ was calculated using the hourly NO_x emission inventory from vehicles in Beijing (Yang et al., 2019) after converted to emission flux of HONO ($F_{HONO}=F_{NOx}\times$ HONO/NO_x) and the PBL height as described in Section 2.2" to make it clearer about F_{HONO} in lines 421-423 in the revised manuscript.

The OH concentration was estimated based on J_{O1D} (Tan et al., 2019;Tan et al., 2018a) or J_{O1D} and J_{NO2} (Li et al., 2018). Photolysis rate constants of NO_2(J_{NO2}), HONO(J_{HONO}) and O_3(J_{O3}) for clear sky conditions were calculated according to the solar zenith angle and the location using a box model (FACSIMILE 4). NO_2 photolysis sensor (J_{NO2}, Metcon) was unavailable during our observation study. However, it was available from Aug 17 to Sep 16, 2018. Calibration function between the measured UVB light intensity and J_{NO2} from Aug 17 to Sep 16, 2008 was established to correct the influence the climatological O_3 column, aerosol optical depth and cloud cover on surface UV light intensity. As shown in Fig. S10A, the model well predicted the J_{NO2}. Then the J_{NO2} during this campaign study was predicted using the model. The details about photolysis rates are shown in the Supplement Information. In lines 458-460 in the revised manuscript, we added a sentence "The method for the photolysis rates calculation were shown in SI and the time series of the photolysis rates were shown in Fig. S7". In lines 472-473 in the revised manuscript, we added a sentence "The time series of OH concentration calculated using different methods was shown in Fig. S11".

Three kinds of OH concentration was used in this work. In lines 460-466 in the revised manuscript, we revised it as "On polluted days, high concentration of NO_2 resulted into lower

OH concentrations estimated using the Eq. (13). Therefore, the corresponding P_{NO-OH} was taken as the low limit for homogeneous reaction between NO and HONO because polluted events were discussed in this work, while P_{NO-OH} calculated using the OH concentration (J_{O1D}×4.33×10^{11} molecules cm^{-3}) (Tan et al., 2018a) was taken as the upper limit and P_{NO-OH} calculated using the OH concentration (J_{O1D}×2×10^{11} molecules cm^{-3}) (Tan et al., 2019) was the middle value".

As for $J_{nitrate}$, we added the number as "The $J_{nitrate}$ varied from 1.22×10^{-5} to 4.84×10^{-4} s^{-1} with the mean value of 8.24×10^{-5} s^{-1}" in line 490-491 in the revised manuscript. About γ_{NO2} on aerosol and ground surface, we pointed out from line 502 to 510 in the revised manuscript "The uptake coefficient (γ) of NO_2 on different particles varied from 5×10^{-9} to 9.6×10^{-6} (Ndour et al., 2009;Underwood et al., 2001;Underwood et al., 1999), while it was recommended to be 1.2×10^{-8} (Crowley et al., 2010), which was used to calculate the $P_{aerosol}$ in the base case. It has been found that the γ highly depends on the relative humidity (RH). The low limit bound of $P_{aerosol}$ was calculated based on the RH dependent uptake coefficient of NO_2 on kaolinite ($\gamma_{NO2}=4.47 \times 10^{39}/(1.75 \times 10^{46} + 1.93 \times 10^{45} RH)$, while the upper limit of $P_{aerosol}$ was calculated according to the RH dependent γ on hematite ($\gamma_{NO2}=4.46 \times 10^{39}/(6.73 \times 10^{44} + 3.48 \times 10^{44} RH)$ (Liu et al., 2015)". In the night, Y_{HONO} was set to 0.5 because of the hydrolysis reaction of NO_2, while it was 0.8 for light enhanced reaction. It has been added "The Y_{HONO} was set to 0.5 because of the hydrolysis reaction of NO_2 (Liu et al., 2015), while it was 0.8 for light enhanced reaction (Liu et al., 2019a;Ndour et al., 2008) and on BC (Han et al., 2013)" in lines 528-530 in the revised manuscript.

Section 3.3 and Figures 3&4: following the first comment, the description and discussion of the HONO budget are also not clear and need clarification. The contributions of heterogeneous reactions of NO_2 on aerosol and ground surfaces were too low, and they were even lower than the OH+NO reactions during the nighttime. This is unusual. Is it reasonable to approximate the nighttime OH concentrations linearly with the temperature? Furthermore, the heterogeneous reactions of NO_2 on aerosol and ground surfaces were highly dependent on the NO_2 concentrations, the uptake coefficients, and surface density, some of which are highly uncertain. It is not clear what values were actually adopted for the uptake coefficients of NO_2 on aerosol

and ground surfaces, and how much were the ambient NO_2 levels and surface density? More details about the calculation of HONO budget are needed.

Response: Thank you for your good suggestion and comments. HONO production from heterogeneous reactions of NO_2 on both aerosol surface and ground surface greatly depend on the uptake coefficient ($\gamma_{NO2, BET}$) and the surface to volume ratio (S/V). The mean and median surface to volume ratio of aerosols are 1.33×10^{-3} and 1.36×10^{-3} m^{-1} during pollution events. This is comparable with the input parameters in modeling studies (Zhang et al., 2016). However, as discussed from line 501 to 503 in the revised manuscript, the $\gamma_{NO2, BET}$ on aerosols varied from 5×10^{-9} to 9.6×10^{-6}. The $\gamma_{NO2, BET}$ on pure oxides was usually higher that on composite oxides. The selection of a proper $\gamma_{NO2, BET}$ is quite tricky. For example, a fixed $\gamma_{NO2, BET}$ was set to 1×10^{-6} in nighttime and 2×10^{-5} in daytime due to photochemical reaction of NO_2 on soot surface in a modelling study (Zhang et al., 2016;Aumont et al., 2003). The nighttime $\gamma_{NO2, BET}$ is ~2 orders of magnitude higher than ours (1.2×10^{-8}) as suggested by Crowley et al. (Crowley et al., 2010). In our previous work, we have measured the $\gamma_{NO2, BET}$ on kaolin and hematite (Liu et al., 2015) and soot (Han et al., 2013). The initial $\gamma_{NO2, BET}$ on kaolin is $4.85\pm0.39\times10^{-8}$ at 47 % RH. It should be pointed out that the $\gamma_{NO2, BET}$ decreases significantly with exposure time due to surface saturation. Fig. R8 shows the typical uptake curve of NO_2 and the $\gamma_{NO2, obs}$ which is not normalized to the specific surface area. The $\gamma_{NO2, BET}$ at steady state (2.56×10^{-9} to 4.56×10^{-9} on kaolin and 1.23×10^{-8} to 1.50×10^{-8} on hematite) is around one order of magnitude lower than the initial $\gamma_{NO2, BET}$ as shown in Fig. R9. Therefore, we used the recommended value (1.2×10^{-8}) (Crowley et al., 2010) in the base case. On the other hand, the $\gamma_{NO2, BET}$ decreases with RH due to competitive adsorption (Liu et al., 2015). High mass concentration of $PM_{2.5}$ usually accompanied with high RH in winter in Beijing. Thus, we calculated the RH dependent $\gamma_{NO2, BET}$ according to the equation we determined previously (Liu et al., 2015) and the measured ambient RH in this work. This should be more reasonable than a fixed uptake coefficient used in modeling studies.

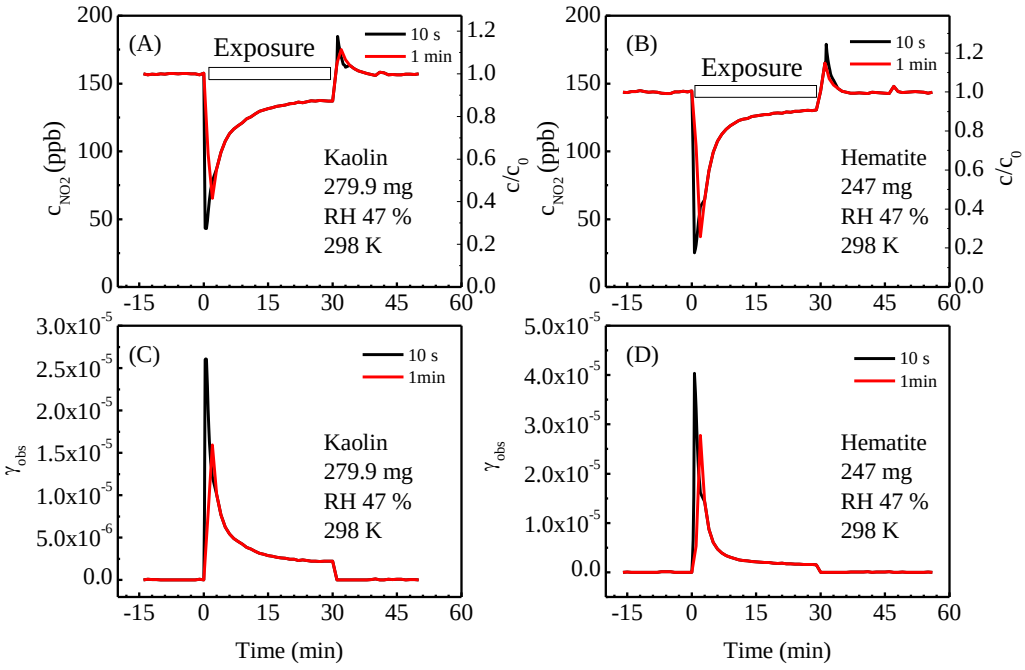

Fig. R8. Uptake curves of NO_2 on (A) kaolin and (B) hematite; and evolution of the observed uptake coefficient on (C) kaolin and (D) hematite at 298 K and at 47 % of RH (Liu et al., 2015).

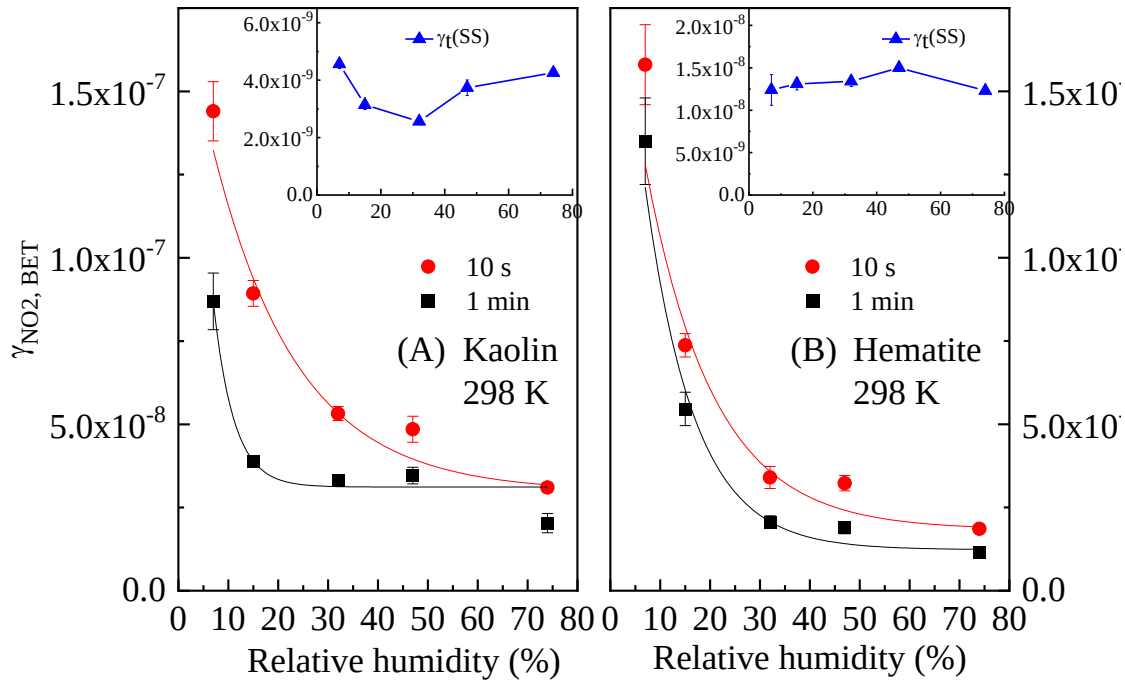

Fig. R9. The dependence of $\gamma_{NO2,BET}$ on relative humidity (Liu et al., 2015).

In the original version of manuscript, we found a bug when calculating the heterogeneous reaction of NO_2 on black carbon. A conversion factor of time from second to hour was missed. So, the contribution of heterogeneous reaction to HONO source was underestimated in the original version. Now, the $P_{aerosol}$ was 0.038±0.030-0.088±0.072, which was dominated by the heterogeneous reaction of NO_2 on black carbon. It was on the same orders as soil emission. However, this was still significantly lower than the contribution of vehicle emission. In the revised manuscript, we updated Figs. 3-5 and the corresponding numbers in section 3.3.

As for heterogeneous reaction of NO_2 on ground surface, we used the same $\gamma_{NO2,BET}$ on dust aerosol in the night, which is similar to the methodology used in modelling studies (Zhang et al., 2016;Aumont et al., 2003). As pointed out in Section 2.2 from line 197 to 209 in the revised manuscript, the S/V was estimated using the surface roughness calculated in the light of satellite image of Beijing. The calculated surface roughness is 3.85, which is slightly higher than the value (2.2) used by Li et al. (2017). Thus, the calculated S/V varied from 0.0015 to 0.0385 m^{-1} (with a mean value of 0.0125 m^{-1}) because of the variation of the PBL height during pollution events. However, a fixed S/V of ground surface was set to 0.3 m^{-1} in the modeling studies (Zhang et al., 2016). This corresponds to a surface roughness ~92, which means the surface area is ~92 times of the projected area of ground. It's too high. If both the $\gamma_{NO2,BET}$ (1×10^{-6}) and surface roughness are increased to the values used in modeling 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. In lines 558-561 in the revised manuscript, we also revised the sentence "These results mean that heterogeneous reaction might not be a major HONO source. This is consistent with a recent work that heterogeneous reaction should be unimportant when compared with traffic emission during haze events in winter in Beijing (Zhang et al., 2019c)" and in lines 605-607 in the revised manuscript, "Heterogeneous reactions of NO_2 on aerosol surface and ground surfaces were not the major HONO source during night unlike the modelled results (Zhang et al., 2016;Aumont et al., 2003) ".

During the Chinese New Year (CNY) and the COVID-19 event in 2020, traffic emission decreased significantly in Beijing. This provides us a unique opportunity to verify the relative importance of each HONO source. We only analyzed the nocturnal data from January 1 to

February 29 because the HONO sources related to photochemical reactions could be avoided. The CNY vacation was from January 23 to February 2. These results are in preparation for a separate paper. Fig. R10 shows the relative change of the concentrations of HONO, NO_x and non-refractory $PM_{2.5}$ (NR-$PM_{2.5}$). The traffic index and the chemical age of the air masses which is defined as -log(NO_x/NO_y) are also shown in Fig. R10. NO_y was measured with a NO_y analyzer (Thermo 42i-Y). The concentration of nighttime HONO decreased significantly during the CNY and after the CNY accompanied with the reduction in vehicle emission as supported by both the concentration of NO_x and traffic index (Fig. R10B). Interestingly, the NR-$PM_{2.5}$ concentration during and after the CNY increased obviously when compared with that before the CNY. The effective conversion of NO_2 aerosol surface was almost constant because both the promotion effect of increased $PM_{2.5}$ concentration and the inhibition effect of reduced NO_2 concentration during and after the CNY as shown in Fig. R10C. On the other hand, we found that the nighttime chemical age of the air masses during and after the CNY was also obviously larger than that before the CNY (Fig. R10D). This means that heterogeneous reaction of NO_2 on both aerosol surface and ground surface should be more effective due to longer residence of the air masses during and after the CNY than that before the CNY. When the reduction of NO_2 concentration was taken into consideration, the product of NO_2 concentration and –log(NO_x/NO_y) in COVID-19 epidemic periods increased slightly (Fig. R11). Therefore, the observed HONO concentration should decreased in COVID-19 epidemic or at least be constant in different periods and be independent on the reduction of vehicle emission if heterogeneous reaction of NO_2 on aerosol and ground surfaces dominates nighttime HONO source or if the vehicle emission is a minor HONO source. However, we observed the decrease of HONO along with reduction of vehicle emission (Fig.R10A). This well supports our (and other researchers' (Meng et al., 2019;Zhang et al., 2019c) conclusion that vehicle emission is an important source of HONO in Beijing.

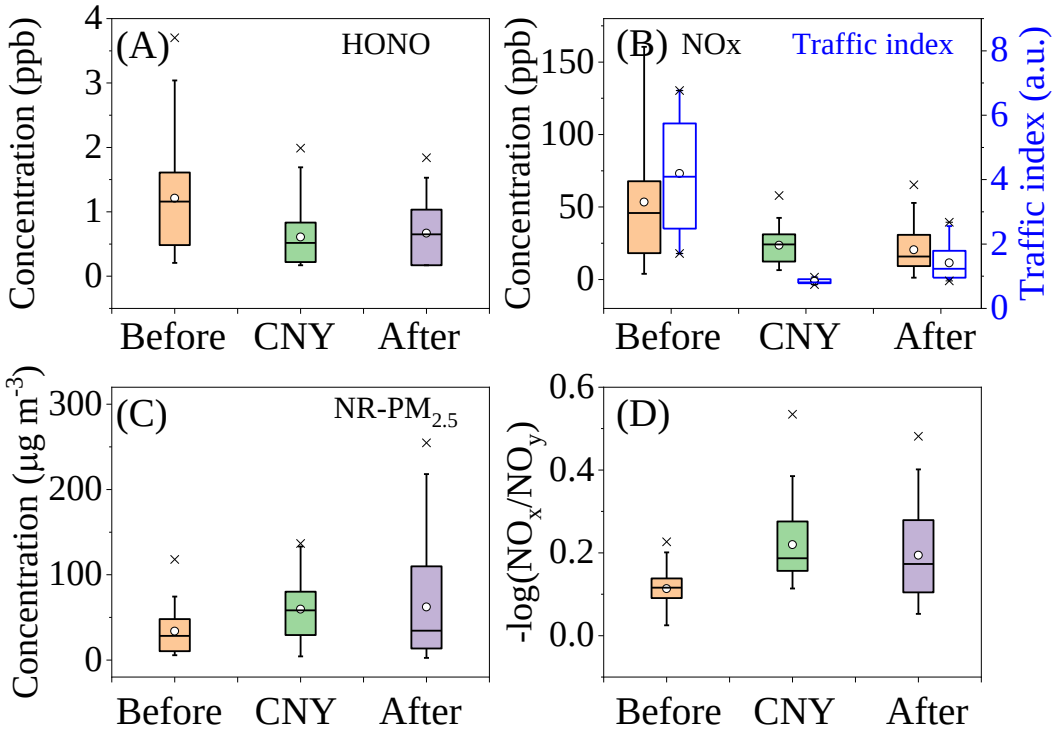

Fig. R10. Relative change of nighttime (A) HONO concentration, (B) NOx concentration and the traffic index, (C) non-refractory $PM_{2.5}$ (NR-$PM_{2.5}$) concentration and (D) relative chemical age (-log(NO_x/NO_y)) of air masses before Chinese New Year (CNY) (2020.1.1-2020.1.22), during CNY (2020.1.23-2020.2.1) and after CNY (2020.2.2-2020.2.29).

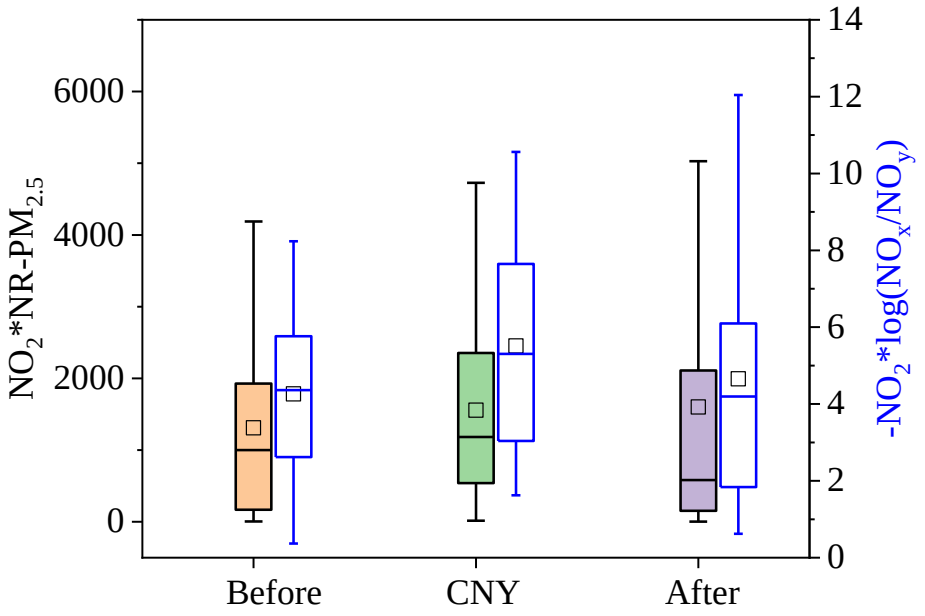

Fig. R11. Relative change of nighttime the product of NO_2 and NR-$PM_{2.5}$ concentration and

the product of NO_2 concentration and $-\log(NO_x/NO_y)$ in different periods.

In lines 523-528 in the revised manuscript, we pointed out "The A_s of aerosols which was measured using a DMPS varied from 1×10^{-4} to 4.8×10^{-3} m^{-1} with a mean value of $1.4\pm0.5\times10^{-3}$ m^{-1} during pollution events. This value is comparable with that used in modeling studies (Zhang et al., 2016;Aumont et al., 2003). The A_s of ground surface which was calculated according to Eq. (6) and (7) varied from 1.5×10^{-3} to 3.85×10^{-2} m^{-1} with a mean value of $1.3\pm0.9\times10^{-2}$ m^{-1} during pollution events. The surface roughness was 3.85 calculated according to Eq. (7)". And from line 544 to 554 in the revised manuscript, we added a paragraph to discuss the reason why we obtained the low production rate of HONO via heterogeneous reaction of NO_2 on ground and aerosol surfaces as "It should be pointed out that HONO production from heterogeneous reaction of NO_2 on both aerosol and ground surface greatly depend on the $\gamma_{NO2,\,BET}$ and A_s. The A_s of aerosols is comparable with the modeling input. However, the small nighttime $\gamma_{NO2,\,BET}$ (10^{-8} – 10^{-7}) were used in this work rather than the $\gamma_{NO2,\,BET}$ (1×10^{-6}) used in modelling studies (Zhang et al., 2016;Aumont et al., 2003). This leads to a lower production rate of HONO from heterogeneous reaction of NO_2 on aerosols. As for heterogeneous reaction of NO_2 on ground surface, besides the small $\gamma_{NO2,\,BET}$ used in this work, the A_s of ground surface (0.0015 to 0.0385 m^{-1}) calculated using the surface roughness and PBL height was also significantly lower than the fixed value of 0.3 m^{-1} used in modeling studies that might overestimate the contribution of HONO production from heterogeneous reaction of NO_2 on ground surface".

As for nighttime OH concentration, we revised it to using the proxy of alkene and O_3 concentration to normalize it from 1×10^5 to 4×10^5 molecules cm^{-3}. In lines 468-472 in the revised manuscript, we revised it as "The nighttime OH concentration was estimated linearly correlated with the product of nighttime O_3 concentration and alkenes concentration, namely,

$$c_{OH,night} = 1\times10^5 + 4\times10^5 \times \frac{(c_{O_3}\times c_{alkenes})_{night} - (c_{O_3}\times c_{alkenes})_{night,min}}{(c_{O_3}\times c_{alkenes})_{night,max} - (c_{O_3}\times c_{alkenes})_{night,min}} \quad (16)$$

The time series of OH concentration calculated using different methods was shown in Fig. S11" At the same time, we updated the data in Figs. 3-5 in the revised manuscript.

The authors attempted to quantify the contributions of vehicle-emitted NO to ambient HONO via NO+OH reaction based on the source apportionment of NO emissions. This is not

convincing because the homogeneous HONO formation is generally limited by OH other than NO. This means that the produced HONO should be not linearly dependent to the NO emissions. It can be concluded that vehicle emission should contribute significantly to not only direct HONO emission but also HONO formation through reactions of NO and NO_2. However, the current quantification analysis needs be more careful.

Response: Thank you so much for your comment. We agree with you that the production rate of HONO ($P_{NO\text{-}OH}$) from this reaction is greatly dependent on or determined by OH concentration as shown in Fig. 3 because the variation degree of OH concentration from nighttime to daytime is obviously larger than that of NO concentration. However, we think $P_{NO\text{-}OH}$ actually reflects both the variations of OH concentration and the emission of NO from vehicles. From the point view of HONO sources, it still represents the indirect source of HONO related to traffic emission although the diurnal variation of OH concentration is mainly determined by light intensity. In the revised manuscript, we added a sentence to discuss this point "As shown in Fig.3, although the diurnal curve of $P_{NO\text{-}OH}$ coincided well with that of OH concentration (Fig. S10), which means the $P_{NO\text{-}OH}$ should be mainly determined by OH concentration, the $P_{NO\text{-}OH}$ should still reflect the indirect contribution of traffic related emission to HONO source because the ambient NO concentration was used to calculate the $P_{NO\text{-}OH}$." in lines 637-641 in the revised manuscript.

Specific Comments:

Line 44: fine particulate matter with diameter less than or equal to 2.5…

Response: Thank you. It has been corrected in line 44 in the revised manuscript.

Line 78: on polluted days

Response: Thank you. It has been corrected throughout the paper.

Lines 84-94: to my knowledge, there have been a number of observational studies of HONO in recent years in China, and similar HONO budget analyses were performed. I suggest the authors to comprehensively review the existing results about the HONO sources in China and compare them against the source analysis results obtained in the present study.

Response: Thank you for you good suggestion. In the revised manuscript, we added two paragraph to review the previous results. "The HONO concentration has been measured with a wide rang from 0.18 to 9.71 ppbv at different locations, such as Beijing (Zhang et al., 2019c;Hu et al., 2002;Hendrick et al., 2014;Wang et al., 2017), Shanghai (Wang et al., 2013;Zhang et al., 2019a), Guangdong (Hu et al., 2002;Su et al., 2008a), Hongkong (Xu et al., 2015), Shandong (Li et al., 2018), Xi'an (Huang et al., 2017) and so on in China since 2000" in lines 85-89 and "At the present time, the study of the HONO budget is still far from closed, which would require a significant effort on both the accurate measurement of HONO and the determination of related kinetic parameters for its production pathways (Liu et al., 2019b). For example, photo-enhanced conversion of NO_2 (Su et al., 2008b) and photolysis of particulate nitrate were found to be the two major mechanisms with large potential of HONO formation during noontime, but the associated uncertainty may reduce their importance (Liu et al., 2019b). Some other researches proposed that heterogeneous reactions on ground/aerosol surfaces were important during nighttime (Wang et al., 2017;Zhang et al., 2019b) and daytime in Beijing-Tianjin-Hebei (BTH) (Zhang et al., 2019b). But the heterogeneous reaction was unimportant in Ji'an compared with the unknown sources and the homogeneous reaction between NO and OH (Li et al., 2018). In addition, the traffic emission was proposed to be an important HONO source during nighttime but not significant during daytime in BTH (Zhang et al., 2019b). However, it was proposed that direct emission of HONO from vehicles should contribute about 51.1 % (Meng et al., 2019) and 52 % of nighttime HONO in Beijing (Zhang et al., 2019c). These results mean that more studies is still required on the HONO budget" in lines 99-115.

Line 138: replace "nitrous acid" by "nitric acid"

Response: Thank you. It has been corrected in line 81 in the revised manuscript.

Line 146: Equation (1) describes the budget analysis other than the stationary state analysis. Both methods are different. Transport terms need be considered here.

Response: Thank you. It has been corrected in line 171 in the revised manuscript.

Lines 198-202 and Fig. 1: it would be much better if the authors could also plot the other related

parameters, such as NOx and meteorological parameters, in Fig. 1. It is difficult for the readers to look at the same measurements separately from main text and supplement.

Response: Thank you for your suggestion. We have combined these parameters in Fig. 1 and Fig. R12.

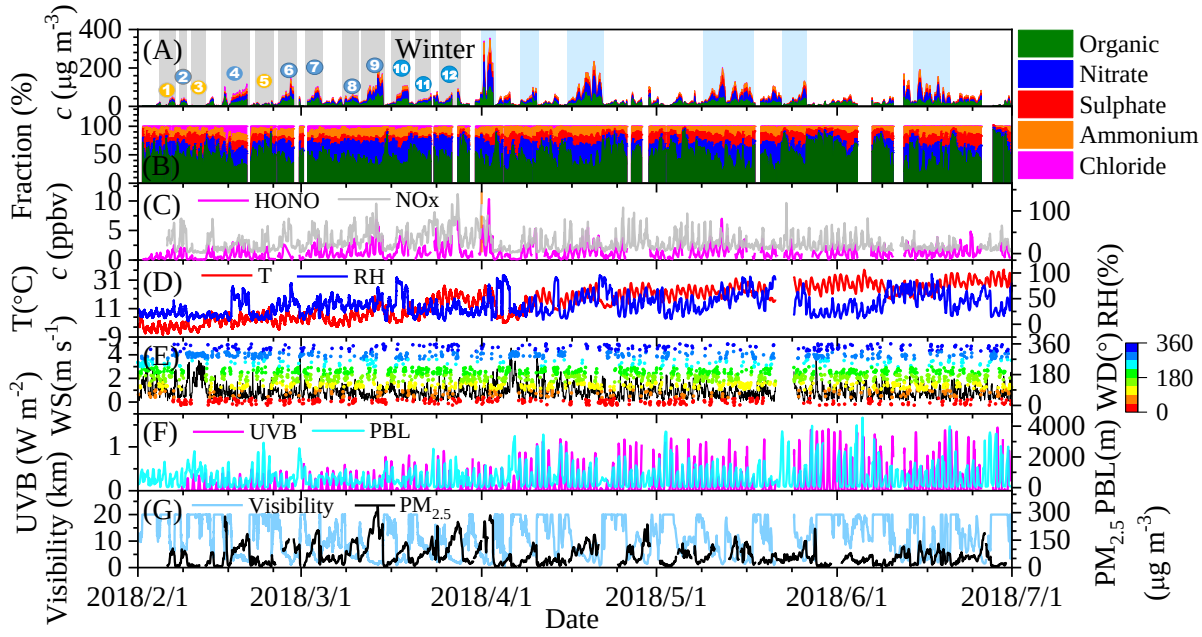

Fig. R12. An overviewed measurement of non-refractory-$PM_{2.5}$ (NR-$PM_{2.5}$), HONO, NOx, $PM_{2.5}$ and meteorological parameters from Feb. 1 to July 1, 2018. (A) the mass concentration of different components of $PM_{2.5}$, (B) the mass fraction of individual component, (C) HONO and NOx concentration, (D) temperature and RH, (E) wind speed and wind direction, (F) UVB and PBL height and (G) visibility and $PM_{2.5}$ concentration during observation.

Line 228: the increase in temperature…

Response: Thank you. It has been corrected in line 268 in the revised manuscript.

Line 262: what does "in RO_2 chemistry" mean? Rephrase this sentence.

Response: Thank you. We revised it to "the reaction between NO and HO_2" in line 298 in the revised manuscript. It means the reaction: $HO_2 + NO \rightarrow OH + NO_2$.

Line 266: replace "dominating" by "dominant"

Response: Thank you. It has been corrected in line 303 in the revised manuscript.

Lines 270-282: it is not clear how the $P_{OH\text{-}HONO}$ and $P_{OH\text{-}O3}$ were calculated from the current discussion. The calculated $P_{OH\text{-}HONO}$ and $P_{OH\text{-}O3}$ levels in winter and April-June seem to be too high. Detailed calculation methods should be given here. Usually, the OH+NO reactions should be subtracted from the photolysis of HONO to denote the real contribution of HONO to the OH source.

Response: Thank you for your good suggestions. The photolysis rates of NO_2(J_{NO2}), HONO(J_{HONO}) and O_3(J_{O3}) under clear sky conditions were calculated according to the solar zenith angle and the location using a box model (FACSIMILE 4). NO_2 photolysis sensor (J_{NO2}, Metcon) was unavailable, while UVB is always available during our observation study. However, the J_{NO2} sensor was available from Aug 17 to Sep 16, 2018. A calibration function between the measured UVB light intensity and the J_{NO2} was established to correct the influence the climatological O_3 column, aerosol optical depth and cloud cover on surface UV light intensity from Aug 17 to Sep 16, 2008. As shown in Fig. S10, the model well predicted the J_{NO2}. Then, the J_{NO2} during this campaign study was predicted using the measured UVB light and the modelled photolysis rates. These information has been shown in the SI. The time series of the daytime photolysis rates were added in the SI (Fig. S7) and shown in Fig. R2. Overall, the *J* values are comparable with literature data during the similar season in Beijing (Tan et al., 2018b;Zhang et al., 2019c). In addition, we recently compared the OH concentration using the J_{O1D} with that derived from measured H_2SO_4 concentration using a box model. We found the OH concentration calculated with the two methods are comparable as shown in Fig. R1.

In lines 313-314 in the revised manuscript, we added a sentence "The details about the J_{HONO} and J_{O1D} calculation were shown in the Supplement Information and their time series were shown in Fig. S7".

Line 291: photolysis of HCHO is actually the primary source of HO_2.

Response: Thank you. OH is formed from the reaction between NO and HO_2, which is related to HCHO photolysis (Alicke et al., 2003). We revised it as "…,while photolysis of O_3 and HCHO related reactions usually dominated primary OH production in summer (Alicke et al., 2003)" in lines 330-331 in the revised manuscript.

Line 330: delete “and”.

Response: Thank you. It has been corrected in line 366 in the revised manuscript.

Lines 333-336: Several recent papers about the nitrate aerosol trend and formation mechanisms in China are highly relevant to this study, and should be acknowledged.

Wen et al., Summertime fine particulate nitrate pollution in the North China Plain: increasing trends, formation mechanisms, and implications for control policy, Atmospheric Chemistry and Physics, 18, 11261-11275, 2018.

Sun et al., Two years of online measurement of fine particulate nitrate in the western Yangtze River Delta: influences of thermodynamics and N2O5 hydrolysis, Atmospheric Chemistry and Physics, 18, 17177-17190, 2018.

Response: Thank you so much. These work have been cited in the revised manuscript (lines 369-370).

Line 363: high or low HONO concentration?

Response: Thank you. We think is should be low HONO concentration if the secondary formation is unimportant.

Line 408: Tan et al., (2019)

Response: Thank you. It has been corrected in line 453 in the revised manuscript.

Line 407-408: it would be better if the authors could provide the estimated OH levels here.

Response: Thank you. The calculated OH concentration was added in the revised SI (Fig. S11) and Fig. R13. And in lines 472-473 in the revised manuscript, we added a sentence “The time series of OH concentration calculated using different methods was shown in Fig. S11”.

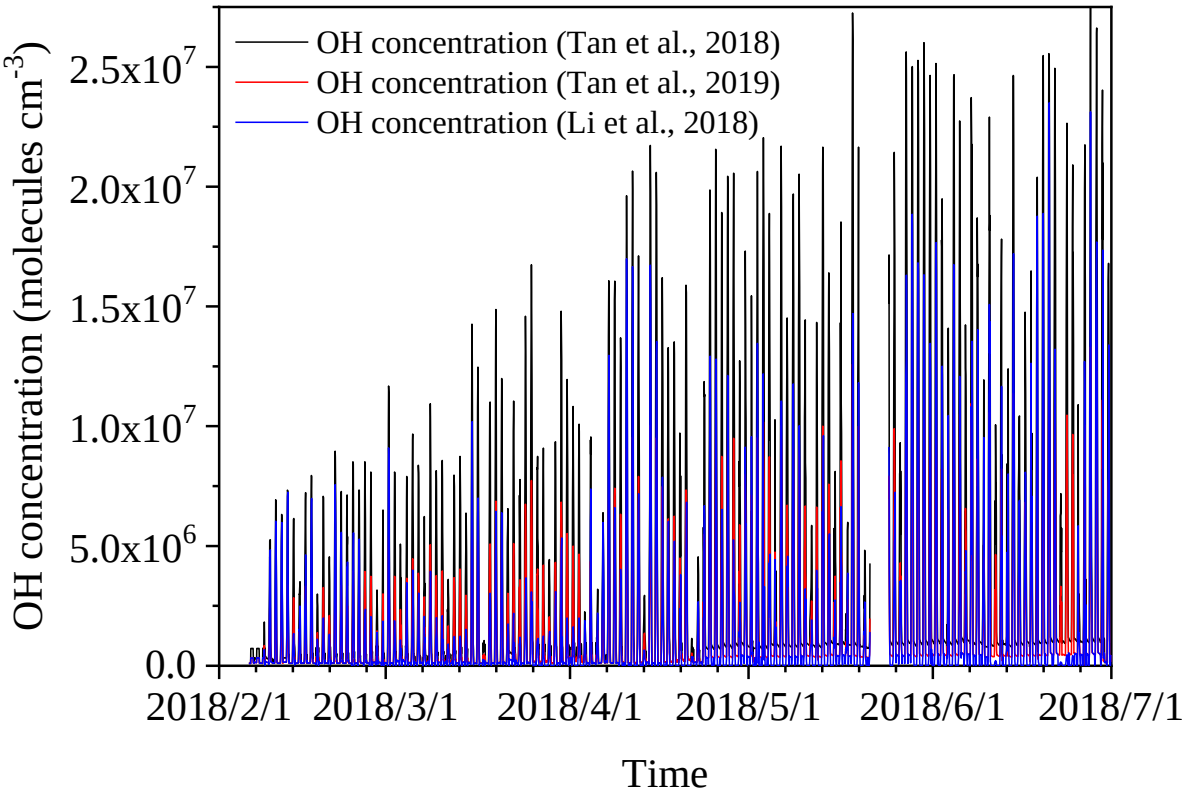

Fig. R13. Estimated OH concentration using different methods.

Lines 430-431: it is not clear how the photolysis frequency of nitrate was corrected? Details are needed here. What are the J values used finally?

Response: Thank you. In the literature (Bao et al., 2018), the authors measured the photolysis of $PM_{2.5}$ samples under irradiation by a Xenon lamp. The authors adjusted the *J* value to ambient sunlight condition at solar zenith angle of 0°. We additionally normalized this value according to the solar zenith angle during our observation according to the latitude, the date and the observed sunlight intensity. They reported a series of $J_{nitrate}$ which varied from 1.22×10^{-5} to 4.84×10^{-4} s^{-1} with a men value of 8.24×10^{-5} s^{-1}. Thus, we used these three values to calculate the lower limit, higher limit and middle value of the $J_{nitrate}$. The time series of the middle value has been added as an example in Fig. S7 in the revised SI and Fig. R2. We added a sentence as "The time series of the measured nitrate concentration and the middle value of $J_{nitrate}$ were shown in Fig. 1 and Fig. S7, respectively" in lines 493-495 in the revised manuscript.

Line 553-554: again, it is budget analysis other than stationary state calculation.

Response: Thank you. It has been corrected in line 683 in the revised manuscript.

Line 568: indirect production

Response: Thank you. It has been corrected in line 698 in the revised manuscript.

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Reviewer 3#

The title of this paper is very intriguing that (1) wintertime HONO promotes aerosol formation and (2) >50% of observed HONO is traffic related in Beijing. After reviewing this paper, I think it will be a grave mistake if the editor decides to publish this paper with these two conclusions in any form. The conclusions are pure speculations. I find no evidence to support either of the two claims in this paper.

Response: Thank you for your comments. We will answer your questions in the following section point by point.

The discussion for conclusion (1) is in section 3.2. One of the many mistakes in this section is that the authors do not understand that the largest source of OH is from the reaction of HO_2+NO. Even when OH production from HONO photolysis is larger than from O_3 photolysis, the effect on OH is much smaller than the photolysis rate comparison. Line 301-304 is based on another paper; the data in this paper do not either support or dispute that oxidation by OH promotes aerosol formation. Figure 2D is used at the observation evidence supporting conclusion (1). 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. Line 318 states ": : : it was reasonable to mainly ascribe the increase of OA concentration to local secondary formation initiated by OH radical from HONO photolysis." It is a pure speculation. The observation data in this paper do not support this statement. It is the same with Line 328. The vague statement cannot be supported by the data in this paper. Line 332 is again a speculation. Ammonia is mostly neutralized by sulfate in Beijing. Line 338-400 is another speculative and ambiguous statement. Line 345-345 cites other people's work but is not supported by the data in this work.

Response: Thank you for your instructive comment. The budget of HO_x or RO_x radical has been investigated at several locations in China based on field measurements and modelling studies (Tan et al., 2018;Tan et al., 2017;Tan et al., 2019;Tang et al., 2015). Using WRF-Chem model, Tang et al (2015) proposed that HO_2+NO was the major OH source, followed by HONO photolysis and O_3 photolysis in Beijing, Shanghai and Guangzhou when both primary and

secondary OH sources were taken into consideration (Fig. R14). As shown in this figure, however, photolysis of HONO was still an important OH sources and the dominate primary OH source in Beijing. Other studies also confirmed that HONO photolysis is an important OH sources, in particular, dominated the primary OH source at various locations (Fig. R15) (Tan et al., 2019;Liu et al., 2019;Tan et al., 2018;Tan et al., 2017).

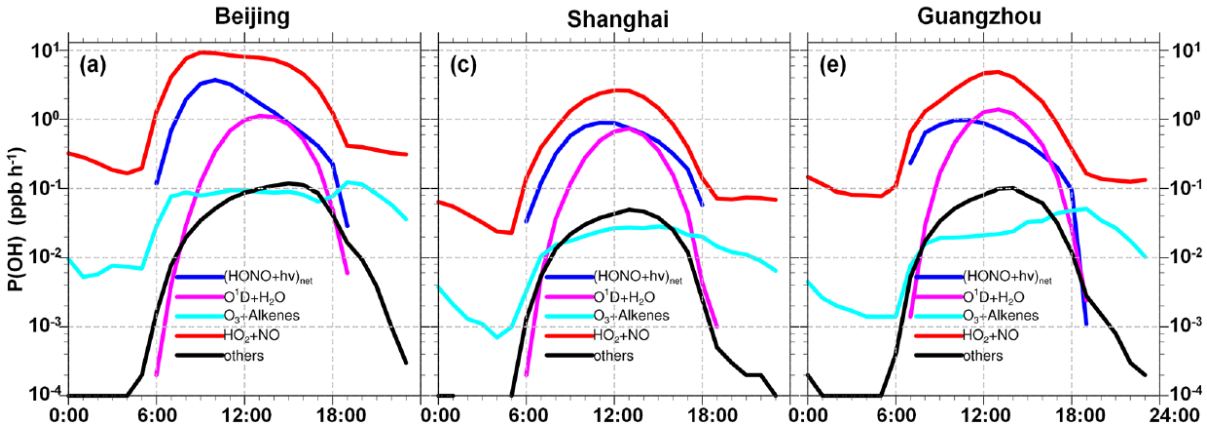

Fig. R14. Averaged production rate of OH in Beijing, Shanghai and Guangzhou (Tang et al., 2015).

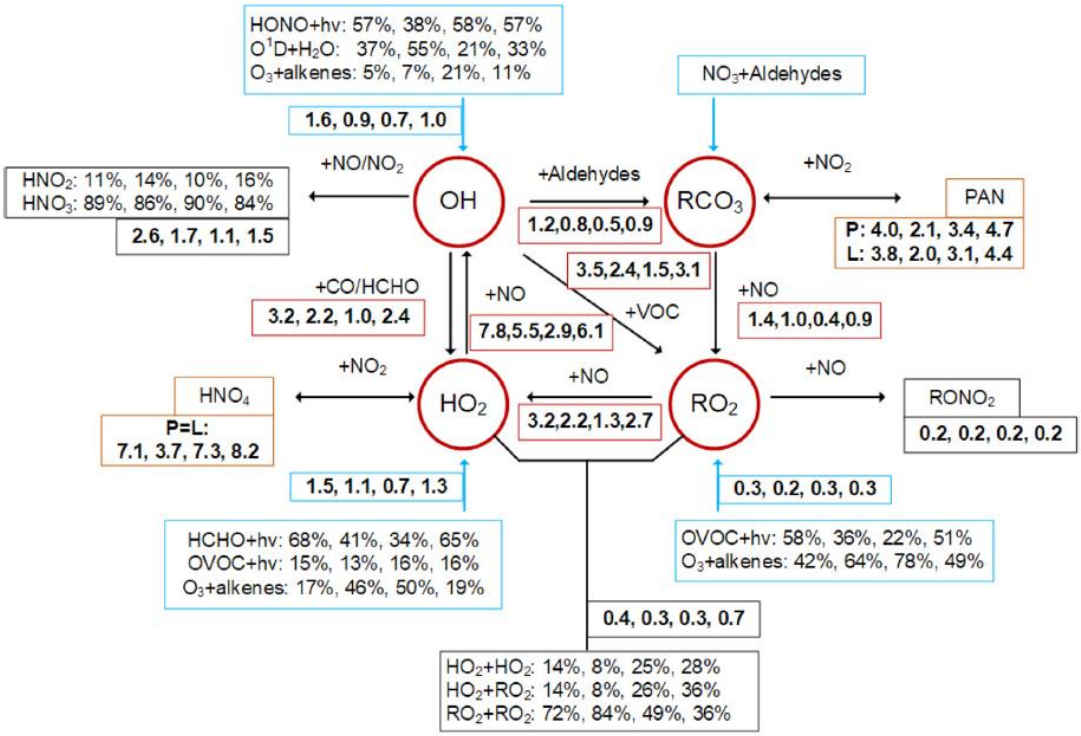

Fig. R15. Comparison of the OH–HO_2–RO_2 radical budget in four cities under daytime conditions (06:00 to 18:00 LT). The numbers are sorted from left to right in the order of Beijing, Shanghai, Guangzhou, and Chongqing. The blue, black, red, and yellow boxes denote the

primary radical sources, radical termination, radical propagation, and equilibrium between radicals and reservoir species, respectively (Tan et al., 2019).

We agree with you that HO_2+NO is the major OH source when both the primary and secondary OH sources are taken into consideration. In section 3.2, we were not going to discuss the budget of OH or RO_x. We want to confirm that HONO should play an important role in the initiation of RO_x chemistry during our observation. From line 285 to 289, in the original version of the manuscript, we may mislead you because of the improper statements ("This means that the photolysis of HONO dominates the daytime OH production in polluted days in winter, while photolysis of O_3 behaves as a bigger OH source from April to June. This is consistent with the previous findings that HONO photolysis is the dominant OH source in winter of BTH"). In lines 324-328 in the revised manuscript, we revised it "These results mean that the photolysis of HONO should play an important role in the initiation of the daytime HO_x and RO_x chemistry on polluted days in winter, while photolysis of O_3 becomes more important from April to June. This is consistent with the previous findings that HONO photolysis dominants the primary OH source in winter of BTH…". At the same time, a sentence has also been added in lines 305-307 in the revised manuscript "In addition, it has been confirmed that HONO dominates the primary OH source at various locations (Tan et al., 2018;Liu et al., 2019;Tan et al., 2017;Aumont et al., 2003)".

We agree that the relationship among different pollutants are very complicated in the atmosphere because many variables are entangled. So, it is difficult to isolate the cause and effect relationship between two variables. In both laboratory and modeling studies, one can change the experiment conditions or the input parameters to test the sensitivity of a target parameter to a given variable. For example, a modeler can change the HONO concentration to simulate the change of aerosol concentration and quantify the influence of HONO on secondary aerosol formation. However, this is impossible for field measurements. Thus, correlation analysis is a common method to reasonably deduce the possible mechanism occurring in the atmosphere based on existing knowledge and reasonable assumptions in field measurements (it does so even in modeling studies and laboratory studies). For example, based on correlation analysis, it has been proposed that amines play a crucial role in new particle formation (Kirkby et al., 2011;Almeida et al., 2013) and NH_3/NO_2 can promote sulfate formation in aqueous phase

(Wang et al., 2016).

It has been well recognized that secondary organic aerosol is formed via multiple steps oxidation of VOCs (Kroll and Seinfeld, 2008). At the same time, HOx and ROx play very important role in VOCs oxidation (Atkinson et al., 2006). As discussed above, HONO is the important source of primary OH in the atmosphere. It also has been found that HONO is responsible for the initiation of photochemical reactions in chamber studies (Rohrer et al., 2005). In addition, modelling studies have confirmed that HONO can enhance secondary aerosols formation in Beijing-Tianjin-Hebei (BTH) region (Zhang et al., 2019b) and Pearl-River-Delta (PRD) region of China (Zhang et al., 2019a;Xing et al., 2019). Therefore, it is reasonable to deduce that the increase of OA concentration (Δc_{OA}) should be related to the OH from HONO photolysis (Δc_{HONO}) after normalized to CO as supported by the linear correlation between $\Delta c_{OA}/c_{CO}$ and $-\Delta c_{HONO}/c_{CO}$ in Fig. 2D. CO is a primary pollutant and a stable species in the atmosphere like BC. Thus, it was used to partially alleviate the influence of PBL variation (Cheng et al., 2016). In addition, $\Delta c_{OA}/c_{BC}$ has also been used to characterize SOA formation during air mass transport (Liggio et al., 2016). Therefore, we correlated the $\Delta c_{OA}/c_{CO}$ with the $-\Delta c_{HONO}/c_{CO}$ rather than the c_{OA} with the c_{HONO}. This has been pointed out as in lines 291-293 in the revised manuscript "After partially ruling out the possible influence of PBL variation by normalizing the concentrations of all pollutants to CO (Cheng et al., 2016) or BC (Liggio et al., 2016)…".

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. However, OA concentration is ready to be affected by regional transport. Thus, we chose these pollution events under stagnant metrological conditions. Therefore, we pointed out that "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" from line 317 to 319 in the original versions of the manuscript. It has been recognized that oxidation of NO_2 by OH dominates the daytime nitrate formation (Tian et al., 2019). Thus, we can deduce that OH from photolysis of HONO should promote nitrate formation because of the good correlation between the $\Delta c_{nitrate}/c_{CO}$ and $-\Delta c_{HONO}/c_{CO}$ in lines 375-377 in the revised manuscript.

In North China Plain, NH_3 is enough to neutralize both sulfate and nitrate the due to the intensive emission of NH_3. Fig. R16A shows the correlation between the charge of NH_4^+ and anions (including sulfate, nitrate and chloride) in non-refractory $PM_{2.5}$ measured using the ACSM in this work. In general, ammonium can neutralize both nitrate and sulfate. In addition, as shown in Fig. R16B, the cations can also neutralize the anions measured using a MARGA in Shijiazhuang from March, 2018 to April, 2019. Therefore, the increase of $\Delta c_{ammounium}/c_{CO}$ and $-\Delta c_{HONO}/c_{CO}$ can be ascribed to the fact that ammonium keeps the pace of nitrate through neutralization. In the revised SI, we added the correlation of the charge between the cations and anions in Fig. S8. In the revised manuscript (lines 368-371), we also pointed out that "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" .

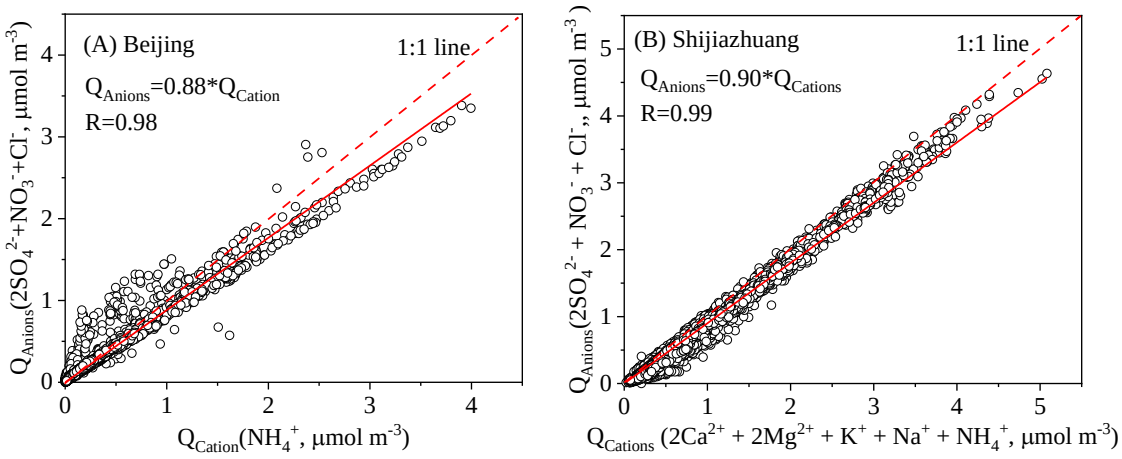

Fig. R16. Correlation of the charge between inorganic anions and cations (A) in non-refractory $PM_{2.5}$ in Beijing and (B) in soluble $PM_{2.5}$ in Shijiazhuang.

From line 338 to 340 in the original manuscript, we concluded that promotion effect of HONO photolysis on nitrate formation could not be excluded. From line 240 to 347, we proposed that HONO photolysis has little influence on sulfate formation based on the correlation between $\Delta c_{sulfate}/c_{CO}$ and $-\Delta c_{HONO}/c_{CO}$ as well as the previous studies, and then made a conclusion that photolysis of HONO could promote aerosol formation during pollution events in winter. From line 348 to 400, we showed the calculation details about HONO emission from vehicle and soil after referring to literatures. From line 345 to 348, we cited the results of

modeling studies. We pointed out that “this work well supported the recent modeling results that HONO could obviously 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”. So, we need to cite these previous work.

Conclusion (2) is based on some calculation that was not described in the paper. Line 376-378 states that the mean emission factor is 1.17% with a lower limit of 0.18% and an upper limit of 1.8%. (Why is the mean so close to the upper limit and 6.6 times larger than the lower limit?) The mean value is similar to previous studies and is not the reason for conclusion (2). Line 381 gives a vehicle HONO emission rate of 0.085 to 0.34 ppbv/h. The unit implies some volume was used in the calculation. No discussion was given on what volume was used and how it varied in a day. Another important factor not considered in this study is the outflow of vehicle HONO and NOx by advection at night. It is the largest sink at night but is not included in the budget discussion. The nighttime source of NO_2 from the ground is 38 times less than vehicle emissions. However, no other paper I know of found that HONO concentrations at night cannot be explained mostly by a ground source. It led me to conclude that the vehicle HONO emission source in this paper is overestimated by 10-100 times. The authors should look at previous modeling papers that included vehicle HONO emissions. What they found is that the effect of vehicle HONO emissions is small.

Response: Thank you for your comments. As for the contribution of vehicle-related emission to HONO source, the details have been discussed in both Section 2.2 and 3.3. In this work, we used two different methods to estimate the emission ratio of HONO to NOx (HONO/NOx) from vehicle exhaust. 1.8 % was calculated based on empirical analysis of field data, while 1.17% was obtained by using the low limit correlation of field data. Table R1 and Table S3 summaries the emission ratio from vehicles estimated or measured in China. The lowest value is 0.18% based on chassis dynamometer tests. From line 376 to 378 in the original manuscript we described as “Thus, three levels of vehicle emission factor were considered. 1.17±0.05% was taken as the middle value, while 0.18% (Liu et al., 2017) and 1.8 % were the lower limit and the upper limit, respectively”. Here, we used a “middle value” (using the low limit correlation method of filed data) but not a “mean value”. Actually, this value is very close to

the mean emission ratio (1.21) if we consider all these reported values in Table R1. In the revised manuscript, we revised this sentence "Thus, three levels of vehicle emission factor were considered. 1.17±0.05% was taken as the middle value which was very close to the mean emission ratio (1.21) for all of these reported values in China (Li et al., 2018;Xu et al., 2015;Yang et al., 2014;Liu et al., 2017;Gall et al., 2016;Meng et al., 2019), while 0.18% (Liu et al., 2017) and 1.8 % were the lower limit and the upper limit, respectively" from line 415 to 420 in the revised manuscript.

Table R1. Summary of the measured emission ratio of HONO to NOx from vehicles in China.

Time	Place	Methods	ΔHONO/ΔNOx		Reference
			Range	Mean	
2015/9/1-2016/8/31	Ji'nan, Shandong	Empirical analysis of field data	0.19%-0.87%	0.53±0.20%	(Li et al., 2018)
2011/8/3-2012/5/31	Hongkong	Empirical analysis of field data	0.5%-1.6%	1.2±0.4%	(Xu et al., 2015)
2015/3/11-2015/3/21	Hongkong	Tunnel experiment	-	1.24±0.35%	(Liang et al., 2017)
2014	Beijing	Tunnel experiment	-	2.1%	(Yang et al., 2014)
2017	Beijing	Chassis dynamometer test	0.03%-0.42%	0.18%	(Liu et al., 2017)
2016/12/16-2016/12/24	Beijing	Empirical analysis of field data	-	1.3%	(Zhang et al., 2019c)
2016/12/7-2016/12/13	Beijing	Low limit correlation of field data	-	1.41%	(Meng et al., 2019)
2018/2/1-2018/6/30	Beijing	Empirical analysis of field data	1.3-2.4%	1.8±0.5%	This study
2018/2/1-2018/6/30	Beijing	Low limit correlation of field data	-	1.17±0.05%	This study

In Section 2.2, we defined the calculation method for the emission rate of HONO from vehicles "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)" from line 152 to 156 in the original manuscript. The emission flux of HONO was calculated according to the the hourly emission flux of NOx from vehicle sector (Yang et al., 2019) and the relative emission ratio of HONO to NO_x as discussed above. It was pointed out as "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." from line 379 to 381 in the original manuscript. To make it clearer, we revised this sentence "The $E_{vehicle}$ was calculated using the hourly NO_x emission inventory from vehicles in Beijing (Yang et al., 2019) after converted to emission flux of HONO ($F_{HONO}=F_{NOx}\times$ HONO/NO_x) and 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" in lines 421-425 in the revised manuscript.

As you suggested, the outflow HONO by advection is an important sink of HONO in the night (Gall et al., 2016;Meng et al., 2019). The the loss of HONO ($T_{advenction}$) via vertical advection can be calculated according to the following equation,

$$T_{vertical} = -K_h(z,t)\frac{\partial c(z,t)}{\partial z}\frac{1}{h} \quad \text{(R3)}$$

where K_h(z,t) is the eddy diffusivity of heat (m^2 s^{-1}) at height *z* (m) and time *t*, *h* is the height of the second layer (Gall et al., 2016). We added two paragraphs to discuss the transport in lines 222-232 "Vertical transport by advection ($T_{vertical}$), which is an important sink of HONO in the night (Gall et al., 2016;Meng et al., 2019), can be calculated according to equation (12).

$$T_{vertical} = -K_h(z,t)\frac{\partial c(z,t)}{\partial z}\frac{1}{h} \quad (12)$$

where K_h(z,t) is the eddy diffusivity of heat (m^2 s^{-1}) at height *z* (m) and time *t*, *h* is the height of the second layer (18 m in this study) (Gall et al., 2016). On the other hand, both the vertical and horizontal transport can be estimate according to Eq. (13),

$$T_{vertical} = k_{dilution}(c_{HONO} - c_{HONO,background}) \quad (13)$$

where $k_{dilution}$ is a dilution rate (0.23 h^{-1}, including both vertical and horizontal transport) (Dillon et al., 2002), c_{HONO} and $c_{HONO,background}$ is the HONO concentration at the observation site and background site, respectively (Dillon et al., 2002)" and lines 574-598 "As pointed in Section 2.2, vertical transport by advection is an important nocturnal sink of HONO (Gall et al., 2016). In this work, the vertical distribution of HONO concentration is unavailable.

Recently, Meng et al. (2019) measured the vertical distribution of HONO in Beijing in December, 2016. 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). The nighttime concentration gradient was 0.0047±0.0025 ppb m^{-1} derived from the nighttime dataset (Meng et al., 2019). In the daytime, we assume a zero concentration gradient. On the other hand, the eddy diffusivity of heat in urban environment was measured in New Delhi, Indian (Yadav et al., 2003). Using their dataset with the wind speed lower than 2.0 m s^{-1}, we derived the relationship between the K_h and the wind speed (WS) (K_h=0.9389×WS-0.3374 m^2 s^{-1}). The nighttime $T_{vertical}$ changed from 0.15 to 0.37 ppbv h^{-1} in winter, while it was from 0.12 to 0.68 ppbv h^{-1} according to Eq. (12) from April to June. Because the wind speed was usually lower than 1.0 m s^{-1} in pollution events (Fig. S6), horizontal transport should have little influence on the daytime sources or sinks of HONO because of the short lifetime of HONO. In the night, 79 % of the wind speed was lower than 1.0 m s^{-1} in winter, thus the air masses from suburban areas should have influence on the sources and sinks of HONO in Beijing. If the HONO concentration at background was zero, the vertical and horizontal transport rate of HONO varied from 0.17 to 0.61 ppbv h^{-1} calculated according to Eq. (13) on haze days in winter and from 0.15 to 0.74 ppbv h^{-1} in pollution events from April to June. These values are higher than that calculated according to Eq. (12). Because the background HONO concentration was unavailable, we only considered the nighttime transport calculated according to Eq. (12) in the following section". At the same time, the relative contribution of each source in Section 3.3 was updated based on the total sinks.

HONO production from heterogeneous reactions of NO_2 on both aerosol surface and ground surface greatly depend on the uptake coefficient ($\gamma_{NO2, BET}$) and the surface to volume ratio (S/V). The mean and median surface to volume ratio of aerosols are 1.33×10^{-3} and 1.36×10^{-3} m^{-1} during pollution events. This is comparable with the input parameters in modeling studies (Zhang et al., 2016). However, as discussed from line 501 to 503 in the revised manuscript, the $\gamma_{NO2, BET}$ on aerosols varied from 5×10^{-9} to 9.6×10^{-6}. The $\gamma_{NO2, BET}$ on pure oxides was usually higher that on composite oxides. The selection of a proper $\gamma_{NO2, BET}$ is quite tricky. For example, a fixed $\gamma_{NO2, BET}$ was set to 1×10^{-6} in nighttime and 2×10^{-5} in daytime due to photochemical reaction of NO_2 on soot surface in a modelling study (Zhang et al.,

2016;Aumont et al., 2003). The nighttime $\gamma_{NO2,\,BET}$ is ~2 orders of magnitude higher than ours (1.2×10^{-8}) as suggested by Crowley et al. (Crowley et al., 2010). In our previous work, we have measured the $\gamma_{NO2,\,BET}$ on kaolin and hematite (Liu et al., 2015) and soot (Han et al., 2013). The initial $\gamma_{NO2,\,BET}$ on kaolin is $4.85\pm0.39\times10^{-8}$ at 47 % RH. It should be pointed out that the $\gamma_{NO2,\,BET}$ decreases significantly with exposure time due to surface saturation. Fig. R8 shows the typical uptake curve of NO_2 and the $\gamma_{NO2,\,obs}$ which is not normalized to the specific surface area. The $\gamma_{NO2,\,BET}$ at steady state (2.56×10^{-9} to 4.56×10^{-9} on kaolin and 1.23×10^{-8} to 1.50×10^{-8} on hematite) is around one order of magnitude lower than the initial $\gamma_{NO2,\,BET}$ as shown in Fig. R9. Therefore, we used the recommended value (1.2×10^{-8}) (Crowley et al., 2010) as the base case. On the other hand, the $\gamma_{NO2,\,BET}$ decreases with RH due to competitive adsorption (Liu et al., 2015). High mass concentration of $PM_{2.5}$ usually accompanied with high RH in winter in Beijing. Thus, we calculated the RH dependent $\gamma_{NO2,\,BET}$ according to the equation we determined previously (Liu et al., 2015) and the measured ambient RH in this work. This should be more reasonable than a fixed uptake coefficient used in modeling studies.

In the original version of manuscript, we found a bug when calculating the heterogeneous reaction of NO_2 on black carbon. A conversion factor of time from second to hour was missed. So, the contribution of heterogeneous reaction to HONO source was underestimated in the original version. Now, the $P_{aerosol}$ was 0.038±0.030-0.088±0.072, which was dominated by the heterogeneous reaction of NO_2 on black carbon. It was on the same orders as soil emission. However, this was still significantly lower than the contribution of vehicle emission. In the revised manuscript, we updated Figs. 3-5 and the corresponding numbers in section 3.3.

As for heterogeneous reaction of NO_2 on ground surface, we used the same $\gamma_{NO2,BET}$ on dust aerosol in the night, which is similar to the methodology used in modelling studies (Zhang et al., 2016;Aumont et al., 2003). As pointed out in Section 2.2 from line 197 to 209 in the revised manuscript, the S/V was estimated using the surface roughness calculated in the light of satellite image of Beijing. The calculated surface roughness is 3.85, which is slightly higher than the value (2.2) used by Li et al. (2017). Thus, the calculated S/V varied from 0.0015 to 0.0385 m^{-1} (with a mean value of 0.0125 m^{-1}) because of the variation of the PBL height during pollution events. However, a fixed S/V of ground surface was set to 0.3 m^{-1} in the modeling studies (Zhang et al., 2016). This corresponds to a surface roughness ~92, which means the

surface area is ~92 times of the projected area of ground. It's too high. If both the $\gamma_{NO2,BET}$ (1×10^{-6}) and surface roughness are increased to the values used in modeling 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. In lines 558-561 in the revised manuscript, we also revised the sentence "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)" and in lines 605-607 in the revised manuscript, "Heterogeneous reactions of NO_2 on aerosol surface and ground surfaces were not the major HONO source during night unlike the modelled results (Zhang et al., 2016;Aumont et al., 2003) ".

During the Chinese New Year (CNY) and the COVID-19 epidemic in 2020, traffic emission decreased significantly in Beijing. This provides us a unique opportunity to verify the relative importance of each HONO source. We only analyzed the nocturnal data from January 1 to February 29 because the HONO sources related to photochemical reactions could be avoided. The CNY vacation was from January 23 to February 2. These results are in preparation for a separate paper. Fig. R10 shows the relative change of the concentrations of HONO, NO_x and non-refractory $PM_{2.5}$ (NR-$PM_{2.5}$). The traffic index and the chemical age of the air masses which is defined as $-\log(NO_x/NO_y)$ are also shown in Fig. R10. NO_y was measured with a NO_y analyzer (Thermo 42i-Y). The concentration of nighttime HONO decreased significantly during the CNY and after the CNY accompanied with the reduction in vehicle emission as supported by both the concentration of NO_x and traffic index (Fig. R10B). Interestingly, the NR-$PM_{2.5}$ concentration during and after the CNY increased obviously when compared with that before the CNY. The effective conversion of NO_2 aerosol surface was almost constant because both the promotion effect of increased $PM_{2.5}$ concentration and the inhibition effect of reduced NO_2 concentration during and after the CNY as shown in Fig. R10C. On the other hand, we found that the nighttime chemical age of the air masses during and after the CNY was also obviously larger than that before the CNY (Fig. R10D). This means that heterogeneous reaction of NO_2 on both aerosol surface and ground surface should be more effective due to longer residence of the air masses during and after the CNY than that before the CNY. When

the reduction of NO_2 concentration was taken into consideration, the product of NO_2 concentration and $-\log(NO_x/NO_y)$ in different periods increased slightly (Fig. R11). Therefore, the observed HONO concentration should be at least constant in different periods and independent on the reduction of vehicle emission if heterogeneous reaction of NO_2 on aerosol and ground surfaces dominates nighttime HONO source or if the vehicle emission is a minor HONO source. However, we observed the decrease of HONO along with reduction of vehicle emission (Fig.R10A). This well supports our (and other researchers' (Meng et al., 2019;Zhang et al., 2019c) conclusion that vehicle emission is an important source of HONO in Beijing.

In lines 523-528 in the revised manuscript, we pointed out "The A_s of aerosols which was measured using a DMPS varied from 1×10^{-4} to 4.8×10^{-3} m^{-1} with a mean value of $1.4\pm0.5\times10^{-3}$ m^{-1} during pollution events. This value is comparable with that used in modeling studies (Zhang et al., 2016;Aumont et al., 2003). The A_s of ground surface which was calculated according to Eq. (6) and (7) varied from 1.5×10^{-3} to 3.85×10^{-2} m^{-1} with a mean value of $1.3\pm0.9\times10^{-2}$ m^{-1} during pollution events. The surface roughness was 3.85 calculated according to Eq. (7)". And from line 544 to 554 in the revised manuscript, we added a paragraph to discuss the reason why we obtained the low production rate of HONO via heterogeneous reaction of NO_2 on ground and aerosol surfaces as "It should be pointed out that HONO production from heterogeneous reaction of NO_2 on both aerosol and ground surface greatly depend on the $\gamma_{NO2,\,BET}$ and A_s. The A_s of aerosols is comparable with the modeling input. However, the small nighttime $\gamma_{NO2,\,BET}$ (10^{-8} – 10^{-7}) were used in this work rather than the $\gamma_{NO2,\,BET}$ (1×10^{-6}) used in modelling studies (Zhang et al., 2016;Aumont et al., 2003). This leads to a lower production rate of HONO from heterogeneous reaction of NO_2 on aerosols. As for heterogeneous reaction of NO_2 on ground surface, besides the small $\gamma_{NO2,\,BET}$ used in this work, the A_s of ground surface (0.0015 to 0.0385 m^{-1}) calculated using the surface roughness and PBL height was also significantly lower than the fixed value of 0.3 m^{-1} used in modeling studies that might overestimate the contribution of HONO production from heterogeneous reaction of NO_2 on ground surface".

In summary, I think that the calculation and reasoning of this paper are either incorrect or ambiguous. It does seem likely that any revision can correct the flaws in the two main conclusions. I suggest that the authors scratch the conclusions and redo the analysis of their

observation data.

Response: Thank you for your comments again. We have answered your questions above.

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The promotion effect of nitrous acid on aerosol formation in wintertime Beijing: possible contribution of traffic-related emission

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Abstract

Secondary aerosol is a major component of $PM_{2.5}$, yet its formation mechanism in the ambient atmosphere is still an open question. Based on field measurements in downtown Beijing, we show that the photolysis of nitrous acid (HONO) could promote the formation of organic and nitrate aerosol in wintertime Beijing as evidenced by the growth of the mass concentration of organic and nitrate aerosols linearly increasing as a function of consumed HONO from early morning to noon. The increased nitrate also lead to the formation of particulate matter ammonium by enhancing the neutralization of nitric acid by ammonia. We further illustrate that over 50 % of the ambient HONO during pollution events in wintertime Beijing might be related to traffic-related emission including direct emission and formation via the reaction between OH and vehicle-emitted NO. Overall, our results highlight that the traffic-related HONO plays an important role in the oxidative capacity and in turn, contribute to the haze formation in winter Beijing. Mitigation of HONO and NO_x emission from the vehicles might be an effective way to reduce secondary aerosol mass formation and severe haze events in wintertime Beijing.

1. Introduction

China is one of the most suffering countries from the pollution of fine particulate matter with diameter less than or equal to 2.5 μm ($PM_{2.5}$) (Lelieveld et al., 2015). Although the regional air quality has been continuously improving since the central government of China issued the Clean Air Act in 2013 (Vu et al., 2019), $PM_{2.5}$ concentration is still significantly higher than that in developed countries (Fu et al., 2014;An et al., 2019). Nowadays, a consensus has been reached that haze events are driven by local emissions (An et al., 2019), regional transport (Zheng et al., 2015b) and secondary formation (Huang et al., 2014;He et al., 2018) of pollutants under unfavorable meteorological conditions (stagnant atmosphere and high relative humidity) (Zhu et al., 2018;Liu et al., 2017c). A feedback loop between meteorological parameters and haze formation has also been found playing an important role in the evolution of haze events (Zhang et al., 2018).

Secondary aerosol can contribute up to ~70 % to the aerosol mass concentration on polluted days (Huang et al., 2014). Several reaction pathways have been proposed in the atmospheric chemistry community, such as sulfate formation via heterogeneous oxidation of SO_2 promoted by H_2O_2 and/or NO_2 on mineral dust (Huang et al., 2015;He et al., 2014), aqueous oxidation of SO_2 promoted by NO_2 in the presence or absence of NH_3 in particle-bound water film (He et al., 2014;Wang et al., 2016), catalytic conversion of SO_2 to sulfate by black carbon (Zhang et al., 2020), nitrate formation via efficient hydrolysis of N_2O_5 on aerosol surfaces (Wang et al., 2017c;Wang et al., 2019;Kulmala, 2018;Li et al., 2017), and the haze formation initiated by new particle

formation and growth (Guo et al., 2014;Guo et al., 2020). During the past years, strict control of coal combustion has successfully reduced the SO_2 concentration, resulting in a reduction of sulfate (SO_4^{2-}) component in $PM_{2.5}$; in stark contrast, the contributions from organic and nitrate become increasingly more significant in China (Lang et al., 2017).

The formation of secondary organic aerosol (SOA) starts from the gas-phase oxidation of volatile organic compounds (VOCs) leading to various oxidized low-volatility and semi-volatile products (Bianchi et al., 2019), followed by their partitioning into the particle phase (Hallquist et al., 2009). Similarly, the formation of nitrate aerosol in the daytime is largely due to the partitioning of gaseous nitric acid, which is formed via the oxidation of NO_2 by OH (Seinfeld and Pandis, 2006;Wang et al., 2019). It is traditionally believed that the wintertime atmospheric oxidation capacity is weak due to the weak solar radiation, which limits the formation of SOA and nitrate (Sun et al., 2013). However, it is very recently shown that the peak OH concentration on polluted days in winter Beijing varies from 2×10^6 to 6×10^6 molecules cm^{-3}, which is 6-10 times higher than what is predicted by the global model (Tan et al., 2018). This discrepancy can be largely reduced after accounting for other OH production processes in model simulations, which shows that the photolysis of nitrous acid (HONO) dominates the initiation of HO_x (OH and HO_2) and RO_x (RO and RO_2) radical chain in wintertime Beijing (Tan et al., 2018), and some other cities (Ren et al., 2006;Stutz et al., 2013).

The HONO concentration has been measured with a wide rang from 0.18 to 9.71

ppbv at different locations, such as Beijing (Zhang et al., 2019d;Hu et al., 2002;Hendrick et al., 2014;Wang et al., 2017b), Shanghai (Wang et al., 2013;Zhang et al., 2019b), Guangdong (Hu et al., 2002;Su et al., 2008a), Hongkong (Xu et al., 2015), Shandong (Li et al., 2018), Xi'an (Huang et al., 2017b) and so on in China since 2000. More recently, modelling studies have suggested that nitrous acid (HONO) could enhance secondary aerosols formation in Beijing-Tianjin-Hebei (BTH) region (Zhang et al., 2019c), Pearl-River-Delta (PRD) region of China (Zhang et al., 2019a;Xing et al., 2019) and Houston (Czader et al., 2015). These results imply that the role of HONO in haze chemistry might be crucial in wintertime Beijing, while the direct evidence from observation has not been reported, yet. On the other hand, the HONO budget has been investigated via modelling studies (Liu et al., 2019c;Zhang et al., 2019c) and photostationary state calculations (Wang et al., 2017b;Li et al., 2018;Huang et al., 2017b;Lee et al., 2016;Oswald et al., 2015;Zhang et al., 2019d) at different locations. At the present time, the study of the HONO budget is still far from closed, which would require a significant effort on both the accurate measurement of HONO and the determination of related kinetic parameters for its production pathways (Liu et al., 2019c). For example, photo-enhanced conversion of NO_2 (Su et al., 2008b) and photolysis of particulate nitrate were found to be the two major mechanisms with large potential of HONO formation during noontime, but the associated uncertainty may reduce their importance (Liu et al., 2019c). The heterogeneous reactions of NO_2 on ground/aerosol surfaces were proposed to be an important HONO source during nighttime (Wang et al., 2017b;Zhang et al., 2019c) and daytime in Beijing-Tianjin-

Hebei (BTH) (Zhang et al., 2019c), but it was unimportant compared with the unknown sources and the homogeneous reaction between NO and OH in Ji'an (Li et al., 2018) or compared with the traffic emission on haze days in Beijing (Zhang et al., 2019d). The traffic emission was found to be an important HONO source during nighttime and a minor daytime HONO source in BTH (Zhang et al., 2019c). However, it was proposed that direct emission of HONO from vehicles should contribute about 51.1 % (Meng et al., 2019) and 52 % of HONO source on haze days in Beijing (Zhang et al., 2019d). These results mean that more studies are still required on the HONO budget. In particular, it is meaningful to analyze the HONO budget in polluted events for understanding the possible influence of HONO sources on secondary pollutants formation.

In this work, we carried out comprehensive measurements at a newly constructed observation station (Aerosol and Haze Laboratory, Beijing University of Chemical Technology, AHL/BUCT Station) located in the western campus of Beijing University of Chemical Technology in downtown Beijing. We show observational evidence that HONO has a prominent promotion effect on the secondary aerosol mass formation in winter. Traffic-related emission seems to be a vital contributor to ambient HONO during the pollution events in winter in Beijing.

2. Materials and methods

2.1 Field measurements. Field measurements were performed at AHL/BUCT Station (Lat. 39°56′31″ and Lon. 116°17′52″) from February 1 to June 30, 2018. The observation station is on a rooftop of the main building, which is 550 m from the 3rd

ring road in the East, 130 m from the Zizhuyuan road in the North and 565 m from the Nandianchang road in the West (Figure S1). The station is surrounded by both traffic and residential emissions, thus, is a typical urban observation site.

Ambient air was sampled from the roof of the main building with five floors (~18 m above the surface). A $PM_{2.5}$ inlet (URG) was used to cut off the particles with diameter larger than 2.5 μm before going to a Nafion dryer (MD-700-24, Perma Pure). Then a Time-of-Flight Aerosol Chemical Speciation Monitor equipped a $PM_{2.5}$ aerodynamic lens (ToF-ACSM, Aerodyne) and an Aethalometer (AE33, Magee Scientific) were connected to the manifold of aerosol sampling tube. The Reynolds number in the aerosol sampling tube was 800 with the total flow rate of 16.7 lpm and the residence time of 6.5 s. The details about ToF-ACSM measurement was described in the Supplement information. Ambient air was drawn from the roof using a Teflon sampling tube (BMET-S, Beijing Saak-Mar Environmental Instrument Ltd.) with the residence time <10 s for gas phase pollutants measurements. Trace gases including NOx, SO_2, CO and O_3 were measured with the corresponding analyzer (Thermo Scientific, 42i, 43i, 48i and 49i). Volatile organic compounds (VOCs) was measured using an online Single Photon Ionization Time-of-flight Mass Spectrometer (SPI-ToF-MS 3000R, Hexin Mass Spectrometry) with unit mass resolution (UMR). The principle and the configuration of the instrument has been described in detail elsewhere (Gao et al., 2013) and the Supplement information. HONO concentration was measured using a home-made Long Path Absorption Photometer (LOPAP) (Tong et al., 2016). The details are described in the Supplement information. Particle size and number concentration

from 1 nm to 10 μm were measured with Scanning Mobility Particle Sizer (SMPS 3936, TSI), particle size magnifier (PSM, Airmodus) and Neutral Cluster and Air Ion Spectrometer (NIAS, Airel Ltd.). Meteorological parameters including temperature, pressure, relative humidity (RH), wind speed and direction were measured using a weather station (AWS310, Vaisala). Visibility and planetary boundary layer (PBL) height were measured using a visibility sensor (PWD22, Vaisala) and a ceilometer (CL51,Vaisala), respectively

2.2 HONO budget calculation. Multiple sources of ambient HONO have been identified, such as emission from soil (E_{soil}) (Oswald et al., 2015;Meusel et al., 2018) and vehicle exhaust ($E_{vehicle}$) (Trinh et al., 2017), production through homogeneous reaction between NO and OH ($P_{NO\text{-}OH}$) in the atmosphere, photolysis of nitrate ($P_{nitrate}$) (Bao et al., 2018), nitrous acid (P_{HNO3}) and nitrophenenol ($P_{nitrophenol}$) (Sangwan and Zhu, 2018), heterogeneous reaction of NO_2 on aerosol surface ($P_{aerosol}$) (Liu et al., 2015) and ground surface (P_{ground}) (Liu et al., 2019c;Li et al., 2018;Wang et al., 2017b). However, the photolysis of HNO_3 and nitrophenol were excluded in this work because they were believed as minor sources (Lee et al., 2016) and their concentrations were unavailable during our observation. The removal pathways of HONO including photolysis ($L_{photolysis}$), the homogeneous reaction with OH radical ($L_{HONO\text{-}OH}$) and dry deposition ($L_{deposition}$) (Liu et al., 2019c) were considered.

The HONO budget could be calculated by,

$$\frac{dc_{HONO}}{dt} = E_{HONO} + P_{HONO} - L_{HONO} + T_{vertical} + T_{horizontal} \quad (1)$$

where $\frac{dc_{HONO}}{dt}$ is the observed change rate of HONO mixing ratios (ppbv h^{-1}); E_{HONO}

represents the emission rate of HONO from different sources (ppbv h^{-1}); P_{HONO} is the in-*situ* production rate of HONO in the troposphere (ppbv h^{-1}); L_{HONO} is the loss rate of HONO (ppbv h^{-1}) (Li et al., 2018); $T_{vertical}$ and $T_{horizontal}$ are the vertical and horizontal transport (Soergel et al., 2011), which can mimic source or sink terms depending on the HONO mixing ratios of the advected air relative to that of the measurement site and height (Soergel et al., 2011).

The emission rate (E_{HONO}, ppbv h^{-1}) was calculated based on the emission flux (F_{HONO}=EI_{HONO}/A, 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, EI_{HONO}, is the emission inventory of HONO (g s^{-1}), A is the urban area of Beijing (m^2), α is the conversion factor ($\alpha = \frac{1\times10^9 \cdot 3600 \cdot R \cdot T}{M \cdot P} = \frac{2.99\times10^{13} \cdot T}{M \cdot P}$), M is the molecular weight (g mol^{-1}), T is the temperature (K) and P is the atmospheric pressure (Pa).

The production rates of HONO (P_{HONO}, ppbv h^{-1}) in the troposphere was calculated by,

$$P_{HONO} = 3600 \cdot k_1 \cdot c_{precursor} \quad (3)$$

where, k_1 is the quasi first-order reaction rate constant (s^{-1}), $c_{precursor}$ is the concentration of precursor (ppbv). For homogeneous reaction between NO and OH,

$$k_1 = k_2 \cdot c_{OH} \quad (4)$$

where, k_2 is the second-order reaction rate constant (7.2×10^{-12} cm^3 $molecule^{-1}$ s^{-1}) (Li et al., 2012), c_{OH} is the OH concentration (molecules cm^{-3}). For heterogeneous reaction,

$$k_1 = \frac{\gamma \cdot A_S \cdot \omega}{4} \cdot Y_{HONO} \quad (5)$$

where, A_s is the surface area concentration of the reactive surface (m^2 m^{-3}), ω is the

molecular mean speed (m s^{-1}), γ is the uptake coefficient of the precursor, Y_{HONO} is the yield of HONO. For ground surface, the surface area concentration is

$$A_s = \frac{\delta}{H} \quad (6)$$

where δ is the surface roughness, which is calculated according to the mean project area, perimeter and height of the buildings in Beijing.

$$\delta = \frac{f_{building} * (A_{projected} + h * P_{building})}{A_{projected}} + f_{blank} \quad (7)$$

where $f_{building}$ (0.31) and f_{blank} (0.69) are the fraction of the projected area ($A_{projected}$) of buildings and blank space, respectively; $P_{building}$ and h are the perimeter and the height of the building, respectively. The $f_{building}$ and $P_{building}$ are measured from ~1000 buildings randomly selected on the Google Map using ImageJ software. The mean height (44.5 m) of the building in Beijing is linearly extrapolated from the literature data based on remote measurement using Light Detection and Ranging (LiDAR) sensor from 2004 to 2008 (Cheng et al., 2011). The δ in Beijing is calculated to be 3.85, which is slightly higher than the value (2.2) used by Li et al. (2018).

As for photolysis reaction, the first-order reaction rate was

$$k_1 = J \quad (8)$$

where, J is the photolysis rate to produce HONO (s^{-1}).

The loss rates of HONO by photolysis ($L_{photolysis}$), homogeneous reaction with OH radicals ($L_{HONO\text{-}OH}$) and dry deposition ($L_{deposition}$) (Liu et al., 2019c) were calculated according to the following equations.

$$L_{photolysis} = 3600 \cdot J_{HONO} \cdot c_{HONO} \quad (9)$$

$$L_{HONO-OH} = 3600 \cdot k_{HONO-OH} \cdot c_{OH} \cdot c_{HONO} \quad (10)$$

$$L_{deposition} = \frac{3600 \cdot v_d \cdot c_{HONO}}{H} \quad (11)$$

where, J_{HONO} is the photolysis rate of HONO (s^{-1}), $k_{HONO\text{-}OH}$ is the second-order reaction rate constant between HONO and OH (6×10^{-12} cm^3 $molecule^{-1}$ s^{-1}) (Atkinson et al., 2004), and v_d is the dry deposition rate of HONO (0.001 m s^{-1}) (Han et al., 2017).

Vertical transport by advection ($T_{vertical}$), which is an important sink of HONO in the night (Gall et al., 2016;Meng et al., 2019), can be calculated according to equation (12).

$$T_{vertical} = -K_h(z,t)\frac{\partial c(z,t)}{\partial z}\frac{1}{h} \quad (12)$$

where K_h(z,t) is the eddy diffusivity of heat (m^2 s^{-1}) at height z (m) and time t, h is the height of the second layer (18 m in this study) (Gall et al., 2016). On the other hand, both the vertical and horizontal transport can be estimate according to Eq. (13),

$$T_{vertical} = k_{dilution}(c_{HONO} - c_{HONO,background}) \quad (13)$$

where $k_{dilution}$ is a dilution rate (0.23 h^{-1}, including both vertical and horizontal transport) (Dillon et al., 2002), c_{HONO} and $c_{HONO,background}$ is the HONO concentration at the observation site and background site, respectively (Dillon et al., 2002).

In addition, even though all the current known sources had been considered in models, the modelled daytime HONO concentrations were still lower than the observed concentration (Tang et al., 2015;Michoud et al., 2014). Therefore, the HONO concentration could be described in equation (14).

$$\frac{dc_{HONO}}{dt} = E_{soil} + E_{vehicle} + P_{NO-OH} + P_{nitrate} + P_{aerosol} + P_{ground} + P_{unknown} - L_{photolysis} - L_{HONO-OH} - L_{deposition} + T_{vertical} + L_{horizontal} \quad (14)$$

3. Results and discussion

3.1 Overview of the air pollution. The mass concentration of non-refractory $PM_{2.5}$ ($NR\text{-}PM_{2.5}$) and HONO along with metrological parameters are shown in Fig. 1. The time series of other pollutants (SO_2, CO, O_3, benzene, toluene and black carbon) are shown in Fig. S2 in the Supplement information.

Similar to previous measurements (Guo et al., 2014;Wang et al., 2016), the air pollution events showed a periodic cycle of 3-5 days during the observation, as indicated by the concentration of $NR\text{-}PM_{2.5}$ (Fig. 1A), gaseous pollutants and the visibility. During the observation period, 20-60% of hourly $PM_{2.5}$ concentration was higher than 75 μg m^{-3} (the criterion for pollution according to the national air quality standards) in each month (Fig. S3A). Both the frequency of severe polluted episodes and the mean mass concentration of $PM_{2.5}$ and $NR\text{-}PM_{2.5}$ were obviously higher in March than that in the rest months (Fig. 1 and S3). This can be explained by both the intensive emission during the heating season as evidenced by the high concentration of primary pollutants including CO, SO_2 and BC (Table S1) and the stagnant meteorological conditions supported by the low wind speed (<2 m s^{-1}) and the low planetary boundary layer (PBL) height, in particular, in March (Fig. S4A).

OA and nitrate dominated the $NR\text{-}PM_{2.5}$, while their relative contribution varied significantly during the observation (Fig. 1B and Table S1). This is similar to the previously reported $NR\text{-}PM_{1.0}$ composition (Sun et al., 2015). The monthly mean fraction of OA varied from 45.9±10.2 % to 52.6±18.7 %, which was accompanied by a slight increase of sulfate from 16.0±9.1 % to 18.2±8.0 % (Fig. S4D). At the same time, the monthly mean fraction of nitrate and chloride decreased from 26.7±8.8 % to

16.7±12.8 % and from 7.7±6.1 % to 0.3±0.2 %, respectively. Ammonium showed a peak value (14.2±2.8 %) in March, then slightly decreased to 12.2±5.2 %. The intensive emission of chloride from coal combustion during heating season (Cho et al., 2008) and firework burning (Zhang et al., 2017), which was transported from Tangshan during Chinese New Year (Fig. S5A and B), led to high fraction of chloride in February and March. The decrease in nitrate and ammonium fractions from February to June should be related to the increase in temperature (Fig. S2) which was in favor of NH_4NO_3 decomposition (Wang et al., 2015). Besides the reduction of the contribution from other components, secondary formation due to increased UV light (Fig. S4C) might also favor the increased OA fraction (Huang et al., 2014). This means that chemical transformation in March should still be vigorous although the UV light intensity in March is lower than in summer (Fig. S4C). It also implies other factors may compensate the weak UV light intensity in March.

HONO, which has been recognized as the important precursor of primary OH radical (Ren et al., 2006;Alicke et al., 2003), ranged from 0.05 to 10.32 ppbv from February 1 to June 30, 2018 (Fig. 1C) with the mean value of 1.26±1.06 ppbv. In winter (February and March), HONO concentration was 1.15±1.10 ppbv and comparable to the previous results (1.05±0.89 ppbv) measured in the winter of Beijing (Wang et al., 2017b;Hou et al., 2016), while it was slightly lower than that from April to June (1.35±1.11 ppbv) in this work and those measured in the summer of Shanghai (2.31 ppbv, in May) (Cui et al., 2018) and Guangzhou (2.8 ppbv, in July) (Qin et al., 2009). The mean HONO concentration in March (1.53±1.25 ppbv) was higher than that in

February and April (Fig. S3D), while was slightly higher or close to that in May and June. Chamber studies have found that HONO is responsible for the initiation of photosmog reactions (Rohrer et al., 2005). It is reasonable to postulate that HONO probably play an important role in the secondary chemistry of particle formation in March.

3.2 Promotion effect of HONO photolysis on aerosol formation in winter. Oxidation of precursors by OH radicals is the main mechanism regarding to secondary aerosol formation in the troposphere. After partially ruling out the possible influence of PBL variation by normalizing the concentrations of all pollutants to CO (Cheng et al., 2016) or BC (Liggio et al., 2016), we found all secondary species including sulfate, nitrate and ammonium show obvious daytime peaks from 7:00 am to 6:00 pm (Figure S5C) (Cheng et al., 2016). The similar trends were observed after the concentrations of pollutants were normalized to BC (not shown). This suggests they might connect with photochemistry.

Photolysis of H_2O_2, HCHO, O_3 and HONO, and the reaction between NO and HO_2 are known as sources of OH radical in the atmosphere (Alicke et al., 2003;Volkamer et al., 2010;Tan et al., 2018;Tang et al., 2015). In this work, the concentration of H_2O_2, HCHO and HO_2 are unavailable. Thus, their contributions to OH production were not discussed here. However, it has been well recognized that the photolysis of HONO is the dominant source of OH in the dawn and dusk period (Holland et al., 2003), even contributes up to 60% of daytime OH source in winter (Spataro et al., 2013;Rohrer et al., 2005). In addition, it has been confirmed that HONO dominates the primary OH

source at various locations (Tan et al., 2018;Liu et al., 2019c;Tan et al., 2017;Aumont et al., 2003). Therefore, it is meaningful to discuss the contribution of HONO to secondary aerosol formation through OH production. We simply compared the OH production via photolysis of HONO ($P_{OH\text{-}HONO}=J_{HONO}\times c_{HONO}$) and O_3 ($P_{OH\text{-}O3}=J_{O1D}\times c_{O3}$) 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. Under these conditions, local chemistry should be more important as 75 % of the wind speed was less than 1.0 m s^{-1} (Fig. S6). The details about the J_{HONO} and J_{O1D} calculation were shown in the Supplement information and their time series were shown in Fig. S7. On polluted days in winter, the daytime $P_{OH\text{-}HONO}$ was always significantly higher than the $P_{OH\text{-}O3}$ in winter and the maximal $P_{OH\text{-}HONO}$ and $P_{OH\text{-}O3}$ were 1.73±0.86 × 10^7 molecules cm^{-3} s^{-1} (2.43±1.21 ppb h^{-1}) and 1.03±1.06 × 10^7 molecules cm^{-3} s^{-1} (1.45±1.49 ppb h^{-1}), respectively (Fig. 2A). Owing to the high HONO concentration accumulated throughout the night, the maximal $P_{OH\text{-}HONO}$ in winter was as about 2-6 times of that was observed in the wintertime of Colorado, USA (~0.59 ppb h^{-1}) (Kim et al., 2014), New York, USA (~0.40 ppb h^{-1}) (Kanaya et al., 2007) and Nanjing, China (0.90±0.27 ppb h^{-1}) (Liu et al., 2019b). In the period from April to June, the daily maxima of $P_{OH\text{-}HONO}$ and $P_{OH\text{-}O3}$ were 2.48±1.42 × 10^7 molecules cm^{-3} s^{-1} (3.48±1.99 ppb h^{-1}) and 6.51±4.17 × 10^7 molecules cm^{-3} s^{-1} (9.15±5.86 ppb h^{-1}), respectively. These results mean that the photolysis of HONO should play an important role in the initiation of the daytime HO_x and RO_x chemistry on polluted days in winter, while photolysis of O_3 becomes more important from April to June. This is consistent with the previous

findings that HONO photolysis dominants the primary OH source in winter of BTH (Xing et al., 2019;Tan et al., 2018), Colorado and New York City (Ren et al., 2006;Kim et al., 2014), while photolysis of O_3 and HCHO related reactions usually dominated primary OH production in summer (Alicke et al., 2003).

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). We partially ascribe this to the high HONO concentration in winter Beijing. To confirm this assumption, 12 episodes in winter were chosen (Fig. 1) to uncover the connection between aerosol formation and HONO photolysis. The 1st, 3rd and 5th episodes were clean days and the other 9 episodes were typical haze events with duration above 2 days. The features of these episodes were summarized in Table S2. Fig. 2C shows the CO-normalized daytime profiles of OA and HONO in the 7th and 12th episodes as two examples. In all selected cases, HONO exhibited quick reduction due to the photolysis after sunrise, and simultaneously, OA concentration started to increase. This is similar to the evolution of the concentration of pollutants in a typical smog chamber experiment. We further show the formation of OA ($\Delta C_{OA}/C_{CO}$) as a function of the consumed HONO ($-\Delta C_{HONO}/C_{CO}$) in Fig. 2D. Except for the 4th episode that was highly affected by firework emission during the Spring Festival, $\Delta C_{OA}/C_{CO}$ showed a linear dependence on $-\Delta C_{HONO}/C_{CO}$ in winter, and the correlation coefficient was 0.75. 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 HO_x and RO_x chemistry. This kind of correlation could not be seen for the pollution events from April to June because the primary OH production was no longer dominated by HONO photolysis as indicated by Fig. 2D. It should be noted that oxidation of biogenic alkenes by O_3 might also contribute to OA formation. However, anthropogenic VOCs instead of biogenic VOCs dominated the wintertime VOCs in Beijing (Liu et al., 2017a). Although vehicles can emit isoprene (Zou et al., 2019), the contribution of isoprene to the observed increase of OA concentration should be unimportant due to the low concentration of isoprene in winter (Zou et al., 2019). Therefore, it is reasonable to conclude that the increase of OA concentration in daytime might be mainly resulted from oxidation of VOCs by OH.

Similar to OA, $\Delta C_{nitrate}/C_{CO}$ in winter also showed good linear correlation with $-\Delta C_{HONO}/C_{CO}$ (R=0.67, Fig. S5E), suggesting that the increase of particle-phase nitrate in the daytime should also be promoted by OH radical from HONO photolysis. Interestingly, $\Delta C_{ammonium}/CO$ also showed a good correlation with $-\Delta C_{HONO}/C_{CO}$ (R=0.61, Fig. S5E), although particle-phase ammonium should not be directly related to oxidation of NH_3 by OH. 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. This was consistent with the recent work which observed the important role of

372 photochemical reactions in daytime nitrate formation, while hydrolysis of N_2O_5 mainly
373 contributed to nighttime nitrate (Tian et al., 2019). Although a recent work has found
374 that daytime hydrolysis of N_2O_5 on hygroscopic aerosols is also an important source of
375 daytime nitrate in winter Beijing (Wang et al., 2017a), the linearly correlation between
376 $\Delta C_{nitrate}/C_{CO}$ and $\Delta C_{HONO}/C_{CO}$ at least implies that the promotion effect of HONO on
377 nitrate formation could not be excluded. On the other hand, the correlation between
378 $\Delta C_{sulfate}/C_{CO}$ and $-\Delta C_{HONO}/C_{CO}$ was much weaker (R=0.26), suggesting a weak
379 connection between particle-phase sulfate and gas-phase H_2SO_4. This was also
380 consistent with the previous understanding that heterogeneous reactions of SO_2 were
381 the dominant pathway for sulfate formation (Zheng et al., 2015a;He et al., 2018;Zhang
382 et al., 2020). Overall, this work well supported the recent modeling results that HONO
383 could obviously promote the aerosol production in winter (Zhang et al., 2019a;Zhang
384 et al., 2019c;Xing et al., 2019;An et al., 2013) from the point of view of observation.
385 **3.3 HONO budget in polluted events.** To understand the possible sources of HONO
386 in polluted events in winter, the HONO budget was calculated for the events when the
387 $PM_{2.5}$ concentration was larger than 50 μg m^{-3} and the RH was less than 90 % according
388 to the method described in Section 2.2.
389 **Vehicle emission.** The $E_{vehicle}$ was calculated according to Eq. (2) using the relative
390 emission rate of HONO to NO_x and the emission inventory of NO_x from vehicles. Firstly,
391 the ratio of HONO/NO_x was calculated according to the method reported by Xu et al.
392 (Xu et al., 2015) and Li et al. (Li et al., 2018) from the fresh nighttime plumes which
393 were strictly satisfy the following criteria: 1) NO_x > 45 ppb (highest 25% of NO_x data);

2) $\Delta NO/\Delta NO_x > 0.8$, with good correlation between NO and NO_x ($R > 0.9$, $P < 0.05$); 3) Good correlation between HONO and NO_x ($R^2>0.65$, $P < 0.05$); and 4) Dataset from 5:00 am to 8:00 am. The mean emission ratio of HONO to NO_x was 1.8±0.5% based on 5 fresh vehicle exhaust plumes during our observation (Table S3). This value is higher than that in Hongkong (1.2±0.4%) (Xu et al., 2015), Beijing (1.3%) (Zhang et al., 2019d) and Jinan (0.53±0.20%) (Li et al., 2018) using the same method, while is comparable with the result measured in tunnel experiments (2.1%) carried out in Beijing (Yang et al., 2014). Secondly, low HONO concentration should be companied with high NO_x and high ratio of $\Delta NO/\Delta NO_x$ if direct emission from vehicles was the major source of HONO and the source from secondary formation was negligible in the urban atmosphere. Therefore, we further estimated the HONO/NO_x ratio using a low limit correlation method (Li et al., 2012). In the 2D space of HONO verse NO_x (Fig. S8), the lowest marge with ΔNO/ΔNOx larger than 0.8 were chosen for linear correlation. The ratio of ΔHONO/ΔNOx is 1.17±0.05%. This value is lower than that estimated through empirical method discussed above, while is very close to that measured in Hongkong (1.2±0.4%) (Xu et al., 2015) and (1.23±0.35%) (Liang et al., 2017), Guangzhou (1.0%) (Li et al., 2012) and Beijing (1.3% and 1.41 %) (Zhang et al., 2019d;Meng et al., 2019). Finally, several studies have measured the direct emission of HONO from vehicle exhaust. The HONO/NO_x was 0.18% from gasoline cars through chassis dynamometer tests in China (Liu et al., 2017d), while it was 0-0.95% for gasoline vehicles and 0.16-1.0 % for diesel vehicles measured under real-world driving test cycles in Japan (Trinh et al., 2017). Thus, three levels of vehicle emission factor

were considered. 1.17±0.05% was taken as the middle value which was very close to the mean emission ratio (1.21) for all of these reported values in China (Li et al., 2018;Xu et al., 2015;Yang et al., 2014;Liu et al., 2017d;Gall et al., 2016;Meng et al., 2019), while 0.18% (Liu et al., 2017d) and 1.8 % were the lower limit and the upper limit, respectively.

The $E_{vehicle}$ was calculated using the hourly NO_x emission inventory from vehicles in Beijing (Yang et al., 2019) after converted to emission flux of HONO ($F_{HONO}=F_{NOx}\times$ HONO/NO_x) and 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. The calculated hourly middle value of $E_{vehicle}$ using the HONO/NO_x of 1.17% was from 0.085±0.038 to 0.34±0.15 ppbv h^{-1}, which was slightly higher than the daytime emission rate of HONO in Xi'an (Huang et al., 2017b). This is reasonable when the vehicle population in Beijing is taken into consideration. The lower limit of $E_{vehicle}$ was 0.013±0.006-0.053±0.023 ppbv h^{-1}, which was close to the estimated emission rate of HONO in Jinan (Li et al., 2018). The upper limit was in the range of 0.13±0.06-0.53±0.23 ppbv h^{-1}.

Soil emission. The emission flux of HONO from soil depends on the water content, the nitrogen nutrient content and the temperature of soil (Oswald et al., 2013). Oswald et al. (2013) measured the emission flux of HONO from 17 soil samples, including eucalyptus forest, tropical rain forest, coniferous forest, pasture, woody savannah, grassland, stone desert, maize field, wheat field, jujube field an cotton field etc. Tropical rain forest, coniferous forest and grassland are the typical plants in downtown Beijing

(Huang et al., 2017a). At the same time, their emission fluxes of HONO are comparable (Oswald et al., 2013). Thus, we used the emission flux from grassland to calculate the emission rate of HONO from soil in Beijing because the temperature and water holding content dependent emission flux of HONO was available for grassland soil. Three levels of water content including 25-35%, 35-45% and 45-55% were considered. The temperature dependence of F_{HONO} was calculated using the mean value of the F_{HONO} with different water content, while the low limit and upper limit of F_{HONO} were calculated using the emission flux from 45-55% of water content and 25-35% of water content, respectively. The lower limit, the middle value and the upper limit of the E_{soil} are 0.0032±0.0027-0.013±0.014, 0.0046±0.0039-0.020±0.20 and 0.0057±0.0047-0.025±0.024 ppbv h^{-1}, respectively, calculated according to Eq. (2).

Homogeneous reaction between NO and OH. Direct measurement of OH concentration was unavailable in this work, while several methods were used to estimate the ambient OH concentration. In winter in Beijing, it has been found that the OH concentration is linearly correlated with J_{O1D}, that's, $c_{OH}=J_{O1D}\times 2\times 10^{11}$ molecules cm^{-3} (Tan et al., 2019). However, Tan et al. (2018) reported a larger conversion factor (4.33×10^{11} molecules cm^{-3}). Li et al. (2018) estimated the OH radical concentration considering both photolysis rate and NO_2 concentration, namely,

$$c_{OH} = \frac{4.1\times 10^{9}\times (J_{O1D})^{0.83}\times (J_{NO_2})^{0.19}\times (140 c_{NO_2}+1)}{0.41 c_{NO_2}^{2}+1.7 c_{NO_2}+1} \quad (15)$$

Overall, the estimated OH concentrations according to Eq. (15) were comparable with that estimated by Tan et al. (2019) (Fig. S10C). The method for the photolysis rates calculation were shown in the SI and the time series of the photolysis rates were shown

in Fig. S7. On polluted days, high concentration of NO_2 resulted into lower OH concentrations estimated using the Eq. (15). Therefore, the corresponding $P_{NO\text{-}OH}$ was taken as the low limit for homogeneous reaction between NO and HONO because polluted events were discussed in this work, while $P_{NO\text{-}OH}$ calculated using the OH concentration (J_{O1D}×4.33×10^{11} molecules cm^{-3}) (Tan et al., 2018) was taken as the upper limit and $P_{NO\text{-}OH}$ calculated using the OH concentration (J_{O1D}×2×10^{11} molecules cm^{-3}) (Tan et al., 2019) was the middle value. In the night, OH concentration usually varied from 1.0×10^5 molecules cm^{-3} (Li et al., 2012;Tan et al., 2018) in winter to 5×10^5 molecules cm^{-3} in summer (Tan et al., 2017). The nighttime OH concentration was estimated linearly correlated with the product of nighttime O_3 concentration and alkenes concentration, namely,

$$c_{OH,night} = 1 \times 10^5 + 4 \times 10^5 \times \frac{(c_{O_3} \times c_{alkenes})_{night} - (c_{O_3} \times c_{alkenes})_{night,min}}{(c_{O_3} \times c_{alkenes})_{night,max} - (c_{O_3} \times c_{alkenes})_{night,min}} \quad (16)$$

The time series of OH concentration calculated using different methods was shown in Fig. S11. Thus, the lower limit, the middle value and the upper limit of $P_{NO\text{-}OH}$ were 0.007±0.019-0.43±0.26, 0.026±0.053-0.99±0.79 and 0.028±0.053-2.14±1.71 ppbv h^{-1}, respectively, calculated according to Eqs. (3) and (4). The calculated middle value of $P_{NO\text{-}OH}$ (with mean daytime value of 0.49±0.35 ppb h^{-1}) was comparable with these estimated values by Li et al. (2018) (0.4 ppb h^{-1}) and Huang et al. (2017b) (0.28 ppb h^{-1}). It should be noted that measured NO concentration was used to calculate the $P_{NO\text{-}OH}$. Besides vehicle emission, power plant and industries also contribute NO emission. 40 % of NOx was from vehicle emission according to the emission inventory of NO_x in Beijing (He et al., 2002).

It should be noted that OH concentration was estimated based on J_{O1D} (Tan et al., 2019;Tan et al., 2018) or J_{O1D} and J_{NO2} (Li et al., 2018). As discussed in Section 3.2, HONO was an important primary OH source in the daytime. Unfortunately, it could not be parameterized for calculating OH concentration because the measured or modelled OH concentration was unavailable in this work. This might underestimate the early daytime OH concentration, subsequently, the contribution of homogeneous reaction of NO with OH to HONO source. This need to be further investigated in the future.

Photolysis of nitrate. A recent work reported the photolysis rate of nitrate ($J_{nitrate}$) in ambient $PM_{2.5}$ at a solar zenith angle of 0° (Bao et al., 2018). The $J_{nitrate}$ varied from 1.22×10^{-5} to 4.84×10^{-4} s^{-1} with the mean value of 8.24×10^{-5} s^{-1}. These values were further normalized according to the zenith angle and UV light at our observation station to calculate the low limit, the upper limit and the middle $J_{nitrate}$. The time series of the measured nitrate concentration and the middle value of $J_{nitrate}$ were shown in Fig. 1 and Fig. S7, respectively. Therefore, the corresponding daytime lower limit, the middle value and the upper limit of HONO from photolysis of nitrate were 0.0011±0.0021-0.096±0.092, 0.0072±0.0021-0.66±0.092 and 0.042±0.082-3.86±0.008 ppbv h^{-1}, respectively, calculated in the light of Eqs. (3) and (8).

Heterogeneous reactions of NO_2 on aerosol and ground surface. The production of HONO from heterogeneous reactions of NO_2 on aerosol surface was calculated according to Eqs. (3) and (5). The aerosol surface concentration was measured with a SMPS. The uptake coefficient (γ) of NO_2 on different particles varied from 5×10^{-9} to 9.6×10^{-6} (Ndour et al., 2009;Underwood et al., 2001;Underwood et al., 1999), while it

was recommended to be 1.2×10^{-8} (Crowley et al., 2010), which was used to calculate the $P_{aerosol}$ in the base case. It has been found that the γ highly depends on the relative humidity (RH). The low limit bound of $P_{aerosol}$ was calculated based on the RH dependent uptake coefficient of NO_2 on kaolinite ($\gamma_{NO2}=4.47\times10^{39}/(1.75\times10^{46}+1.93\times10^{45}RH)$), while the upper limit of $P_{aerosol}$ was calculated according to the RH dependent γ on hematite ($\gamma_{NO2}=4.46\times10^{39}/(6.73\times10^{44}+3.48\times10^{44}\,RH)$ (Liu et al., 2015). Heterogeneous reaction of NO_2 on black carbon (BC) was also considered in the night. The surface area concentration of BC was calculated according to its specific area (87 $m^2\ g^{-1}$) (Su et al., 2018) and the measured mass concentration. The γ_{NO2} on BC is 1.17×10^{-5}, with a HONO yield of 0.8 (Han et al., 2013). The light enhanced uptake γ of NO_2 (1.9×10^{-6}) on mineral dust was further parameterized (Ndour et al., 2008) after normalized to the solar radiation intensity in Beijing.

The contribution of heterogeneous reaction of NO_2 on ground surface was calculated similar to that on mineral dust. The same kinetics for heterogeneous reaction of NO_2 on aerosol surface were used to calculate the nighttime contribution of ground surface. A recent work observed a significant enhancement of NO_2 and HONO formation by UV light on the real urban grime (Liu et al., 2019a). Thus, RH dependent kinetic data measured on urban grime ($\gamma_{NO2}=7.4\times10^{-7}+5.5\times10^{-8}\ RH$) was used to calculate the daytime upper limit for heterogeneous uptake of NO_2 on the ground surface. The A_s of aerosols varied from 1×10^{-4} to 4.8×10^{-3} m^{-1} with a mean value of $1.4\pm0.5\times10^{-3}$ m^{-1} during pollution events. This value is comparable with that used in modeling studies (Zhang et al., 2016;Aumont et al., 2003). The A_s of ground surface

526 which was calculated according to Eq. (6) and (7) varied from 1.5×10^{-3} to 3.85×10^{-2} m^{-1}
527 with a mean value of $1.3\pm0.9\times10^{-2}$ m^{-1} during pollution events. The surface roughness
528 was 3.85 calculated according to Eq. (7). The Y_{HONO} was set to 0.5 because of the
529 hydrolysis reaction of NO_2 (Liu et al., 2015), while it was 0.8 for light enhanced
530 reaction (Liu et al., 2019a;Ndour et al., 2008) and on BC (Han et al., 2013).

531 The lower limit, the middle value and the upper limit of $P_{aerosol}$ were 0.038±0.030-
532 0.087±0.072, 0.038±0.030-0.088±0.072 and 0.041±0.032 - 0.092±0.073 ppbv h^{-1},
533 respectively. The corresponding values were 0.00027±0.00017-0.0020±0.0012,
534 0.0014±0.00095-0.0089±0.006 and 0.0025±0.0023-0.060±0.032 ppbv h^{-1} for P_{ground}.
535 Although the A_s of ground surface was higher than that of aerosol, the larger γ_{NO2}
536 (1.17×10^{-5}) on soot particles than that on other aerosols and ground surface led to a
537 larger production rate of HONO in this work. The $P_{aerosol}$ calculated in this work was
538 on the same orders as soil emission, while it was lower than the $P_{aerosol}$ estimated by
539 Huang et al. (Huang et al., 2017b) because different calculation methods have been
540 used. In their work, the production rate of HONO was estimated based on the
541 conversion rate (Huang et al., 2017b), whilst it was calculated based on the measured
542 aerosol surface area concentration and uptake coefficient of NO_2 on different particles
543 in this work.

544 It should be pointed out that HONO production from heterogeneous reaction of
545 NO_2 on both aerosol and ground surface greatly depend on the $\gamma_{NO2, BET}$ and A_s. The A_s
546 of aerosols was comparable with the modeling input. However, the small nighttime $\gamma_{NO2,}$
547 $_{BET}$ (10^{-8} - 10^{-7}) on dust were used in this work rather than the $\gamma_{NO2, BET}$ (1×10^{-6}) used in

548 modelling studies (Zhang et al., 2016;Aumont et al., 2003;Gall et al., 2016). This leads
549 to a lower production rate of HONO from heterogeneous reaction of NO_2 on aerosols.
550 As for heterogeneous reaction of NO_2 on ground surface, besides the small $\gamma_{NO2,\ BET}$
551 used in this work, the A_s of ground surface (0.0015 to 0.0385 m^{-1}) calculated using the
552 surface roughness and PBL height was also significantly lower than the fixed value of
553 0.3 m^{-1} in modeling studies that might overestimate the contribution of HONO
554 production from heterogeneous reaction of NO_2 on ground surface. It should be noted
555 that the initial uptake coefficient (γ_{ini}) was parameterized in this work. This will
556 overestimate the contribution of heterogeneous reaction of NO_2 to HONO source
557 because the steady-state uptake coefficient is usually one order of magnitude lower than
558 γ_{ini} (Han et al., 2013;Liu et al., 2015). These results mean that heterogeneous reaction
559 might not be a major HONO source. This is consistent with a recent work that found
560 heterogeneous reaction being unimportant when compared with traffic emission during
561 haze events in winter in Beijing (Zhang et al., 2019d).
562 **Sinks of HONO.** The loss rates of HONO by photolysis ($L_{photolysis}$), homogeneous
563 reaction with OH radicals ($L_{HONO\text{-}OH}$) and dry deposition were calculated according to
564 Eqs. (9)-(11). The daytime J_{HONO} varied from 1.71×10^{-5} to 1.13×10^{-3} s^{-1} on polluted
565 days in winter, while it was in the range of 5.89×10^{-5} to 1.53×10^{-3} s^{-1} from April to June.
566 These values are comparable to modelling results (3.9×10^{-5}-1.8×10^{-3} s^{-1}) (Gall et al.,
567 2016). The daytime $L_{photolysis}$ were in the range of 0.03-5.23 ppb h^{-1} and 0.25-7.10 ppb
568 h^{-1} in winter and the rest months, respectively. It was the major sink of HONO in the
569 daytime. The $L_{HONO\text{-}OH}$ varied from 0.0049 to 0.069 ppbv h^{-1} in winter using the $k_{HONO\text{-}}$

570 $_{OH}$ of 6×10^{-12} cm^3 $molecule^{-1}$ s^{-1} (Atkinson et al., 2004) and the middle value of OH
571 concentrations. It was from 0.0050 to 0.085 ppbv h^{-1} from April to June. The $L_{deposition}$
572 was in the range of 0.004-0.056 ppbv h^{-1} in winter and 0.004-0.030 ppbv h^{-1} from April
573 to June, calculated according to Eq. (11).

574 As pointed in Section 2.2, vertical transport by advection is an important nocturnal
575 sink of HONO (Gall et al., 2016). In this work, the vertical distribution of HONO
576 concentration is unavailable. Recently, Meng et al. (2019) measured the vertical
577 distribution of HONO in Beijing in December, 2016. The concentration of HONO
578 showed nearly flat profiles from ground level to 240 m in pollution events after sunset,
579 while negative profiles of HONO were observed in pollution events during night (Meng
580 et al., 2019). The nighttime concentration gradient was 0.0047±0.0025 ppb m^{-1} derived
581 from the nighttime dataset (Meng et al., 2019). In the daytime, we assume a zero
582 concentration gradient. On the other hand, the eddy diffusivity of heat in urban
583 environment was measured in New Delhi, Indian (Yadav et al., 2003). Using their
584 dataset with the wind speed lower than 2.0 m s^{-1}, we derived the relationship between
585 the K_h and the wind speed (WS) (K_h=0.9389×WS-0.3374 m^2 s^{-1}). The nighttime $T_{vertical}$
586 changed from 0.15 to 0.37 ppbv h^{-1} in winter, while it was from 0.12 to 0.68 ppbv h^{-1}
587 according to Eq. (12) from April to June. Because the wind speed was usually lower
588 than 1.0 m s^{-1} in pollution events (Fig. S6), horizontal transport should have little
589 influence on the daytime sources or sinks of HONO because of the short lifetime of
590 HONO (Spataro and Ianniello, 2014). In the night, 79 % of the wind speed was lower
591 than 1.0 m s^{-1} in winter, thus the air masses from suburban areas should have influence

on the sources and sinks of HONO in Beijing. If the HONO concentration at background was zero, the vertical and horizontal transport rate of HONO varied from 0.17 to 0.61 ppbv h^{-1} which is calculated in the light of Eq. (13) on haze days in winter and from 0.15 to 0.74 ppbv h^{-1} in pollution events from April to June. These values were higher than that calculated according to Eq. (12). Because the background HONO concentration was unavailable, we only considered the nighttime transport calculated according to Eq. (12) in the following section.

Comparison among different HONO sources. Fig. 3 summarizes the diurnal patterns of each sources with different parameterizations during the pollution events from February to March. The black dots and lines mean the middle values, while the shadow indicates the corresponding lower bound and upper bound. In the nighttime, vehicle and soil emission, and homogeneous reaction between NO and OH were the important sources of HONO. In the daytime, however, photolysis of nitrate and homogeneous reaction between NO and OH dominated the sources of HONO. Heterogeneous reactions of NO_2 on aerosol surface and ground surfaces were not the major HONO source during night unlike the modelled results (Zhang et al., 2016;Aumont et al., 2003).

Fig. 4A-F shows the HONO budget estimated using the middle values among these parameters during the polluted events. The mean production rate of HONO varied in the range of 0.25 - 1.81 ppbv h^{-1} from these identified sources, while the corresponding loss rate was from 0.21 to 2.34 ppbv h^{-1} during the polluted events in winter. The main loss of HONO was the photolysis during the daytime (1.74± 0.44 ppbv h^{-1}), whereas it was vertical transport in the nighttime (0.28±0.08 ppbv h^{-1}). Direct emission from

vehicles exhaust was the largest nighttime source of HONO (0.23±0.06 ppbv h^{-1}), followed by heterogeneous reactions of NO_2 on the ground surface (0.07±0.01 ppbv h^{-1}), homogeneous reaction between NO and OH (0.04±0.01 ppbv h^{-1}), emission from soil (0.014±0.005 ppbv h^{-1}), and heterogeneous reactions of NO_2 on aerosol surface (0.006±0.002 ppbv h^{-1}). $P_{NO\text{-}OH}$ and $P_{nitrate}$ dominated the daytime HONO production, with daytime mean values of 0.49±0.35 ppbv h^{-1} and 0.34±0.23 ppbv h^{-1}, respectively. As shown in Fig. 4, these six sources still underestimated the daytime sources of HONO. The $P_{unknown}$ was 0.20±0.24 ppbv h^{-1} in February and March, while it was 0.50±0.24 ppbv h^{-1} from April to June.

The $E_{vehicle}$ contributed 57.0±10.0% and 51.5±20.1% to the nighttime HONO sources from February to March and the rest months, respectively, even when the $P_{unknown}$ was taken into consideration. The relative contribution of daytime $E_{vehicle}$ decreased to 15.2±15.4% in winter and 9.7±7.8% from April to June. Thus, the daily mean fraction of the $E_{vehicle}$ was 39.6±24.3% and 34.0±24.3% from February to March and from April to June, respectively. This means that the $E_{vehicle}$ dominates the nighttime HONO source during the polluted events in Beijing, which is consistent with the previous result that vehicle emission was the major nighttime or haze day HONO source (51.1 % -52 %) in Beijing (Zhang et al., 2019c;Meng et al., 2019). As pointed out in Section 3.3, $E_{vechicle}$ was calculated based on the NO_x inventory from vehicle sector. On the other hand, NO is prone to be quickly converted to NO_2 and NO_z (including HONO, HNO_3, N_2O_5, PAN and organonitrate etc) by O_3, HO_2, RO_2 and OH in the atmosphere. It is reasonable to assume that local traffic emission dominates the ambient NO source

636 in the urban environment. Thus, homogeneous reaction between NO and OH in the
637 atmosphere could also be related to vehicle exhaust. As shown in Fig.3, although the
638 diurnal curve of $P_{NO\text{-}OH}$ coincided well with that of OH concentration (Fig. S10), which
639 means the $P_{NO\text{-}OH}$ should be mainly determined by OH concentration, the $P_{NO\text{-}OH}$ should
640 still reflect the indirect contribution of traffic related emission to HONO source because
641 the ambient NO concentration was used to calculate the $P_{NO\text{-}OH}$. Traffic-related HONO
642 sources ($E_{vehicles}$ +$P_{NO\text{-}OH}$) might contribute 57.8±15 .8% and 48.6±15.9 % to the daily
643 HONO source in winter and the rest months, respectively. Even if 40 % of NO_x was
644 from vehicle exhaust in Beijing (He et al., 2002), traffic-related source ($E_{vehicles}$ +
645 0.4$P_{NO\text{-}OH}$) might still contribute 46.9±20.5 % in winter and 39.9±20.5 % from April to
646 June to the corresponding daily HONO source. The contribution of traffic-related
647 source was still an important daytime source of HONO (43.9±10.6 % for $E_{vehicles}$ +$P_{NO\text{-}OH}$, and 26.7±12.4 % for $E_{vehicles}$ + 0.4$P_{NO\text{-}OH}$) on polluted days in winter.

649 As shown in Fig. 3, uncertainties existed when calculating each HONO source. To
650 further understand the role of traffic emission, we also estimated the lower limit of the
651 traffic-related contribution as follows: 1) the lower limit of $E_{vehicle}$ was obtained by
652 using the lowest reported emission ratio of HONO/NO_x from vehicles (0.18%) (Liu et
653 al., 2017d) rather than 1.17%, which was the empirical value calculated based on the
654 field measurement in Fig. S7; 2) the lower limit for homogeneous reaction between NO
655 and OH radical was calculated according to the method by Li et al. (2018); 3) the upper
656 limit of the emission rate from soil was estimated using the emission flux of HONO
657 with low water content (Oswald et al., 2013); 4) the upper limit of HONO production

rate from heterogeneous reaction of NO_2 on the aerosol was calculated using the large RH-dependent uptake coefficient of NO_2 on hematite (Liu et al., 2015) rather the value recommended by Crowley et al. (Crowley et al., 2010); 5) the upper limit for heterogeneous reaction on ground surface was calculated using the RH-dependent kinetic data measured on urban grime (Liu et al., 2019a). As shown in Fig. 5, traffic-related source ($E_{vehicles}$ + $P_{NO\text{-}OH}$) contributed 25.7±15.8 % to the daily HONO sources in winter if all NO was assumed to be dominated by local traffic emission, while it was 14.5±15.8 % when 40 % of NO was considered as local traffic emission (He et al., 2002). Under this circumstance, the daytime $P_{unknown}$ of HONO in winter increased to 0.83±0.36 ppbv h^{-1}, which was corresponding to 58.1±8.6 % of the HONO source. This means these assumptions might underestimate the contribution of the HONO sources. In addition, P_{ground}, $P_{aerosol}$ and $P_{nitrate}$ could be also partially related to traffic emission of NO_x (Lee et al., 2016;Tan et al., 2017). These results mean that the contribution of traffic-related emission might be larger than our estimation in this work. Therefore, our work at least suggests that traffic related emission should be a very important HONO source in winter Beijing although more work is required based on comprehensive modelling studies.

4. Conclusions and atmospheric implications.

In this work, the promotion effect of HONO on aerosol mass formation in polluted events was observed based on the good correlation between the growth of OA and nitrate mass concentration and the consumed HONO from early morning to noon during the polluted days in winter. This promotion effect could be related to OH production

680 from photolysis of HONO on aerosol formation followed by oxidation process of the
681 corresponding precursors. Our observation supports well the recent modelling studies
682 that HONO may significantly promote secondary aerosol mass formation (Zhang et al.,
683 2019a;Zhang et al., 2019c;Xing et al., 2019;An et al., 2013). Based on budget analysis
684 calculations, traffic-related sources (direction emission and conversion of NO from
685 vehicle emission) was found to be an important contributor to HONO source during
686 polluted days in winter in Beijing. This means that HONO from the traffic-related
687 sources can have an important role in aerosol mass formation in the atmosphere.

688 Vehicle population in China is increasing very quickly (Liu et al., 2017b;Wang et
689 al., 2011). Thus, the negative influences of the vehicle emission on air quality will
690 increase especially in populous metropolitan areas (Yang et al., 2019;Guo et al., 2020),
691 such as Beijing and Shanghai, if targeted pollution control technologies are not applied.
692 It has been estimated that the vehicles emission accounted for over 40% of total urban
693 NO_x emissions in Beijing (He et al., 2002). In the atmosphere, NO_x involves very
694 complicated reaction network, from which finally leads to aerosol mass formation and
695 production of ozone in VOC limited environment. At the same time, reactions of NO_x
696 also leads to some reactive NO_z species (Seinfeld and Pandis, 2006). In particular,
697 HONO is an important precursor of OH, which governs the conversion of primary
698 pollutants to secondary pollutants in the atmosphere. Besides indirect production of
699 HONO from NO, the vehicles also directly emits HONO as discussed in this work.
700 Even if the low limit of emission factor was used to calculating the HONO source from
701 the vehicles, the traffic-related emission can still be an important source of HONO in

winter Beijing. Therefore, this work implies that mitigation of HONO and NO_x emission from vehicles might be an effective way to reduce secondary aerosol mass formation and can have a positive effect on severe haze events in wintertime Beijing.

It should be pointed out that we only considered O_3 and HONO when discussing the sources of OH. Other sources such as HO_2 (and RO_2) with NO, ozonolysis of alkenes and photolysis of OVOCs might also contribute to OH radicals in the atmosphere (Tan et al., 2018). In the future it will be vital to comprehensively analyze OH sources and to quantify the role of HONO in secondary aerosol mass formation although photolysis of HONO is the major OH source in winter. On the other hand, as discussed in Section 3.3, uncertainties about the HONO budget might originate from the emission factors, OH concentration, and reaction kinetics and so on. The source of HONO from vehicles was calculated based on the emission inventories, which should have a significant bias (Squires et al., 2020). For example, the emission flux of NO_x calculated using the emission inventory from Yang et al. (2019) is as 2.4±0.5 times as the reported emission flux reported by Squires et al. (2020). To take the next step, it is required to measure the emission factors from vehicle exhaust under real road conditions in the future. When calculating the OH concentration, the factor between OH concentration and J_{O1D} might vary over locations and seasons due to different NO_x/VOCs ratio (Holland et al., 2003). Direct measurements of OH concentration would be helpful for decreasing the uncertainty of both OH sources and HONO budget analysis. Finally, it is necessary to quantify the contribution of traffic-related source of HONO on secondary aerosol formation based on modelling studies in the future.

Data availability. The experimental data are available upon request to the corresponding authors.

Supplement. The supplement related to this article is available online at:

Competing interests. The authors declare that they have no conflict of interest.

Author information

Author contributions. YL, WW and MK designed the experiments. YL wrote the paper and performed HONO budget analysis. YZ, CL, WW, YC, MG and XW carried out HONO measurement. ZF, FZ, JC, WD and KD did aerosol composition measurements. BC and JK did particle size measurements. YW, BH and YW analyzed meteorological data analysis. CY, FB, JK, TP, HH, MG and MK revised the manuscript.

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Figure captions

Fig. 1. An overviewed measurement of non-refractory-$PM_{2.5}$ (NR-$PM_{2.5}$), HONO, NOx, $PM_{2.5}$ and meteorological parameters from Feb. 1 to July 1, 2018. (A) the mass concentration of different components of $PM_{2.5}$, (B) the mass fraction of individual component, (C) HONO and NOx concentration, (D) temperature and RH, (E) wind speed and wind direction, (F) UVB and PBL height and (G) visibility and $PM_{2.5}$ concentration during observation. We consider the period before Apr. 1 as winter. During the winter period, 12 cases are selected and numbered, including three clean cases (1, 3, and 5, marked in yellow) and the rest 9 pollution episodes (marked in blue).

Fig. 2. Contribution of HONO to OH production and correlation between OA and HONO concentration. Diurnal production rates of OH from photolysis of HONO and O_3 on polluted days with $PM_{2.5}$ concentration larger than 50 μg m^{-3} and RH less than 90 % (A) from Feb 1 to Mar 31, (B) from Apr 1 to Jun 30; (C) Daytime variation of OA/CO and HONO/CO concentration for the 7^{th} and 12^{th} episodes and (D) correlation of the daytime OA/CO increased and consumed HONO/CO.

Fig. 3. Diurnal pattern of HONO sources calculated with different parameterizations. The low bound, the middle value, and upper bound of (A) soil emission calculated based on 45-55%, 35-45% and 25-35% of water content, (B) vehicle emission with relative emission factor to NOx of 0.18%, 1.17±0.05% and 1.8 %, (C) production from reaction between NO and OH, whose concentration estimated using Xu (Xu et al., 2015), (Tan et al., 2019)

Fig. 4. The budget of HONO (A) and (B) Diurnal production rates of HONO, (C) and

(D) loss rates of HONO, (E) and (F) relative contribution of each source on polluted days with $PM_{2.5}$ concentrations higher than 50 μg m^{-3} and RH less than 90 %. The left column shows the data from February 1 to March 31) and the right one shows the data from April 1 to June 30.

Fig. 5. (A)-(B) Diurnal production rates and (C)-(D) diurnal loss rates of HONO; (E)-(F) relative contribution of HONO sources on polluted days with $PM_{2.5}$ concentrations higher than 50 μg m^{-3} and RH less than 90 %. The $E_{vehicle}$ is calculated using the low limit of HONO/NOx from vehicles (0.18%) (Liu et al., 2017d) and the $P_{NO\text{-}OH}$ is calculated using the low limit of OH concentration, while the upper limit of E_{soil}, $P_{aerosol}$ and P_{ground} are used as described in the text.

Figures

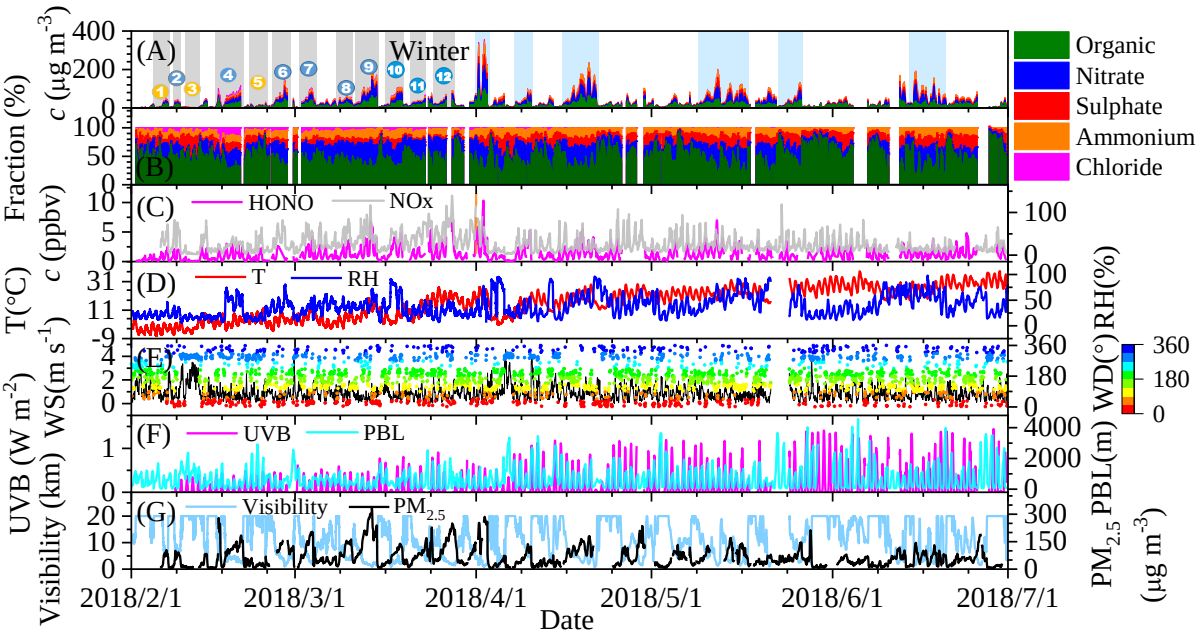


Fig. 1.

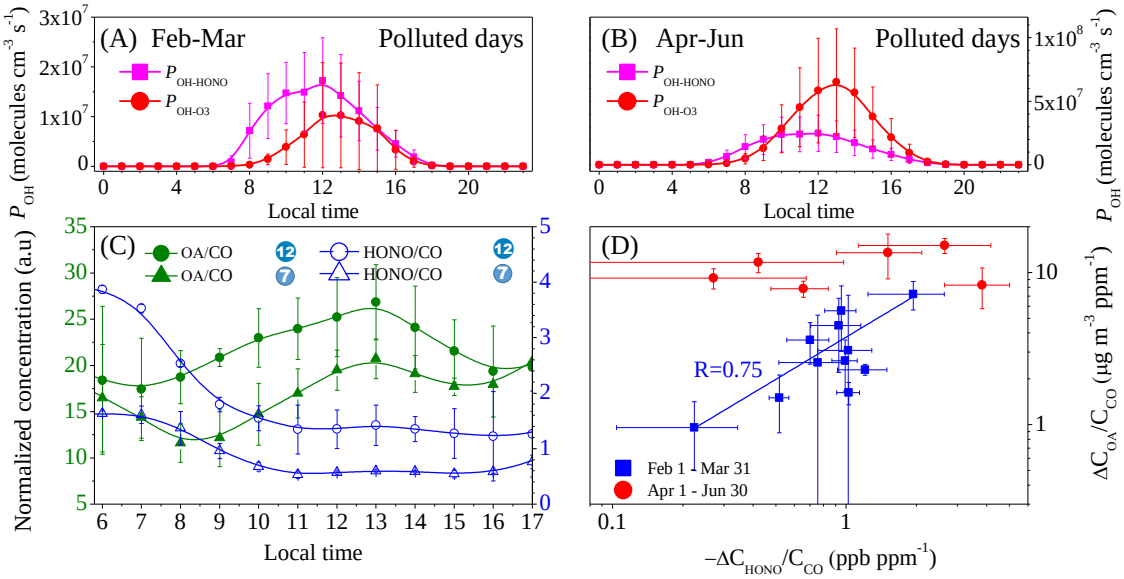
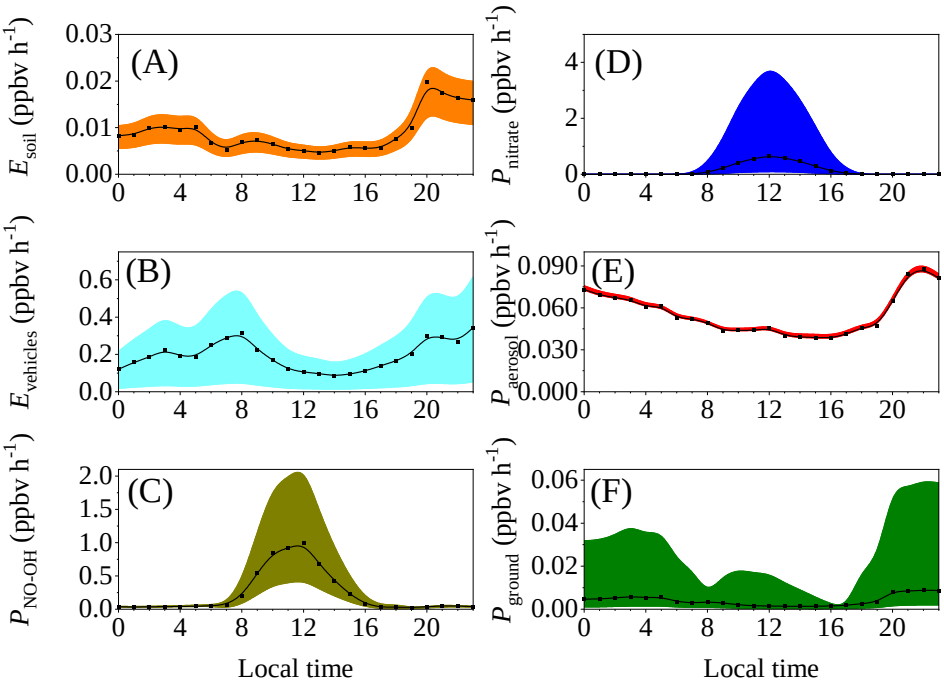

(A) Feb-Mar
Polluted days
$P_{OH-HONO}$
P_{OH-O3}
Local time
(B) Apr-Jun
Polluted days
$P_{OH-HONO}$
P_{OH-O3}
Local time
P_{OH} (molecules cm^{-3} s^{-1})
(C)
OA/CO
OA/CO
HONO/CO
HONO/CO
Normalized concentration (a.u)
Local time
(D)
R=0.75
Feb 1 - Mar 31
Apr 1 - Jun 30
$-\Delta C_{HONO}/C_{CO}$ (ppb ppm^{-1})
$\Delta C_{OA}/C_{CO}$ (μg m^{-3} ppm^{-1})

Fig. 2.



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1182 **Fig. 3**

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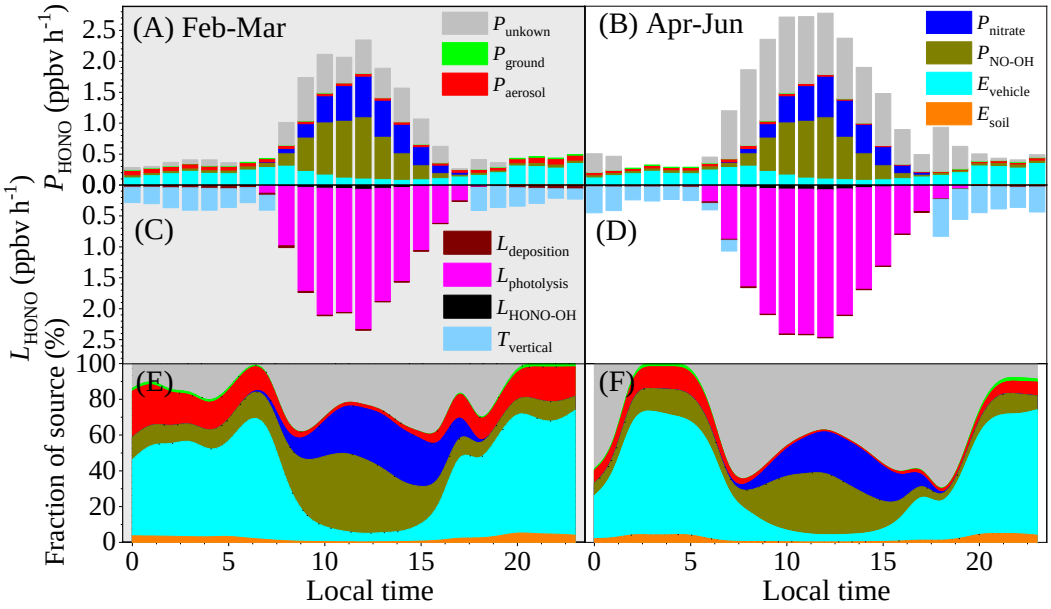

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1185 **Fig. 4**.

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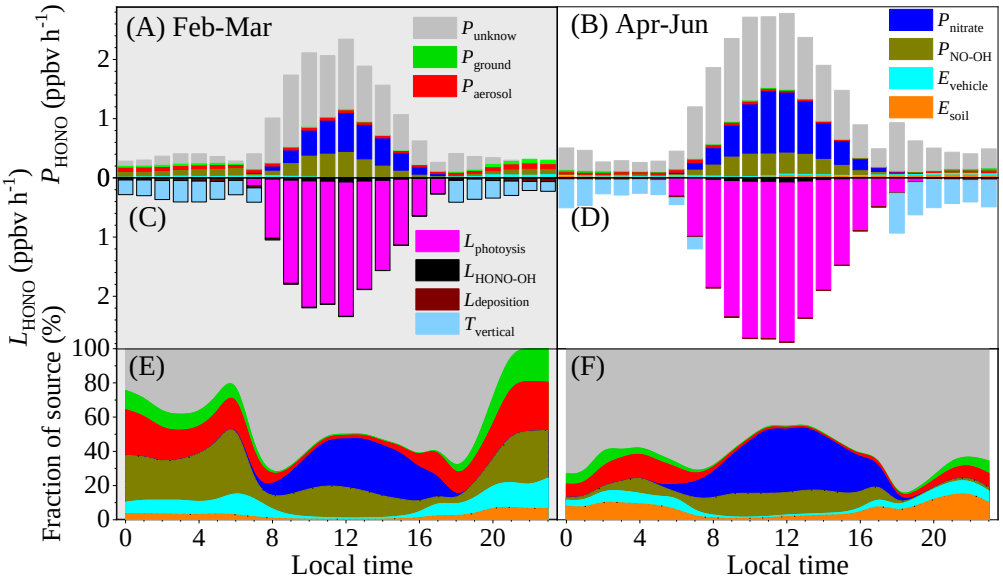

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1188 **Fig. 5**.

The promotion effect of nitrous acid on aerosol formation in wintertime Beijing: possible contribution of traffic-related emission

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Supplement information

Non-refractory $PM_{2.5}$ ($NR\text{-}PM_{2.5}$) measurement. Concentration of $NR\text{-}PM_{2.5}$ was measured with a ToF-ACSM (Aerodyne Co. Ltd., USA). The operation protocol and the configuration of ToF-ACSM has been described well in previous work (Fröhlich et al., 2013). Namely, $PM_{2.5}$ particles from the inlet were focused by a $PM_{2.5}$ aerodynamic lens (Williams et al., 2013), and then vaporized by a standard vaporizer heated at 600 °C followed by electronic ionization (EI, 70 eV). The non-refractory components including chloride, nitrate, sulfate, ammonia and organics were measured using a time-of-flight mass spectrometer with unit mass resolution (UMR). The concentrations of the above species were calculated based on the measured fragments signals, the signal ions (SI), the fragment table, the measured ionization efficiency (IE) of nitrate and the corresponding relative ionization efficiency (RIE) for sulfate, chloride, ammonia and organics. IE calibration of nitrate was performed using 300 nm dry NH_4NO_3 every month during this observation study.

VOCs measurement. VOCs were measured using a Single Photo Ionization Time-of-flight Mass spectrometer (SPI-ToF-MS 3000R, Hexin Mass Spectrometry). 0.8 L min^{-1} of filtered air was sucked from the whole sampling tube and heated to 80 °C in the inlet. VOCs were selectively enriched continuously through a polydimethylsiloxane (PDMS) membrane, and then ionized by VUV light (10.5 eV) with a deuterium lamp. The concentration of VOCs was determined with the time-of-flight mass spectrometer (ToF-MS) based upon external standard curves of PAMS and TO-15 standard gases (Linde Electronics & Specialty Gases, USA). VOCs with m/z from 40 to 300 were

recorded with 3 min of time resolution, while hourly averaged concentration were reported in this work. Calibration was performed every week.

HONO measurement. HONO in ambient air directly sampled from the window of the laboratory was absorbed by a solution containing 0.06 mol L^{-1} sulfnilamide in 1 mol L^{-1} HCl, and then transformed into an azo dye by *N*-(1-naphthyl) ethylene-diaminedihydrochloride (0.8 mml L^{-1}). The azo dye was pumped into Teflon absorption cells (Liquid Core Waveguide, LCW) and detected by a mini-spectrometer with a diode array detector (Ocean Optics, SD2000). The HONO concentrations was obtained by subtracting the calibrated signal of the second coil from the first coil using external nitrile standard solutions. Zero point calibration was performed every day using scrubbed zero air (Tong et al., 2016).

Photolysis rate constants of HONO and O_3. Photolysis rate constants of NO_2(J_{NO2}), HONO(J_{HONO}) and O_3(J_{O3}) under clear sky conditions were calculated according to the solar zenith angle and the location using a box model (FACSIMILE 4). NO_2 photolysis sensor (J_{NO2}, Metcon) was unavailable, while UVB is always available during our observation study. However, it was available from Aug 17 to Sep 16, 2018. A calibration function between the measured UVB light intensity and J_{NO2} was established to correct the influence the climatological O_3 column, aerosol optical depth and cloud cover on surface UV light intensity from Aug 17 to Sep 16, 2008. As shown in Figure S10, the model well predicted the J_{NO2}. Then the J_{NO2} during this campaign study was predicted using the model. We further confirmed the calculated J_{NO2} by comprising the OH concentration estimated by the J_{O1D} according to the equation

(c_{OH}=J_{O1D}×2×10^{11} molecules cm^{-3}) (Tan et al., 2019) and the measured OH concentration at Huairou, which is 60 km northeast from BUCT, form Jan 11 to Mar 10, 2016. As shown in Figure S10C, the estimated diurnal curve of OH is comparable with that measured at Huairou. Fig. S7 shows the calculated photolysis rates.

Supplementary figures

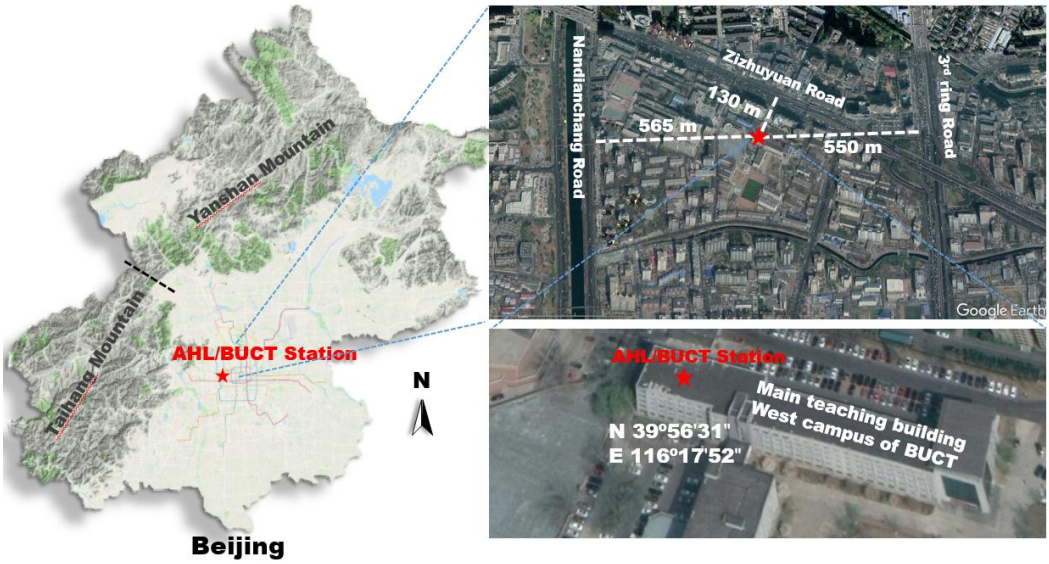


Figure S1. Location of AHL/BUCT observation station. The map was made from Wemap and Google Earth.

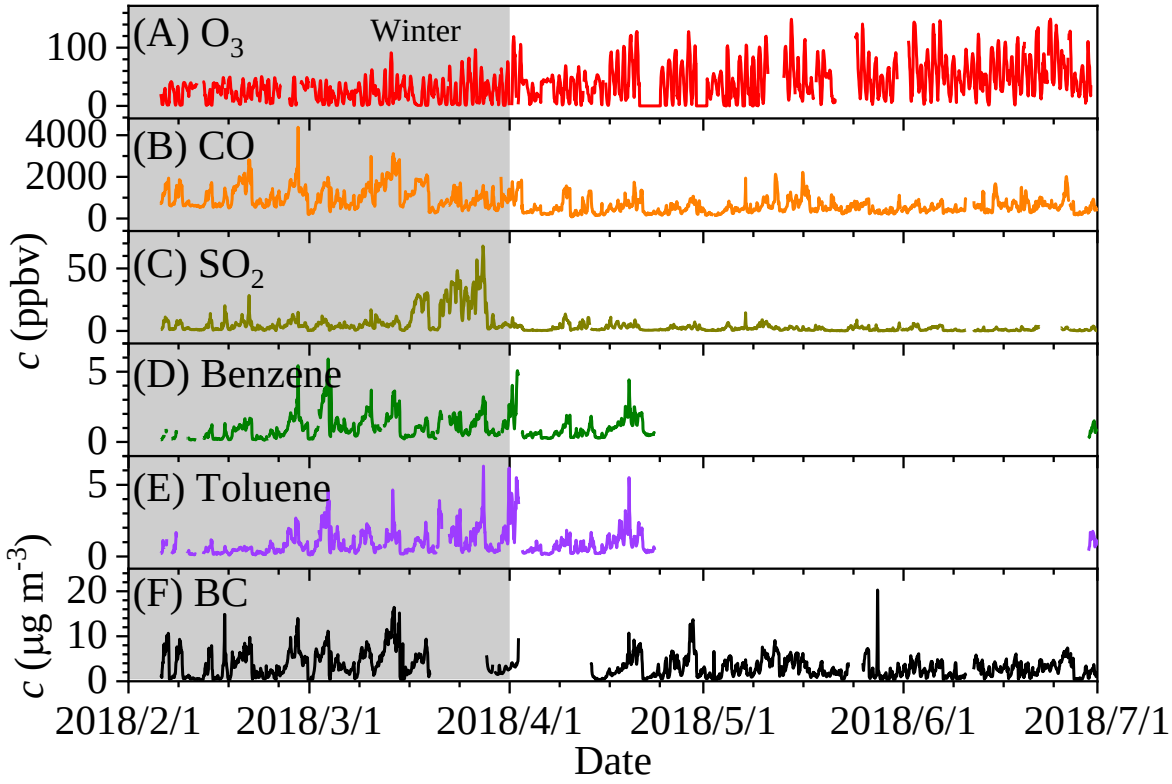


Figure S2. Hourly averaged (A)-(F) concentration of pollutants from Feb 1 to Jun 30, 2018.

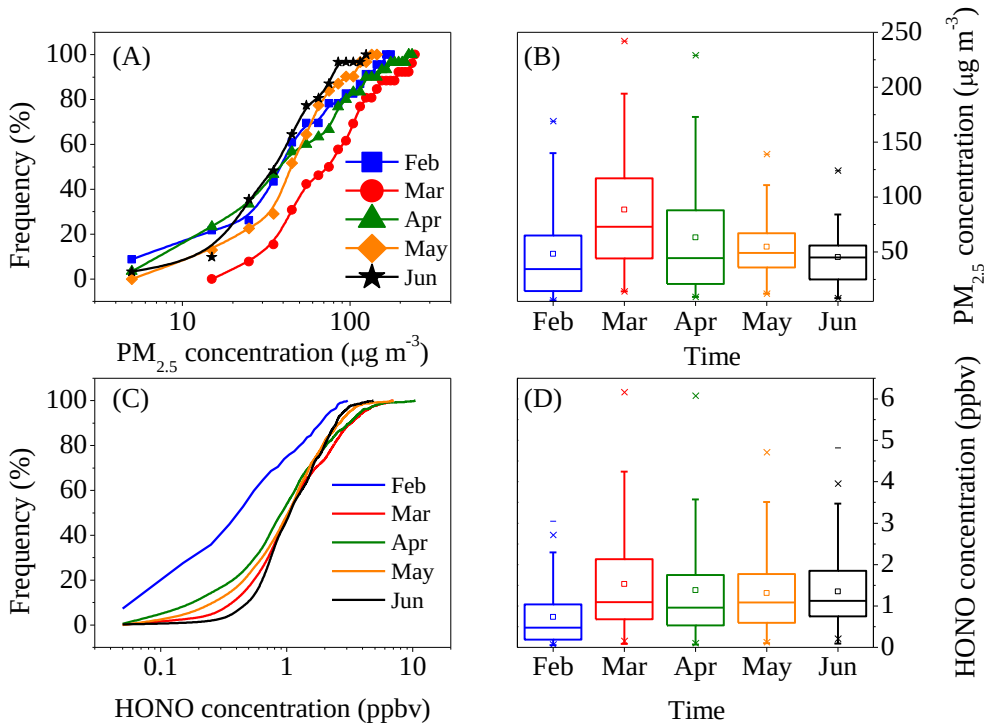


Figure S3. The monthly cumulative frequency of $PM_{2.5}$ and HONO and the monthly mean concentration of $PM_{2.5}$ and HONO.

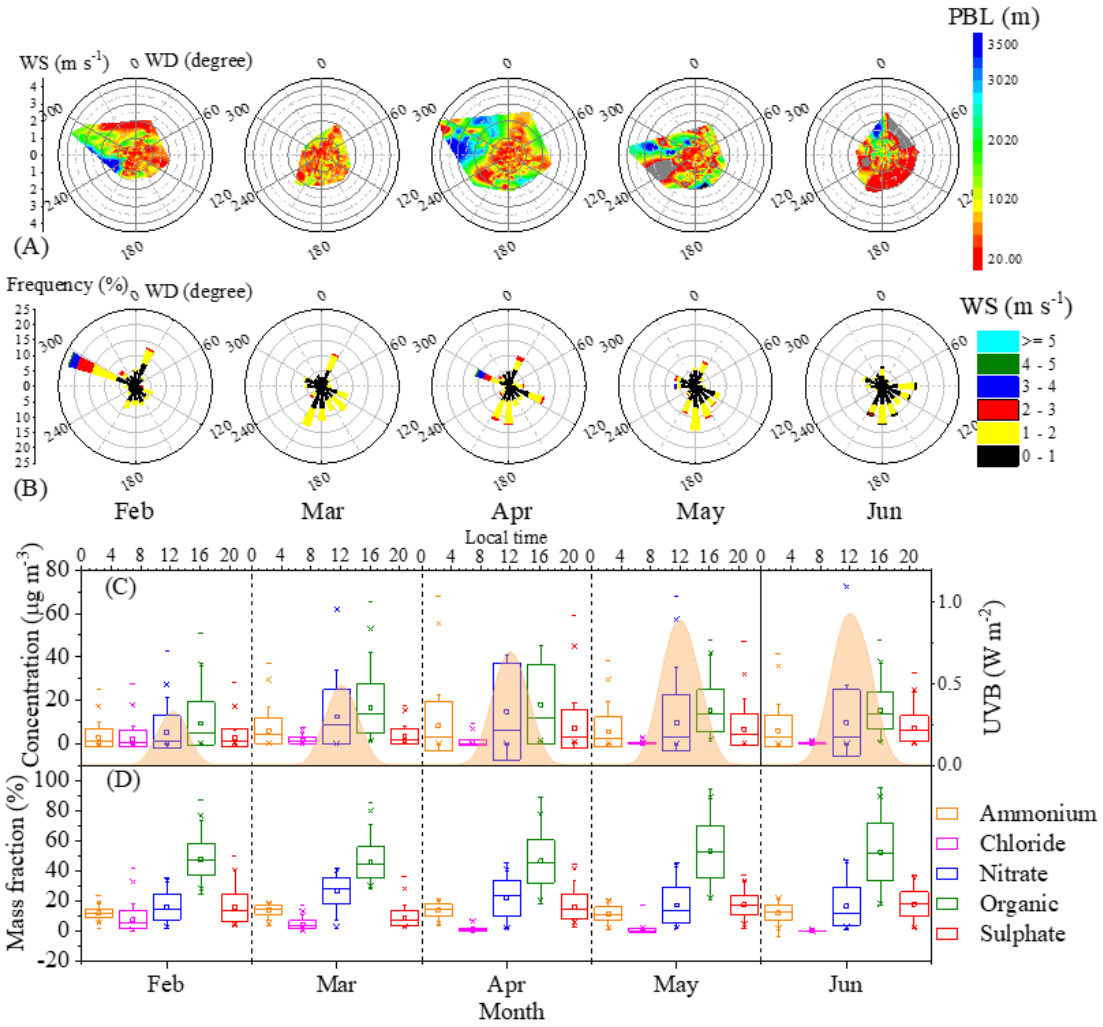
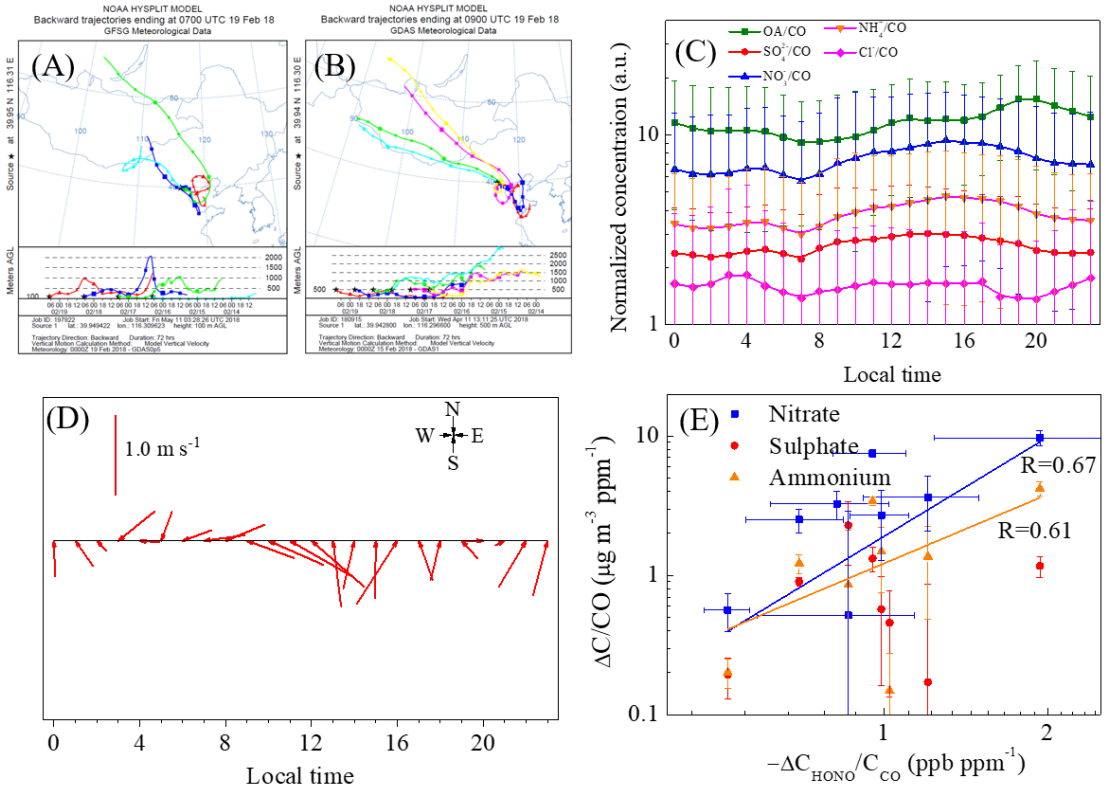


Figure S4. (A)-(B) monthly Windrose-PBL plots, and monthly averaged (C) UVB intensity, mass concentration and (D) fraction of individual component in NR-$PM_{2.5}$ composition from Feb to Jun, 2018.



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93 Figure S5. Transport of air mass during Chinese New Year based on back trajectory

94 analysis (A) at 100 and (B) 500 m height; (C) Diurnal variation of NR-$PM_{2.5}$ normalized

95 to CO concentration from Feb 1 to March 31; (D) Hourly averaged wind speed variation

96 in the 12^{th} episode; (E) Correlation of the concentration increment of individual

97 component and consumed HONO normalized to CO in the daytime.

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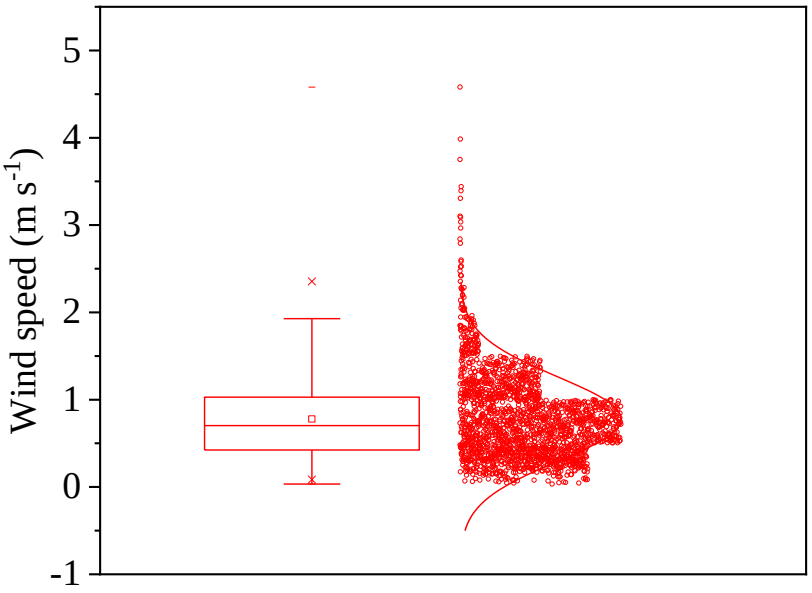


Figure S6. Distribution of wind speed when the $PM_{2.5}$ concentration was larger than 50 μg m^{-3} and the RH was less than 90 %.

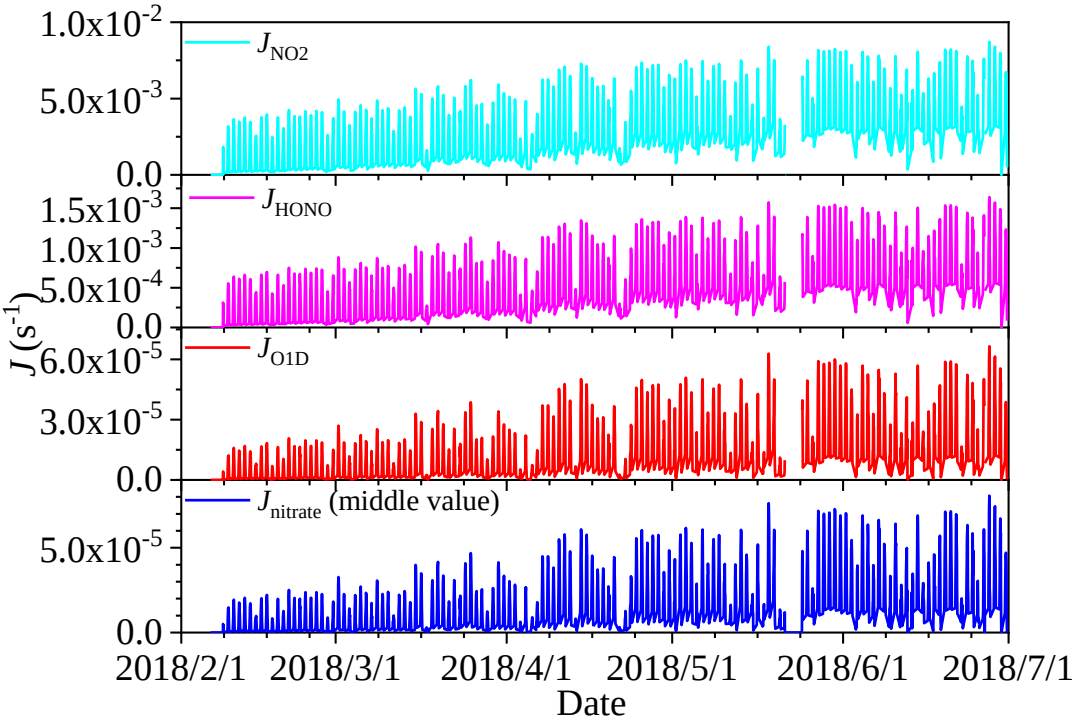
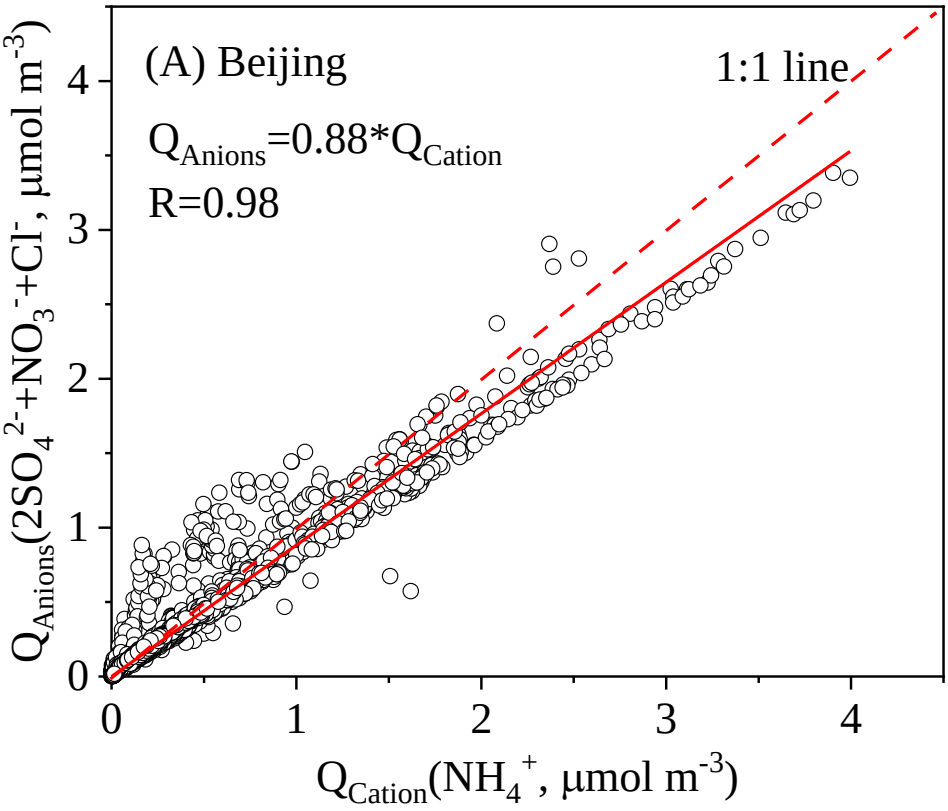


Fig. S7. The photolysis rate of NO_2, HONO, O_3 (O1D) and nitrate (middle value) from 8:00 am to 6:00 pm.



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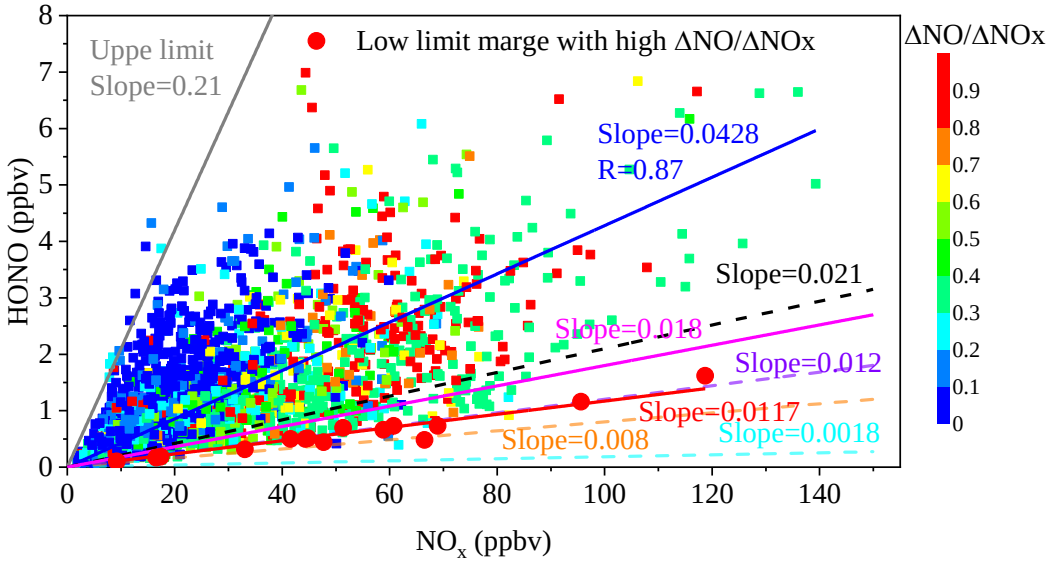
107 Figure S8. Correlation of the charge between inorganic anions and cations in non-

108 refractory $PM_{2.5}$ in Beijing.

109



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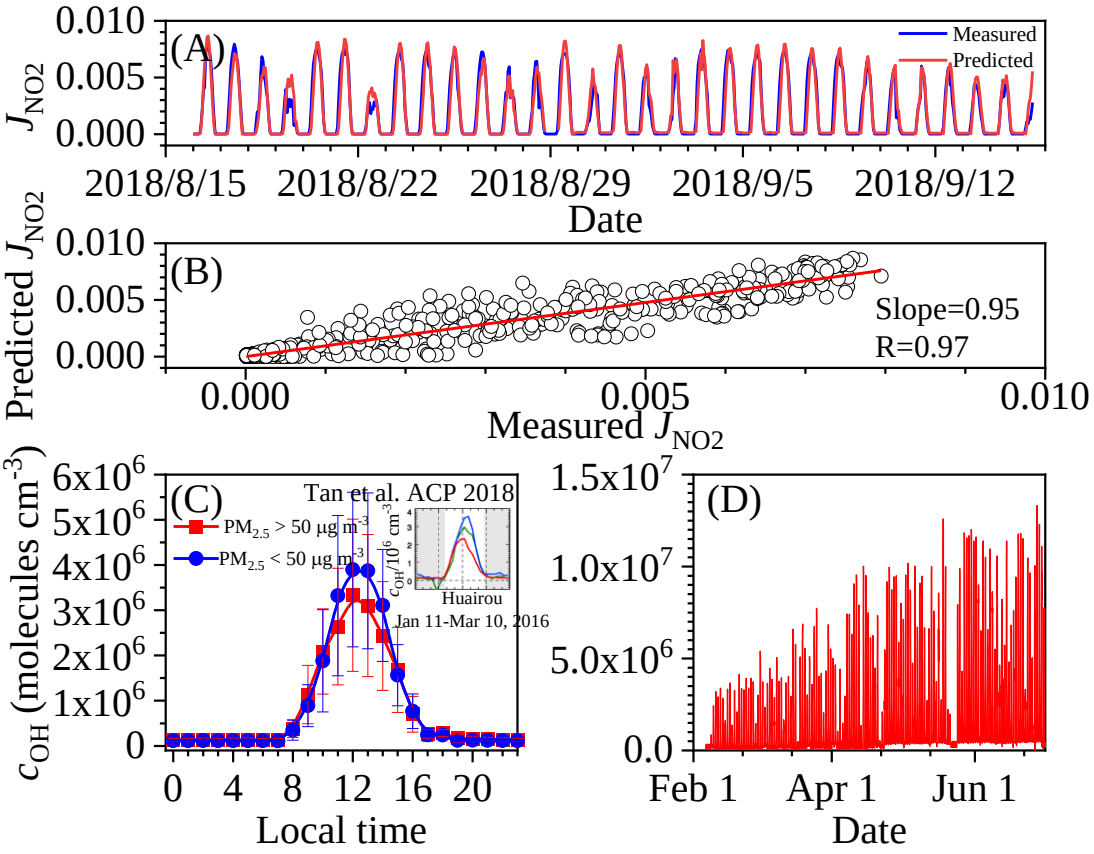
111 Figure S9. Correlation of measured HONO concentration with NO_x concentration.



112

113 Figure S10. (A) Measured and predicted J_{NO2} and (B) the correlation between measured

114 and predicted J_{NO2} from Aug. 15 to Sep. 16; (C) calculated diurnal curve of OH

115 concentration based on J_{O1D} compared with that measured at Huairou (60 km northeast

116 from BUCT) from Jan 11 to Mar 10, 2016; (D) OH concentrations estimated using

117 $c_{OH}=J_{O1D}\times 2\times 10^{11}$(Tan et al., 2019).

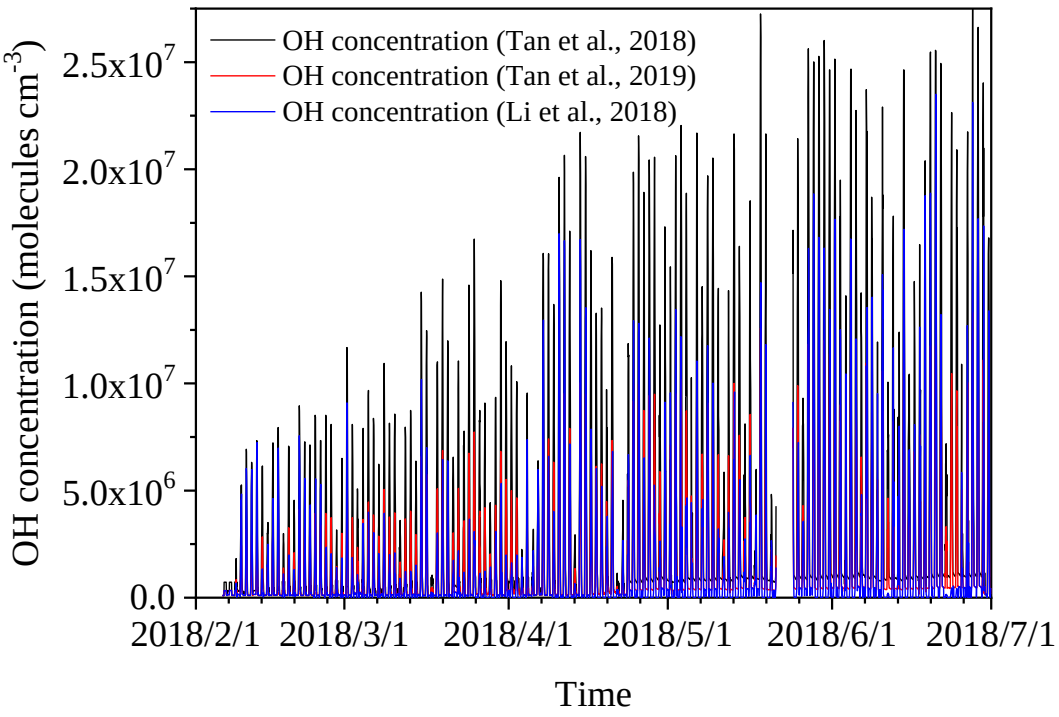


Fig. S11. Estimated OH concentration using different methods.

Supplementary tables

Table S1. ANOVA statistics analysis for the monthly mean fraction of the individual component in NR-$PM_{2.5}$ and HONO concentration.

Component	Fraction of NR-$PM_{2.5}$ (%) or Concentration of gaseous pollutants (ppbv)	Feb	Mar	Apr	May
Ammonium	Feb (12.2±2.9)				
	Mar (14.2±2.8)	Significant			
	Apr (14.0±4.0)	Significant	Not significant		
	May (11.6±4.6)	Not significant	Significant	Significant	
	Jun (12.2±5.2)	Not significant	Significant	Significant	Not significant
Chloride	Feb (7.7±6.1)				
	Mar (4.4±2.6)	Significant			
	Apr (1.1±1.2)	Significant	Significant		
	May (0.7±1.1)	Significant	Significant	Not significant	
	Jun (0.3±0.2)	Significant	Significant	Significant	Not significant
Nitrate	Feb (16.2±8.5)				
	Mar (26.7±8.8)	Significant			
	Apr (22.0±11.7)	Significant	Significant		
	May (17.3±11.8)	Not significant	Significant	Significant	
	Jun (16.7±12.8)	Not significant	Significant	Significant	Not significant
Organic	Feb (47.9±10.7)				
	Mar (45.9±10.2)	Not significant			
	Apr (46.5±14.2)	Not significant	Significant		
	May (52.9±17.0)	Not significant	Significant	Significant	
	Jun (52.6±18.7)	Significant	Significant	Significant	Not significant

Sulfate	Feb (16.0±9.1)				
	Mar (8.8±5.4)	Significant			
	Apr (16.4±8.2)	Not significant	Significant		
	May (17.5±6.6)	Significant	Significant	Not significant	
	Jun (18.2±8.0)	Significant	Significant	Significant	Not significant
BC	Feb (3.0±2.8)				
	Mar (4.6±3.1)	Significant			
	Apr (3.2±2.6)	Not significant	Significant		
	May (2.8±2.1)	Not significant	Significant	Not significant	
	Jun (2.6±1.5)	Significant	Significant	Significant	Not significant
HONO	Feb (0.73±0.70)				
	Mar (1.53±1.25)	Significant			
	Apr (1.38±1.35)	Significant	Not significant		
	May (1.31±1.00)	Significant	Significant	Not significant	
	Jun (1.35±0.80)	Significant	Significant	Not significant	Not significant
NOx	Feb (20.4±17.3)				
	Mar (40.5±24.0)	Significant			
	Apr (22.8±18.6)	Not significant	Significant		
	May (25.0±15.9)	Significant	Significant	Not significant	
	Jun (19.0±12.1)	Not significant	Significant	Significant	Significant
SO_2	Feb (3.8±3.3)				
	Mar (12.1±13.0)	Significant			
	Apr (2.8±2.4)	Significant	Significant		
	May (1.8±1.7)	Significant	Significant	Not significant	
	Jun (1.3±1.2)	Significant	Significant	Significant	Not significant
CO	Feb (959.6±554.6)				

	Mar (1075.0±571.8)	Significant			
	Apr (546.6±378.1)	Significant	Significant		
	May (554.1±336.9)	Significant	Significant	Not significant	
	Jun (583.4±286.2)	Significant	Significant	Not significant	Not significant
	Feb (22.6±14.6)				
	Mar (23.8±19.2)	Not significant			
O_3	Apr (43.5±29.0)	Significant	Significant		
	May (42.5±28.3)	Significant	Significant	Not significant	
	Jun (57.2±30.7)	Significant	Significant	Significant	Significant

Note: “Significant” or “Not significant” denotes that the difference of the monthly mean fractions or concentrations is significant or not significant at the 0.05 level.

Tab. S2. Mean concentrations of HONO and $PM_{2.5}$ in selected episodes

Episode No.	Duration	HONO (ppb)	Average $PM_{2.5}$ concentration	NR-$PM_{2.5}$ Concentration (%)									
				Chloride		Nitrate		Organic		Sulphate		Ammonium	
				(%)	(μg m^{-3})	(%)	(μg m^{-3})	(%)	(μg m^{-3})	(%)	(μg m^{-3})	(%)	(μg m^{-3})
1	Feb 2-5	0.38±0.28	9.3±4.5	4.0±2.3	0.26±0.39	12.3±5.6	0.80±1.17	51.1±10.0	2.68±3.00	20.6±9.2	0.69±0.24	12.0±3.2	0.54±0.49
2	Feb 8-9	0.90±0.72	44.5±3.5	6.3±2.9	1.59±1.46	15.8±7.9	4.20±3.87	49.9±4.8	9.63±7.64	17.3±8.8	2.31±1.42	10.8±1.0	2.14±1.69
3	Feb 10-12	0.31±0.40	9.0±0.8	5.2±3.5	0.18±0.22	6.8±3.9	0.30±0.44	48.6±10.6	1.75±1.72	28.1±11.5	0.74±0.38	11.2±2.5	0.35±0.23
4	Feb 16-19	1.38±0.86	101.5±26.8	15.5±4.2	9.04±4.94	25.0±4.1	13.15±7.73	32.2±3.8	18.21±8.25	14.4±3.7	7.82±4.39	12.9±1.5	6.85±3.78
5	Feb 21-24	0.64±0.58	24.3±7.0	5.5±4.1	0.60±0.51	14.9±6.3	1.80±1.38	56.3±10.0	5.83±2.94	11.8±5.0	1.17±0.67	11.6±2.8	1.24±0.77
6	Feb 25-28	0.87±0.64	108.8±42.9	5.2±1.4	2.94±1.97	27.1±3.9	15.3±8.77	42.5±6.8	22.83±9.68	10.4±3.8	6.44±5.78	14.7±1.8	8.34±5.30
7	Mar 2-3	1.41±0.84	120.0±47.0	8.3±2.2	4.23±1.72	26.5±4.8	15.29±9.44	44.4±6.2	23.40±10.49	7.2±1.9	4.36±3.37	13.5±1.9	7.74±4.76
8	Mar 8-10	1.36±0.89	88.7±34.2	4.8±1.8	1.87±1.09	28.3±5.2	11.00±6.20	43.0±7.0	15.65±7.15	9.0±2.8	3.10±1.42	14.9±2.0	5.58±2.92
9	Mar 11-14	2.27±1.68	170.3±75.4	3.5±0.9	2.48±1.32	34.8±4.3	28.32±19.09	36.8±5.0	27.90±15.78	8.1±1.8	6.60±4.72	16.8±1.5	13.57±8.99
10	Mar 16-19	1.88±1.38	66.0±25.7	3.8±1.7	1.99±1.18	30.2±6.3	17.40±12.45	35.9±2.8	20.87±10.52	13.5±5.1	7.00±4.92	16.5±1.0	9.17±5.86
11	Mar 21-23	1.41±0.72	83.7±22.1	5.3±2.8	2.54±2.30	31.5±3.8	12.23±5.22	45.1±6.7	18.02±5.46	4.4±1.0	1.67±0.92	13.7±1.6	5.38±2.08
12	Mar 25-27	2.22±1.34	129.5±51.9	2.0±0.7	0.94±0.64	35.3±3.6	16.32±9.90	41.5±5.4	20.46±10.18	5.7±1.2	2.56±1.68	15.6±1.6	7.11±4.37

Table S3. The summary of the HONO/NOx ratio from vehicles in this study and the reported emission ratio of HONO/NOx from vehicles in China.

No.	Time	ΔNO/ΔNOx	$R_{\Delta NO/\Delta NOx}$	ΔHONO/ΔNOx	$R_{\Delta HONO/\Delta NOx}$
1	2018/2/6 5:00-8:00	1.00	0.99	1.3%	0.92
2	2018/2/8 5:00-8:00	0.94	0.99	1.8%	0.96
3	2018/3/3 5:00-8:00	0.98	0.99	2.4%	0.96
4	2018/3/13 5:00-8:00	1.00	0.99	1.4%	0.86
5	2018/4/15 5:00-7:00	0.82	0.97	2.3%	0.99
Mean		0.95±0.08	-	1.8±0.5%	-

Time	Place	Methods	ΔHONO/ΔNOx		Reference
			Range	Mean	
2015/9/1-2016/8/31	Ji'nan, Shandong	Empirical analysis of field data	0.19%-0.87%	0.53±0.20%	(Li et al., 2018)
2011/8/3-2012/5/31	Hongkong	Empirical analysis of field data	0.5%-1.6%	1.2±0.4%	(Xu et al., 2015)
2015/3/11-2015/3/21	Hongkong	Tunnel experiment	-	1.24±0.35%	(Liang et al., 2017)
2014	Beijing	Tunnel experiment	-	2.1%	(Yang et al., 2014)
2017	Beijing	Chassis dynamometer test	0.03%-0.42%	0.18%	(Liu et al., 2017)
2016/12/16-2016/12/24	Beijing	Empirical analysis of field data	-	1.3%	(Zhang et al., 2018)
2016/12/7-2016/12/13	Beijing	Low limit correlation of field data	-	1.41%	(Meng et al., 2019)
2018/2/1-2018/6/30	Beijing	Low limit correlation of field data	-	1.17%	This study
2018/2/1-2018/6/30	Beijing	Empirical analysis of field data	1.3-2.4%	1.8±0.5%	This study

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