

## **Response to reviewer #2**

### **General comments**

The paper “NH<sub>3</sub>-promoted hydrolysis of NO<sub>2</sub> induces explosive growth in HONO” by Wanyun Xu et al is joining the long series of scientific work aiming at elucidating the HONO sources that have been published these past twenty years. Considering the major role of HONO in the initiation of the photo-oxidation cycles in the troposphere, any significant work related to the processes that give birth to this key molecule are necessarily important (Kleffmann et al, 2007). Wanyun Xu et al are mostly founding the exploitation of their results on a methodology based on recent papers only and are often disregarding the precious findings of the early times. Nevertheless, they provide here an attempt to exploits a limited set of data obtained in heavily polluted environment that is not without any merit. Overall, I have many minor points to discuss but, for me, one major point is shining a doubtful light over the whole study: it concerns the reliability of the HONO/NO<sub>2</sub>- measurements themselves. The reliable measurement of HONO at low level in the atmosphere has been an analytical challenge for decades. Many groups have worked on various analytical concepts ranging from long path spectroscopy, optical cavities, ionic chromatography or dye formation combined with absorption within waveguide tubing or HPLC analysis.

Because of HONO high reactivity the risk of underestimation of its concentration is often high. In the same time, because of the multiplicity of its heterogeneous sources the risk of positive artefact and unwanted HONO generation in/nearby the system is high too. This is why, even when the measurement principle itself was mature, the sampling condition was often found to be a key parameter for trustable measurements, which has led to important work on the design of inlets, minimizing surfaces, choosing material.

Each of these instrumental concept has required extensive characterization works and a few inter-comparison exercises have demonstrated how large the discrepancies can

be (Keuken et al, 1990; Stutz et al, 2009; Kleffmann et al, 2006; Pinto et al, 2014).

## Major issues

1. In the present paper, the whole experimental strategy relies on the performance of the so-called In situ Gas and Aerosol Compositions Monitor (IGAC, Fortelice International Co., Taiwan) as both HONO/NO<sub>2</sub>- and NH<sub>3</sub> concentrations – the two key species of the present study - are monitored using this instrument. The available information about this device are scarce: IGAC consists in a combination of a wet annular denuder and a particle into liquid sampler. Unfortunately it has been poorly characterized in general and none of the reference provided in the paper are relevant for HONO measurements. In particular, while citing Liu et al, 2017a to claim “the instrument has shown good performance in the past” or quoting Young et al, 2016, one can only regret that nothing in these papers really concern nitrous acid or nitrite ions measurements. Further, Young et al, 2016 indicate that the performance of IGAC were poor concerning the measurement of ammonia.

On my side, considering the IGAC experimental device and condition of use, I especially worry about the use of “a dilute H<sub>2</sub>O<sub>2</sub> solution to collect the gases”. If one refer to Young et al, 2016 the “dilute solution” is a 5x10<sup>-3</sup> M solution (why not mentioning the concentration in the experimental section?) which is used to “assure the oxidation of SO<sub>2</sub> to SO<sub>4</sub><sup>-</sup> and prevents microbial growth “. For me, it is highly probable that such a concentration of such a strong oxidation agent could induced artefacts in the HONO measurement: - in the absence of precursors, it may induce a negative artefact by oxidizing nitrites to nitrates but, on the contrary - in the presence of enough reduced nitrogenous species (such as ammonia) it may forms HONO. In this case this would both affect NH<sub>3</sub> and HONO measurements and would probably lead to a correlation between both species (if ammonia is in excess). Considering the poor level of details provided in the experimental section,

the lack characterization experiments demonstrating the ability of IGAC to measure HONO (especially in the presence of ammonia) and the strong suspicion of artefacts exactly relevant from the main paper conclusion, I strongly recommend to provide the experimental evidences that demonstrate the suitability of the measurement protocol for both  $\text{NH}_3$  and HONO before considering any publication.

***Response:***

During the campaign in 2016, the IGAC instrument was borrowed from the Fortelice International Company. Unfortunately, circumstances do not allow us to borrow the instrument again for additional experiments, but we believe the entire dataset itself may be able to prove itself reliable.

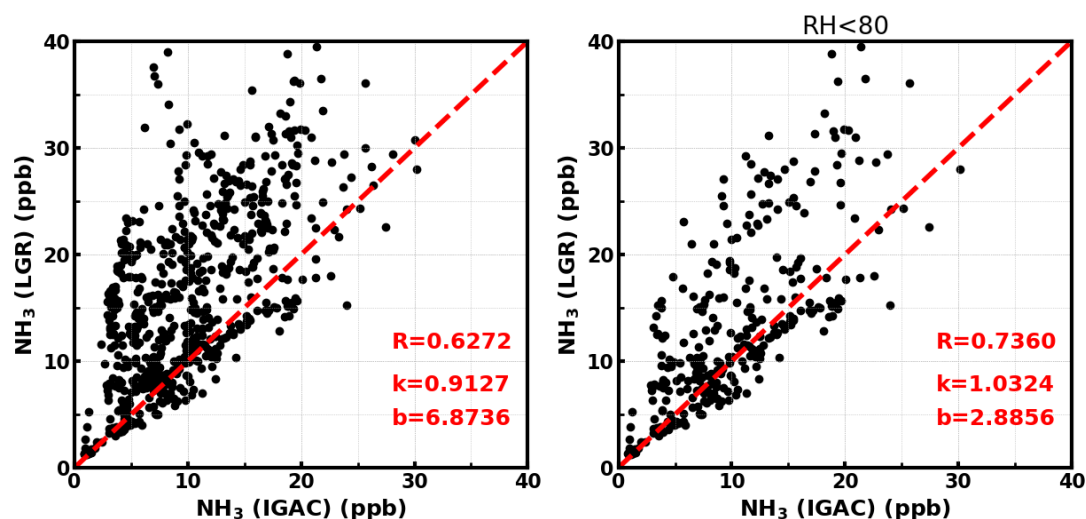
- 1) **On the concern that the IGAC instrument showed “poor” performance in respect of ammonia measurements**, we would thank the reviewer for the careful inspection of our work and for raising this concern, which indeed needs to be addressed to solidify our work.

To evaluate the  $\text{NH}_3$  data quality measured by IGAC, we compared them against  $\text{NH}_3$  measurements of an LGR economical ammonia analyzer (DLT-100, Los Gatos Research, USA). Note that the IGAC instrument, the SMPS+APS system, the humidified nephelometer system and the AL2021  $\text{H}_2\text{O}_2$  analyzer were housed in an air-conditioned container located on the northern edge of the Gucheng site, while the trace gas instruments (including  $\text{SO}_2$ ,  $\text{NO}_x$ , CO and  $\text{NH}_3$ ) that carried out long-term measurements were housed on the second floor of a two story building located on the southern edge of the Gucheng site. Details on the LGR  $\text{NH}_3$  measurements can be found in Meng et al. (2018).

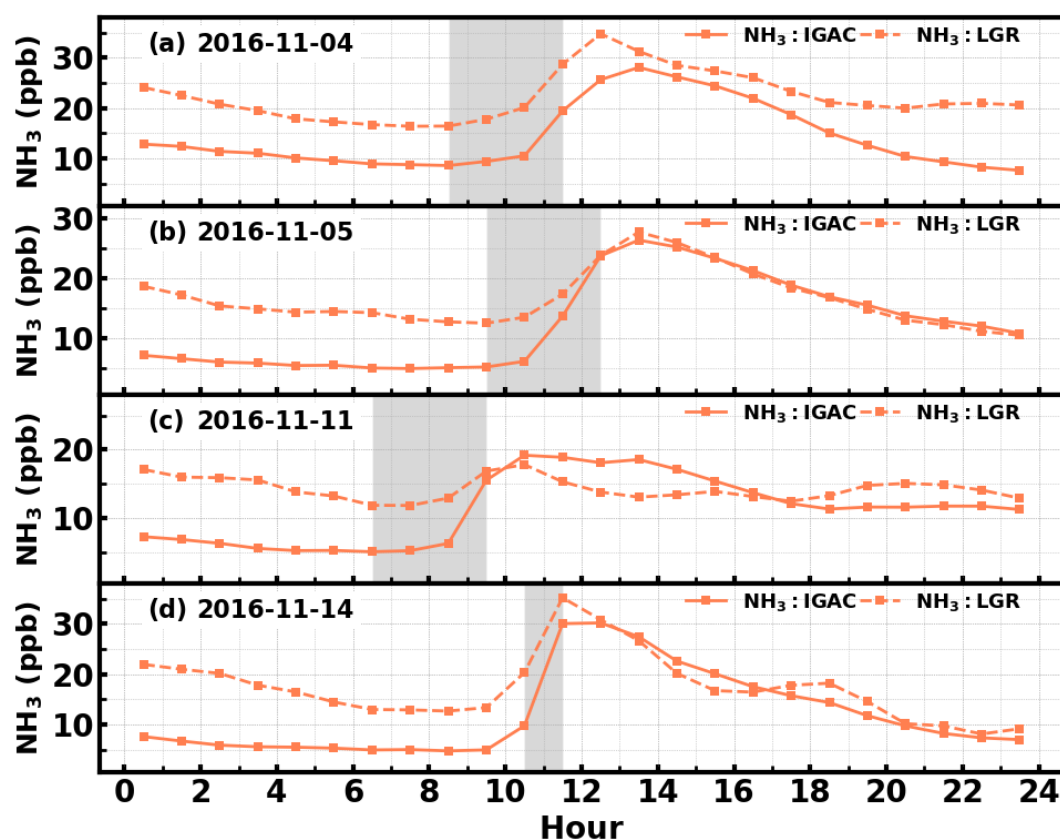
In Young et al. (2016), IGAC showed marginally acceptable performance test result for  $\text{NH}_3$ , with the intercept of the linear fitting meeting the evaluation criteria, while the slope of 0.59 did not. They pointed out that the underestimation in IGAC  $\text{NH}_3$  measurements was probably caused by losses on the sampling tube wall. This indicates that the  $\text{NH}_3$  measured by IGAC are systematically lower,

which high possibly has no great influence on the relative variation pattern of  $\text{NH}_3$ , which we are concerned of in this study. It should be noted that Young et al. (2016) performed  $\text{NH}_3$  measurements and validation in the concentration range of 0 to 16 ppb. Liu et al. (2017) performed  $\text{NH}_3$  measurements with IGAC in urban Beijing, with  $\text{NH}_3$  varying between 0 to 35 ppb, which is closer to the observed  $\text{NH}_3$  range in our campaign. The measurements were validated against ISORROPIA II simulations and reached good agreement ( $R^2 > 0.9$ ). Teng et al. (2017) observed that LGR measurements were far larger than those measured based on wet denuders (with a slope near 0.7) and suggested the overestimation of LGR was possibly caused by interference of water vapor. Overall, we believe that even though the IGAC system may not be as precise as other specific  $\text{NH}_3$  analyzers, if it can capture the variation characteristics of  $\text{NH}_3$ , it would be enough to prove the proposed the HONO production pathway.

Overall, the comparison of the  $\text{NH}_3$  measured with LGR against that of IGAC showed a slope of 0.91 ( $R=0.63$ ) and an intercept of 6.86 (Fig.1a). If data measured under high RH conditions ( $\text{RH} \geq 80$ ) were excluded, an obvious improvement in the comparison results would be achieved (Fig.1b), with a slope of 1.03 ( $R=0.74$ ) and an intercept of 2.89. This indicates that, high discrepancies between the two instruments mostly occur at high relative humidity, where LGR measurements are significantly higher than those of IGAC. Since these discrepancies were linked to high RH conditions, it is more likely that they were caused by the LGR instrument that overestimates  $\text{NH}_3$  due to absorption interference of water vapor. The variation of  $\text{NH}_3$  measured by LGR and IGAC during the four episode cases is shown in Fig. 2. Although LGR showed higher  $\text{NH}_3$  concentrations (especially during nighttime when fog prevailed and RH was near 100), the variation characteristics were the same between the two instruments, all displaying rapid increases during the explosive HONO formation events. Thus, we believe it is appropriate to use the IGAC measured  $\text{NH}_3$  for our discussions.



**Figure 1** Comparison between  $\text{NH}_{3,\text{IGAC}}$  and  $\text{NH}_{3,\text{LGR}}$  using a) all measurement data and b) data associated with  $\text{RH}<80$ .



**Figure 2** Time series of  $\text{NH}_{3,\text{IGAC}}$  (solid) and  $\text{NH}_{3,\text{LGR}}$  (dashed) during a) 4<sup>th</sup> Nov., b) 5<sup>th</sup> Nov., c) 11<sup>th</sup> Nov. 2016 and d) 14<sup>th</sup> Nov. 2016. Gray shaded areas represents periods of rapid increase of HONO.

We hope that this gives the reviewer and readers more confidence in the measurement results of IGAC concerning  $\text{NH}_3$ . In the revised manuscript, the following was added

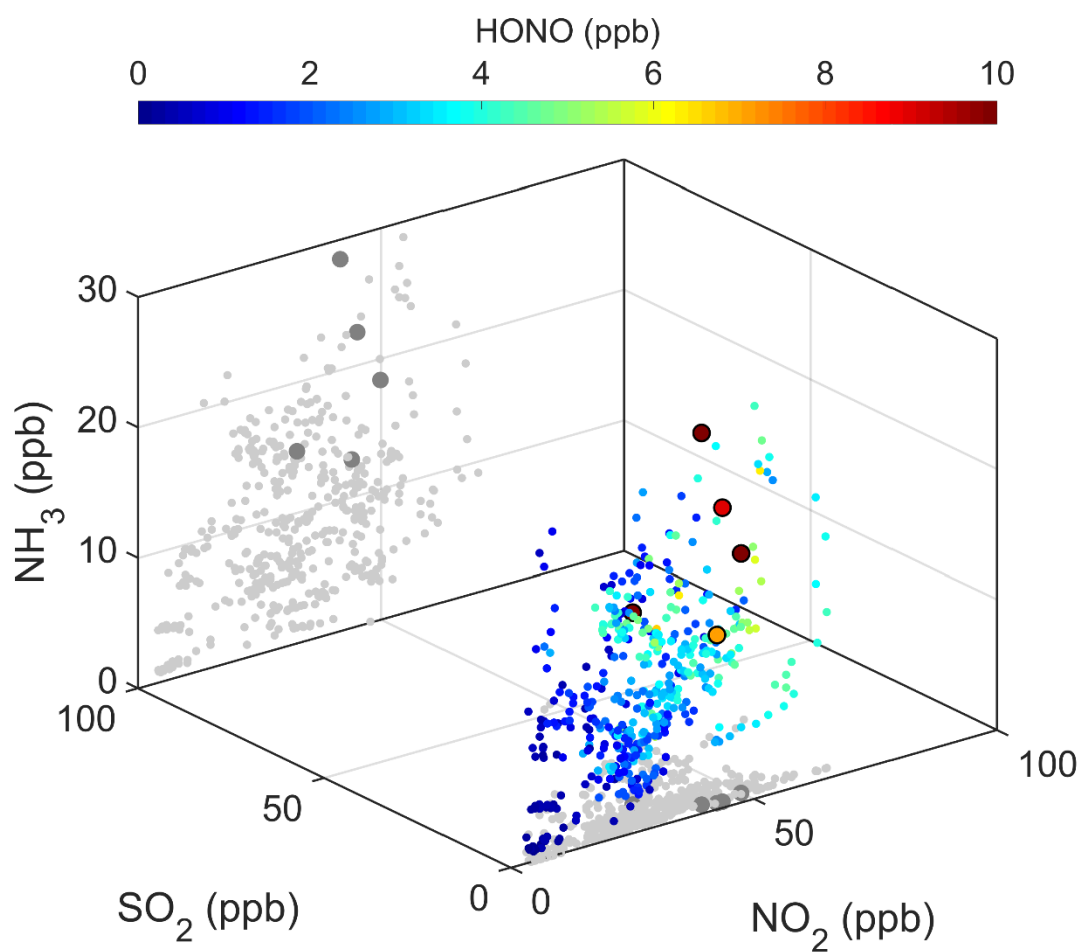
to Sect. 2 to provide the readers with more insight into the  $\text{NH}_3$  measurements and data quality:

“A comparison between  $\text{NH}_3$  observed by IGAC and by an economical  $\text{NH}_3$  analyser (LGR, DLT-100, details see Meng et al. (2018)) yielded an overall slope of 0.91 with  $R=0.63$  (Fig.S1a). A better comparison result (slope of 1.03,  $R=0.74$ ) would be obtained if data associated with  $\text{RH}\geq 80$  were excluded (Fig. S1b). The overestimation of LGR instruments compared to denuder based instruments has also been reported in Teng et al. (2017), suggesting possible interference of water vapor on  $\text{NH}_3$  measurements. As can be seen in Fig S2., both instruments captured the same the diurnal variation of  $\text{NH}_3$  during the four case episodes in this study, which proves that the IGAC instrument was able to capture the overall variation trends of  $\text{NH}_3$ . Since both instruments have their uncertainties, we decided to use the  $\text{NH}_3$  measured by the IGAC instrument for better consistency with the other data.”

2) **On the concern, whether the IGAC instrument can accurately measure HONO**, the performance of IGAC in terms of HONO measurements has indeed not been validated against measurements from other instruments at present. A recent work compared WRF-CHEM simulated HONO against measurements by IGAC and found good agreement between the two of them (Feng et al., 2018). The IGAC instrument is not as widely used as the MARGA system, which shares similar design and principles as IGAC and has been often used to measure HONO in the past (Xie et al., 2015; Nie et al., 2015). Similar measurement systems have been widely applied to study the variation of HONO (Su et al., 2008; Yang et al., 2017; Gu et al., 2009; Qiang et al., 2014). Instruments using wet denuders to collect gaseous HONO can cause sampling artefacts mainly via two pathways: 1) the  $\text{NO}_2$  conversion on the surface of the sampling tube and the wet denuder and 2) the reaction of  $\text{NO}_2$  with S(IV) in the absorption solution in wet denuder (Nie et al., 2015). The second pathway is avoided in IGAC by using the dilute ( $5\times 10^{-3}$  M)  $\text{H}_2\text{O}_2$  solution, which quickly converts S(IV) to S(VI). The first artefact is often

corrected for using a linear correction using slopes of 0.83-0.85. (Su, 2008;Qiang et al., 2014;Nie et al., 2015). Qiang et al. (2014) compared HONO measurements by an instrument called GAC-IC with that of LOPAP and found generally good agreement between both instruments after using a linear correction. Note that such linear adjustments do not alter the overall variation characteristics of HONO. The GAC and MARGA systems all consist of horizontally positioned wet denuders, in which the absorption solution might accumulate and cause additional artifacts. The IGAC system uses a vertically installed wet denuder, guaranteeing for the smooth outflow of the absorption solution. Overall, it is reasonable to believe that IGAC is able to capture the variation characteristics of HONO, even if a slope of 0.83 were used to correct the HONO data, the peaks would still reach 8.8, 7.9, 9.5 and 14.6 ppb, which is still very high.

To further prove that the observed peaks were not caused by instrument sampling artefacts, we analyzed the variation of observed HONO with  $\text{SO}_2$ ,  $\text{NO}_2$  and  $\text{NH}_3$  during 15<sup>th</sup> Oct. to 25<sup>th</sup> Nov. 2016 (Fig.3). High HONO concentrations were typically observed under low  $\text{SO}_2$  conditions, which proves that the sampling artefact due to the reaction of S(IV) and  $\text{NO}_2$  in the wet denuder could be neglected. If the instrument would cause sampling artefacts due to  $\text{NO}_2$  conversions, the high HONO concentrations should have been frequently observed under high  $\text{NO}_2$  concentrations, which was not the case. The  $\text{NO}_2$  concentrations at the occurrence time of the 4 peaks were all below 50 ppb.  $\text{NO}_2$  often exceeded 50 ppb during the campaign, however, HONO stayed below 7 ppb throughout the whole campaign, except for the 4 cases studied in this work.



**Figure 3** Variation of HONO with SO<sub>2</sub> (y-axis), NO<sub>2</sub> (x-axis) and NH<sub>3</sub> (z-axis) during 15<sup>th</sup> Oct. to 25<sup>th</sup> Nov. 2016, with the large dots indicating the data points with HONO exceeding 7 ppb



2. Line 213-214: “The O<sub>3</sub> concentration stayed near zero, which means that UV radiation was weak.” This statement is clearly wrong. From the few NO data that the author disclose to the reader one can see that NO values are typically ranging from 20 to 100 ppb. With such high values, no wonder why O<sub>3</sub> remain low: it is clearly titrated by NO. One can understand that the lack of spectral radiometer measurements is an issue (see later) but O<sub>3</sub> data in a polluted environment can certainly not be used as a proxy for UV radiation strength.

***Response:***

We thank the reviewer for this valuable comment and agree that using O<sub>3</sub> as an indicator for UV radiation under such conditions is indeed not appropriate. As suggested by the reviewer in the following major comment, we used TUV calculation results to prove our point. During the case on the 14<sup>th</sup> Nov. 2016, the relative humidity decreased from 100% (10:00-11:00) to 85% (11:30), suggesting that this was a fog dissipation process. During 10:00 to 11:00, Gucheng was still under foggy conditions, with an estimated HONO lifetime (only considering its photolysis process) of 1.7 hours, proving that the photolysis process was relatively weak during the rapid increase of HONO. The estimated HONO lifetime rapidly decreased to 0.6 h by 12:00, resulting in accelerated HONO dissociation and OH production, explaining the rapid decrease of HONO concentrations.

The discussion in Line 213-214 was deleted and detailed discussions on the HONO photolysis were added in both Sect. 4.1 and Sect. 4.3 of the revised manuscript.

3. Line 226: Equation 1 is strongly oversimplified. On the HONO sinks side one clearly miss - photolysis that can certainly not be neglected. Even if radiation measurements are not available, the authors manage, later on in the paper, to evaluate some values that could be used here. Another approach would be to provide an upper limit evaluating the J value above haze using TUV for example (see Madronich et al, 1988 and Tie et al, 2003) - deposition can be taken into account by using as deposition velocity the value given by Stutz et al., 2002, for

example. In addition in the presence of hydrometeors, one clearly miss the loss processes onto/into haze droplets. On the HONO source side, may well identified processes are missing such as direct emission and heterogeneous HONO formation from conversion of NO<sub>2</sub> on ground surface and aerosol surfaces.

***Response:***

We thank the reviewer for the valuable suggestions in this comment. However, we believe there has been a little misunderstanding, which needs to be clarified. In this section, we tried to speculate if these observed HONO explosive growth events could have been caused by other known sources. In the second paragraph (line 224-236), we wanted to estimate if the homogenous oxidation of NO to HONO could be strong enough to produce such large amounts of HONO. Thus, Equation 1 was not meant to describe the net production of HONO based on all of its sources and sinks. It only describes the net HONO production via homogeneous gas phase reaction. The impact of direct emission is considered in the 3<sup>rd</sup> and 4<sup>th</sup> paragraph (line 233-251), which discuss the potential impact of vehicle and biomass burning emissions. The conversion of NO<sub>2</sub> on ground surface and aerosol surface is exactly what we are mainly discussing in the next paragraphs in this section (line 252-340).

**We try to improve this section considering the reviewers suggestions and discuss all the known sources and sinks together to improve both the readability and scientific quality of the manuscript.** We calculated the following sources and sinks of HONO:

- 1) Gas phase homogeneous production of HONO:

$$P_{NO+OH}^{net} = k_{NO+OH}[NO][OH] - k_{HONO+OH}[HONO][OH], \quad (1)$$

where diurnal variation of OH concentrations was inferred from Whalley et al. (2015), replacing OH under fog conditions with  $1 \times 10^5 \text{ cm}^{-3}$ ).

- 2) Vehicle emissions:  $P_{emi} = \text{Emission factor} \times [\text{NOx}]_{\text{vehicle}}$ , where the emission factor was assumed to be 1% (maximum emission factor of 0.8% used in Huang et al. (2017)) and the total observed NOx was attributed to vehicle emission to obtain

an upper limit for the vehicle emission.

3) Heterogeneous conversion on aerosol and ground surface:

Typically, the conversion of NO<sub>2</sub> on aerosol and ground surface is parameterized as a linear function of NO<sub>2</sub> uptake coefficients and surface to volume ratios (surface area densities) (Xue et al., 2014; Li et al., 2018):

$$P_{het}=(k_g+k_a)\times[NO_2], \quad (2-1)$$

$$\text{Ground: } k_g = \frac{1}{8} \cdot \vartheta_{NO_2} \cdot \gamma_g \cdot \frac{S}{V} \quad (2-2)$$

$$\text{Aerosol: } k_a = \frac{1}{4} \cdot \vartheta_{NO_2} \cdot \gamma_a \cdot S_a \quad (2-3)$$

$\vartheta_{NO_2}$  stands for the mean molecular speed,  $\gamma_g$  and  $\gamma_a$  for the uptake coefficient on ground and aerosol surface,  $S/V$  for the surface to volume ratio and  $S_a$  for the ambient aerosol surface area density. We estimate ground surface HONO production using a  $\gamma_g$  of  $1e^{-6}$  during night time and  $2e^{-5}$  during daytime and an  $S/V$  of  $0.1 \text{ m}^{-1}$ . The heterogeneous HONO production in aerosol and fog droplets were already calculated using a  $\gamma_a$  range of  $1e^{-4}$  to  $1e^{-3}$  as suggested by Li et al. (2018). Since the surface area density under fog conditions were not measured, we can only estimate that  $dHONO/dt$  during fog events would exceed 40 ppb/hour based on calculation results in Fig.S1. For non-fog conditions, we used the ambient aerosol surface area density calculated using the humidified nephelometer and  $\gamma_a=1e^{-4}$  to further calculate the variation of the HONO production on aerosol surface.

4) Loss through photolysis:

$$L_{pho}=J_{Hono}\times[HONO], \quad (3)$$

where  $J_{HONO}$  was modelled using the TUV model, assuming AOD to vary with pH (see Table S1 in revised supplement).

Loss through dry deposition:

$$L_{dep}=v_{dep}/H\times[HONO], \quad (4)$$

where the dry deposition rate  $v_{dep}$  was assumed to be  $0.3 \text{ cm s}^{-1}$  according to Stutz et al. (2002) and the boundary layer height  $H$  was interpolated from ECWMF ERA-interim data ( <http://apps.ecmwf.int/datasets/data/interim-full-daily/>).

Finally, the net production rate can be expressed as:

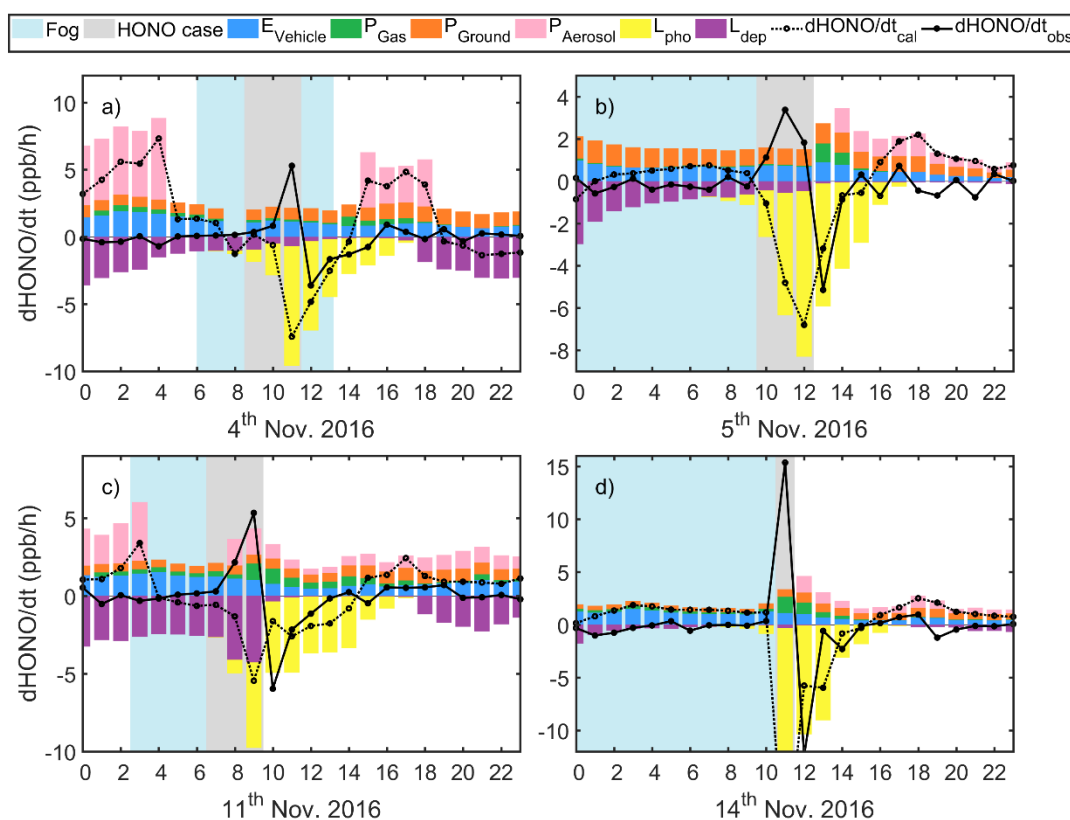
$$P_{HONO}^{net} = P_{NO+OH}^{net} + P_{het} + P_{emi} - L_{pho} - L_{dep} \quad (6)$$

Fig. 4 displays the estimated production and loss of HONO via various routes, as well as the calculated and actually observed dHONO/dt during the 4<sup>th</sup>, 5<sup>th</sup>, 11<sup>th</sup> and 14<sup>th</sup> Nov. 2016. The estimated upper limit for vehicle emissions displays little variability during the day, with slight decreasing trends during the four events, proving that the observed HONO production could not have been caused by direct vehicle emissions. The net gaseous phase production of HONO ( $P_{hom}^{net}$ ) contributed 0.15-0.18, 0.04-0.07, 0.27-1.04 and 0.25-1.53 ppb h<sup>-1</sup> during the 4 case events, displaying little influence during fog events and more during haze events. However, the estimated  $P_{hom}^{net}$  was far from sufficient to explain the observed d[HONO]/dt. Dry deposition was typically high during the night within the shallow nocturnal boundary layer and decreased during the day with the increase of the boundary layer height. The calculated  $L_{dep}$  contributed 0.5-0.9, 0.4-0.6, 2.7-4.3 and 0.05-0.3 ppb h<sup>-1</sup> to the loss of HONO. No significant decreases in  $L_{dep}$  were observed during the two fog events, while increases were detected during the cases on 11<sup>th</sup> and 14<sup>th</sup> Nov. Not only was the variation in  $L_{dep}$  unable to explain observed HONO productions, it further added to the discrepancy between observed and calculated d[HONO]/dt. During the four case events the  $J_{HONO}$  respectively increased from  $0.7 \times 10^{-4}$  to  $2.5 \times 10^{-4}$  s<sup>-1</sup>,  $1.6 \times 10^{-4}$  to  $2.4 \times 10^{-4}$  s<sup>-1</sup>,  $0.03 \times 10^{-4}$  to  $1.4 \times 10^{-4}$  s<sup>-1</sup> and  $1.6 \times 10^{-4}$  to  $4.4 \times 10^{-4}$  s<sup>-1</sup>, with  $L_{pho}$  contributing 0.9-8.9, 2.2-7.8, 0.03-5.5 and 0.8-26.4 ppb h<sup>-1</sup> to the loss of HONO.  $J_{HONO}$  increased significantly by the end of the HONO growth events to  $2.9 \times 10^{-4}$ ,  $4.3 \times 10^{-4}$ ,  $2.6 \times 10^{-4}$  and  $6.6 \times 10^{-4}$  s<sup>-1</sup>, respectively, suggesting that the rapid drop of HONO concentrations was high probably caused by the rapid photolysis. Overall,  $L_{pho}$  contributed most to the discrepancy between observed and calculated d[HONO]/dt.

Generally, the observed and calculated d[HONO]/dt agreed better with each other outside the HONO explosive growth periods, showing overestimations when

aerosol liquid water contents were high, suggesting possible overestimation in the  $\text{NO}_2$  uptake coefficient in the parameterization of  $P_{het}$ . This further suggests that the observed discrepancies in HONO production have mainly been caused by uncertainties in the heterogeneous formation estimates. The fact that HONO drastically increased while  $\text{NO}_2$  varied little (9:30 to 11:30, 5<sup>th</sup> Nov. and 6:30 to 8:30, 11<sup>th</sup> Nov.) or hardly increased even under drastic increases of  $\text{NO}_2$  (8:30 to 11:30, 14<sup>th</sup> Nov.), but displayed explosive growth with increasing  $\text{NH}_3$ , could not be explained by current known HONO sources (direct emission or gas phase reactions). Additionally, these rapid increasing HONO phenomena were all observed under foggy or high RH conditions, which further affirms the suspicion that the HONO increase was caused by heterogeneous conversion of  $\text{NO}_2$ .

The above results were added to the discussions in Sect. 4.1.



**Figure 4** Estimated HONO emission from vehicles (blue), gas phase production (green), production on ground (orange) and aerosol surface (pink), loss through photolysis (yellow) and dry deposition (purple), as well as the calculated (dotted black) and actually observed (solid black)  $d[\text{HONO}]/dt$  on a) 4<sup>th</sup>, b) 5<sup>th</sup>, c) 11<sup>th</sup> and d) 14<sup>th</sup>

Nov. 2016

4. Line 304-306 then line 326-329: In these section the photolysis of HONO is described being rapid (which is probably true) while it has been neglected earlier. I think the manuscript need reorganization to discuss more coherently the photochemistry of HONO under these conditions.

**Response:**

We thank the reviewer for pointing that out. Sect. 4.1 has been reorganized and new results (already mentioned in previous comment) were added. Discussion on the HONO photolysis were also made for the other three cases in the revised manuscript in Sect.4.1:

“During the four case events the  $J_{HONO}$  respectively increased from  $0.7 \times 10^{-4}$  to  $2.5 \times 10^{-4} \text{ s}^{-1}$ ,  $1.6 \times 10^{-4}$  to  $2.4 \times 10^{-4} \text{ s}^{-1}$ ,  $0.03 \times 10^{-4}$  to  $1.4 \times 10^{-4} \text{ s}^{-1}$  and  $1.6 \times 10^{-4}$  to  $4.4 \times 10^{-4} \text{ s}^{-1}$ , with  $L_{pho}$  contributing 0.9-8.9, 2.2-7.8, 0.03-5.5 and 0.8-26.4 ppb h<sup>-1</sup> to the loss of HONO.  $J_{HONO}$  increased significantly by the end of the HONO growth events to  $2.9 \times 10^{-4}$ ,  $4.3 \times 10^{-4}$ ,  $2.6 \times 10^{-4}$  and  $6.6 \times 10^{-4} \text{ s}^{-1}$ , respectively, suggesting that the rapid drop of HONO concentrations was high probably caused by the rapid photolysis. Overall,  $L_{pho}$  contributed most to the discrepancy between observed and calculated d[HONO]/dt.”

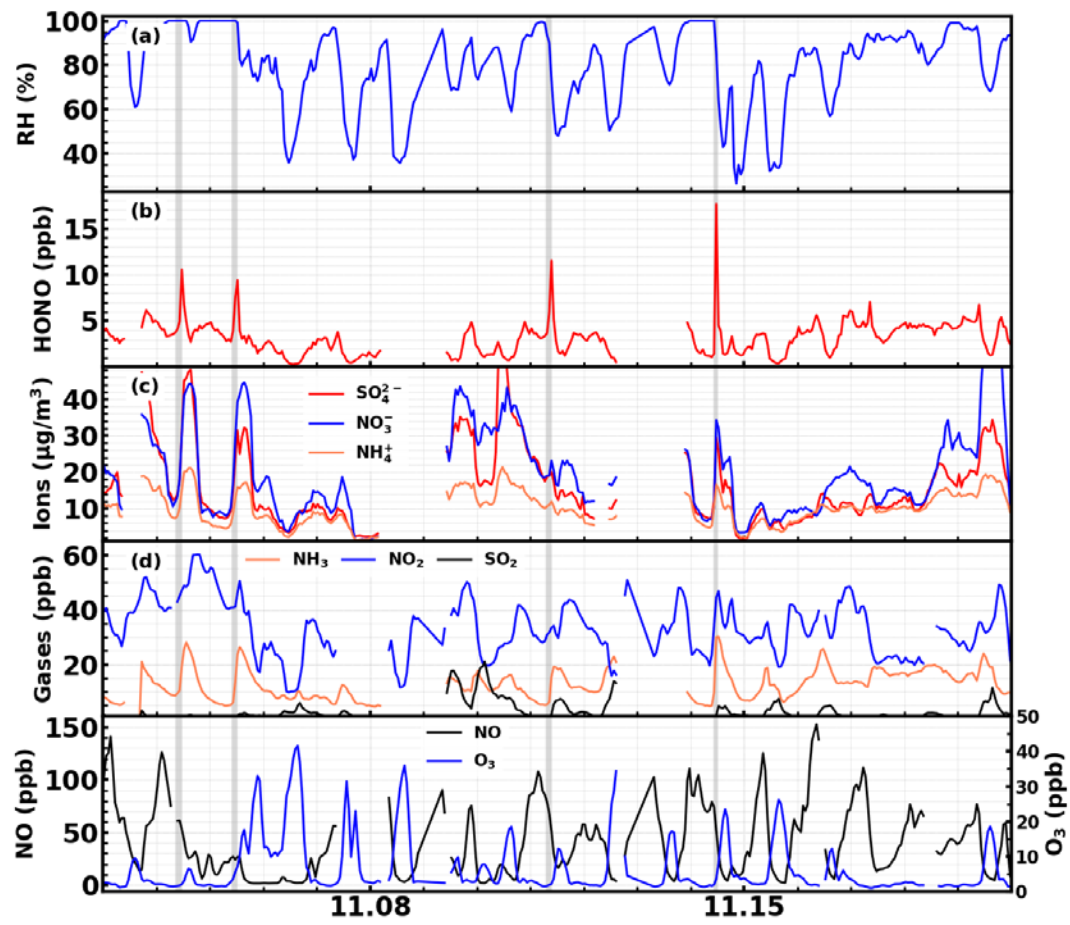
**Minor issues**

1. Figure 2: it is somewhat disturbing that the figure does not displayed all the data acquired. In particular (but not only) the absence of NO and ozone data is clearly a problem. Furthermore, the use of “ppb” for aerosol composition is confusing: is it related to the whole volume of air? Is it related to the whole aerosol quantity. Please use more straightforward units here.

**Response:**

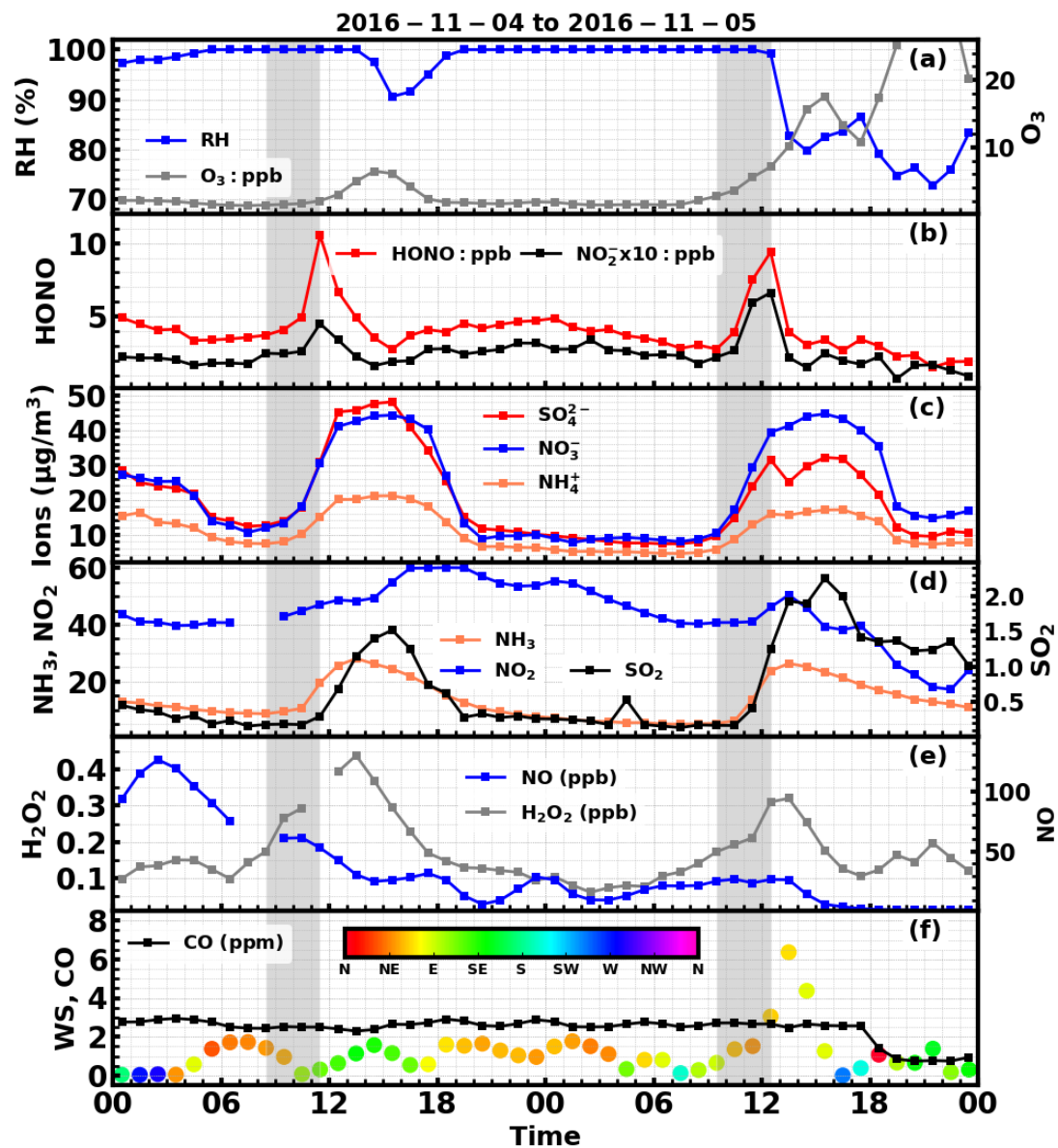
We included NO and O<sub>3</sub> concentrations in Figure 2 revised manuscript (see Fig. 5 below) according to the reviewer’s suggestion. We also agree with the reviewer that the use of “ppb” as a unit for aerosol composition is confusing. The units in the text and in Figs. 2-4 in the revised manuscript were changed to “ $\mu\text{g m}^{-3}$ ” instead (see Figs.

5-7 below).



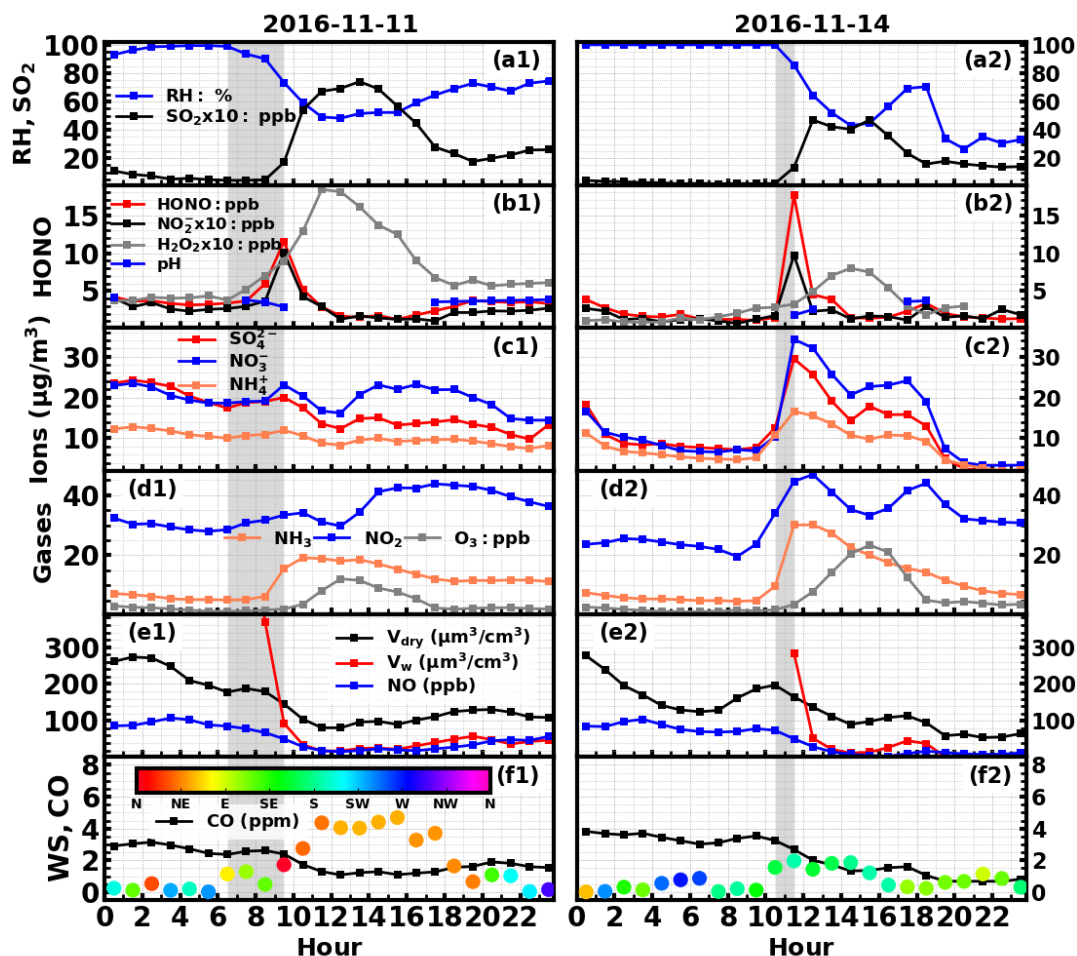
**Figure 5.** Time series of ambient **a)** RH; **b)** HONO; **c)** sulfate, nitrate, ammonium; **d)**  $\text{NH}_3$ ,  $\text{NO}_3$  and  $\text{SO}_2$  during the observation period.





**Figure 6** Time series of ambient a) RH,  $O_3$ , b) HONO,  $NO_2^-$ , c)  $SO_4^{2-}$ ,  $NO_3^-$ ,  $NH_4^+$ , d)  $NH_3$ ,  $NO_2$ ,  $SO_2$ , e) NO,  $H_2O_2$ , f) CO, wind speed and wind direction (colors of scatter points) from 11-04 to 11-05. Gray shaded areas represent periods of rapid increase of HONO.





**Figure 7** Time series of ambient a) RH, SO<sub>2</sub>, b) HONO, NO<sub>2</sub><sup>-</sup>, H<sub>2</sub>O<sub>2</sub>, aerosol pH, c) SO<sub>4</sub><sup>2-</sup>, NO<sub>3</sub><sup>-</sup>, NH<sub>4</sub><sup>+</sup>, d) NH<sub>3</sub>, NO<sub>2</sub>, O<sub>3</sub>, e) NO, volume concentrations of PM<sub>2.5</sub> in dry state ( $V_{dry}$ ), volume concentrations of liquid water ( $V_w$ ), f) CO, wind speed and wind direction during 1) 11<sup>th</sup> Nov. 2016 and 2) 14<sup>th</sup> Nov. 2016. Gray shaded areas represents periods of rapid increase of HONO.

2. Line 98 – 108: The experimental description of the instrument, the inlet and the protocol is insufficient.

**Response:**

We thank the reviewer for pointing it out and added more details to the experimental description on the instrument.

This part was revised as follows:

“During this field campaign, an In situ Gas and Aerosol Compositions Monitor (IGAC, Fortelice International Co., Taiwan) was used for monitoring water-soluble ions (Na<sup>+</sup>, K<sup>+</sup>, Ca<sup>2+</sup>, Mg<sup>2+</sup>, NH<sub>4</sub><sup>+</sup>, SO<sub>4</sub><sup>2-</sup>, NO<sub>3</sub><sup>-</sup>, NO<sub>2</sub><sup>-</sup>, Cl<sup>-</sup>) of PM<sub>2.5</sub> (particulate matter

with aerodynamic diameter less than 2.5  $\mu\text{m}$ ) and trace gases including HONO,  $\text{SO}_2$ ,  $\text{NH}_3$ , HCl, and  $\text{HNO}_3$  with a time resolution of 1h. The IGAC system draws in ambient air through a PM10 inlet and passes the sample through a sharp-cut PM2.5 cyclone at a flowrate of 16.7 L/min. The total length of the stainless steel sampling line is approximately 2 m, with an inner diameter of 3.18 cm (1.25 inch), resulting in a residence time below 6 s, suggesting that underestimates in  $\text{NH}_3$  possibly caused by adsorption on the stainless steel sampling tube as was proposed by Young et al. (2016) might be unimportant. A vertical annular denuder wetted with dilute  $\text{H}_2\text{O}_2$  solution ( $5 \times 10^{-3}$  M) collects the trace gases and converts  $\text{SO}_2$  rapidly to  $\text{SO}_4^{2-}$ , preventing  $\text{SO}_2$  from reacting with  $\text{NO}_2$  in the absorption solution to produce HONO artefacts. A scrub and impact aerosol collector under the denuder is mounted at an inclined angle to capture particles based on impaction after condensation growth. Two separate Ion Chromatographs are used to respectively analyze anions and cations for the gas and aerosol liquid extracts which were injected from the denuder and the aerosol collector once an hour. The detection limits are below 0.12  $\mu\text{g}/\text{m}^3$  and the background concentration of most water-soluble inorganic ions within the instrument were below 0.11  $\mu\text{g}/\text{m}^3$ , only with  $\text{SO}_4^{2-}$  showing a background concentration of 1.10  $\mu\text{g}/\text{m}^3$  (Young et al., 2016). Under highly polluted conditions such as our site, these measurement uncertainties are fully acceptable. The instrument has shown good performance in the past, agreeing well with filter based samples (Liu et al., 2017). Standard LiBr solution was continuously added to the aerosol liquid extracts during the measurements, to ensure the sampling and analyzing process is stable. The swing amplitude was within the range of three standard deviation, confirming the stability of the ion analyzing system throughout the campaign. A mixed standard solution was diluted to perform multipoint calibrations (at 5, 10, 20, 50, 100, 200, 500 and 1000 ppb concentrations) at the beginning and at the end of the campaign for the ions  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{NH}_4^+$ ,  $\text{Li}^+$ ,  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$ ,  $\text{NO}_2^-$ ,  $\text{Cl}^-$ ,  $\text{Br}^-$ , with the  $R^2$  of the calibrations reaching above 0.9999.”

3. Line 120: The authors indicate the use of a  $\text{NO}_x$  monitor 42CTL from thermo. It is not clear if this instrument is equipped with a Mo-based converter, a Blue light

converter or both. In any case, the risk of interferences with HONO on the NO<sub>2</sub> and NO<sub>x</sub> channels are high (through the conversion of HONO on heated Mo – see Dunlea et al, 2007 for example - or through its photolysis by the blue light. During some part of this field campaign the HONO values can be as high as 20 % of NO<sub>2</sub>. In this case it would be necessary to evaluate the cross-sensitivities of NO<sub>2</sub> and HONO in the configuration of the chemiluminescence monitor used.

***Response:***

We thank the reviewer for making a good point. The TE-42CTL NO<sub>x</sub> monitor at the Gucheng site is only equipped with a Mo-based converter, which means that HONO, PAN and HNO<sub>3</sub> can interfere with the NO<sub>2</sub> and NO<sub>x</sub> measurements. This we will clarify in our revised manuscript. During the entire campaign, the median value of HONO/NO<sub>2</sub> reaches 6.8%, while 90% of the data display HONO/NO<sub>2</sub> below 12.7%. The largest HONO/NO<sub>2</sub> were observed during the explosive HONO growth episodes in this study, which are shown in Fig.3. The NO<sub>2</sub> data measured by the TE-42C (red line) is compared against that subtracted by HONO (yellow line). Assuming all the HONO were converted to NO by the Mo-based converter, the actual NO<sub>2</sub> concentration would be similar to the yellow line in Figure 3, which only during the rapid HONO increase shows relatively larger deviation from the red line. Although there is indeed an impact of HONO on NO<sub>2</sub> measurements, NO<sub>2</sub> concentrations subtracted by HONO are still in excess, not limiting its conversion to HONO.

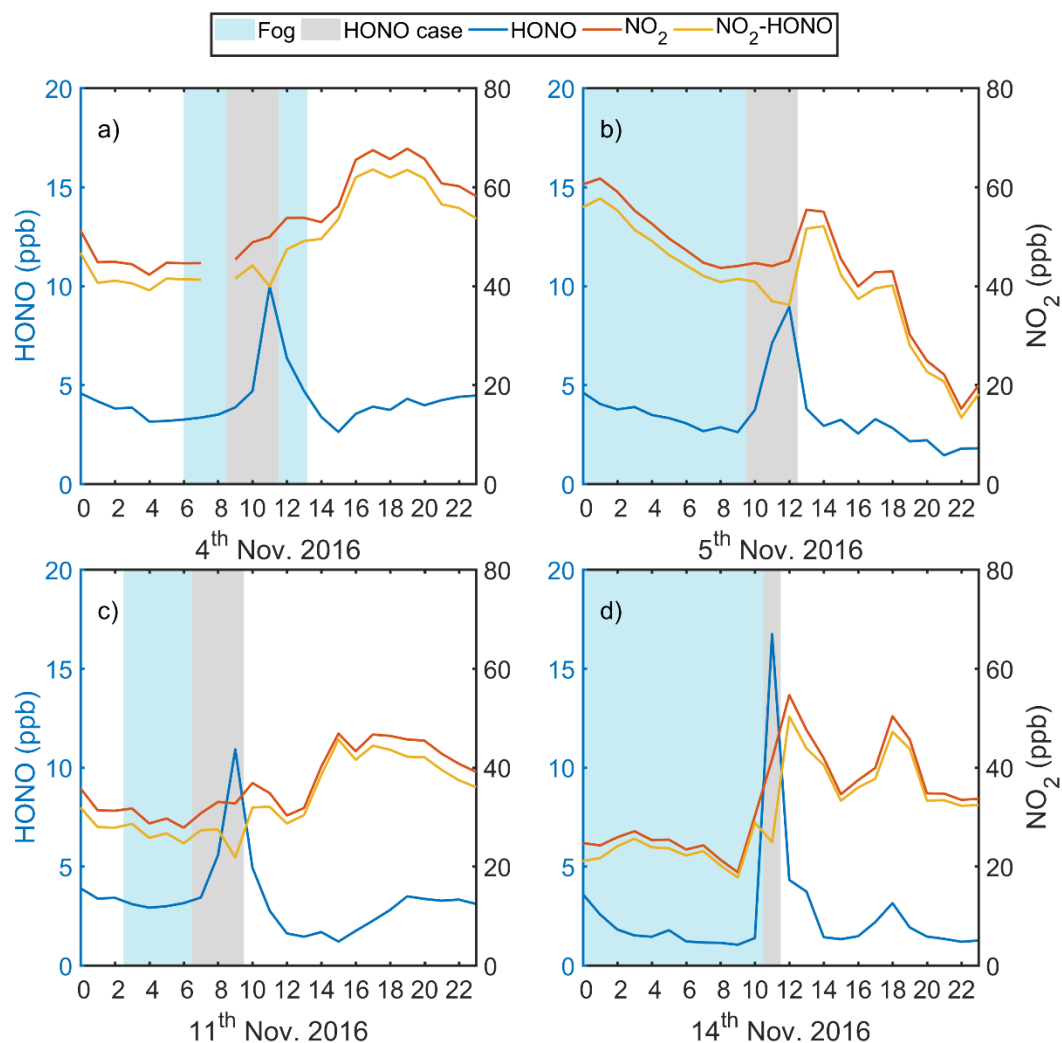


Figure 8 HONO, NO<sub>2</sub>, NO<sub>2</sub>-HONO concentrations on a) 4<sup>th</sup>, b) 5<sup>th</sup>, c) 11<sup>th</sup> and d) 14<sup>th</sup> Nov. 2016

4. Line 127: “wavelength” is misspelled

**Response:**

Thanks, correction made in the revised manuscript.

5. Line 229: The value of  $10^6$  radicals/cm<sup>3</sup> is taken as “typical for noontime haze condition” and later used in the equation 1. Even if the order of magnitude of this guess is probably not too wrong there is no reference provided. Furthermore, I don’t think that the scientific community have the necessary background to raise a “typical value” for these quite peculiar conditions. I would rather recommend to refer to published work such as Whalley et al, 2015 (field) or Tie et al, 2003 (large

scale modeling)

**Response:**

We thank the reviewer for the suggestion and have added the suggested reference by Whalley et al. (2015). The diurnal variation therein was used to estimate the diurnal variation of gas phase HONO production (see response to Major Comment #3).

6. Line 267-269: This statement is quite vague. Which anions are the authors referring to? More explanation are needed.

**Response:**

We added the following explanations to the introduction part, where this was first mentioned:

“Results of Yabushita et al. (2009) suggest that anions (such as Cl<sup>-</sup>, Br<sup>-</sup> and I<sup>-</sup>) greatly enhance the hydrolysis of NO<sub>2</sub> on water, and the NO<sub>2</sub> uptake coefficients of R2 can be enhanced several orders of magnitude by increasing electrolyte concentration.”

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