

The authors gratefully thank the reviewer for the comments and suggestions. We have revised our manuscript according to the reviewer's suggestions and comments. **All the changes and responses to the reviewers' comments are listed below point-by-point in blue according to a new line numbering in the revised manuscript. The major changes are highlighted with red in the revised manuscript.**

**Interactive comment on "Role of the dew water on the ground surface in HONO distribution: a case measurement in Melpitz" by Yangang Ren et al.**

**Anonymous Referee #2**

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General Comments

An exploration of the role of dew from field measurements has been long overdue. This work builds very well on prior field observations and lab experiments regarding effective HONO sequestration in dew. The Authors present a convincing study of the uptake and release of HONO from their observations and controlled field collections of dew nitrite. The production and loss process for HONO are parameterized to rates for HONO uptake into dew as well as subsequent release, which are then coupled to a box-model, finding that their observed rapid HONO increases on mornings with dew evaporation can be reproduced. The rates for NO<sub>2</sub>-to-HONO conversion and HONO deposition are compared against prior uptake observations quite well. Overall, the scientific quality of this manuscript makes it an excellent candidate for publication in Atmospheric Chemistry and Physics following major revisions to improve the manuscript clarity and data quality.

Major Revisions

1. Typos, phrasing, and writing clarity throughout have major issues in communicating the scientific findings of this work. Several instances where this makes following the discussion nearly impossible are noted in the detailed comments below. In other places, sentences are started with abbreviations or chemical structures. In many instances abbreviations are used first with the full spelling in brackets, when these should be presented the other way around. The entire manuscript should be revisited for clarity of writing by all of the Authors.

In three sections of the results and discussion (Sections 3.3, 4.2.1, and 4.2.3) there is no synthesis of the cases or findings to complete the sections. They have been left incomplete and should be revised.

**Response:** The typos, phrasing, and writing of the entire manuscript have been improved and

carefully checked by all of the authors. We also completed the section of 3.3, 4.2.1 and 4.2.3.

2. 2.1 The intercomparison between the MARGA and LOPAP is a very weak component of this manuscript. Detection limits are not given for either technique and cannot be assumed to be the same as from the prior reports cited by the Authors. These need to be determined at each field site from controlled calibrations and careful collection of field blanks. The collection and correction of field blanks from overflowing the MARGA inlet with zero air are not presented. Were they collected and was a correction applied? How were backgrounds in the MARGA determined?

**Response:** During the field campaign in Melpitz, the temperature of the stripping coil of LOPAP was kept constant at 25 °C by a thermostat. Automatic zero air (Air liquid, Alphagaz 2, 99.9999%) measurements were performed for 30 min per 12 h measurements to correct for zero drifts. In addition, three calibrations using NO<sub>2</sub><sup>-</sup> standard solution (Heland et al., 2001) were applied in the beginning, middle and end of the campaign, to derive the HONO mixing ratio of our field campaign with a detection limit of LOPAP as 0.6 pptv. This information was clarified in Line 159-168.

The detection limit of the HONO measurements with the MARGA system is 0.02 µg m<sup>-3</sup> (10 pptv) (Stieger et al., 2018). We performed blank measurements for the MARGA before the intercomparison campaign in 2018. For this, the MARGA was set to the blank measurement mode that has a duration of six hours. Within the first 4 hours, the MARGA air pump was off and the denuder and SJAC liquids were analyzed. The first- and second-hour samples were discarded as they still included residual concentrations. The evaluation of the blank concentrations was performed for the third- and fourth-hour samples. Within these blank samples, 0.00 µg l<sup>-1</sup> of nitrite were measured both in the gas and particle phase indicating no background nitrite collection. This information was added in Line 142-150.

2.2 Calibration techniques for each instrument are also not presented and the arguments for the measurement bias being high for the MARGA are incorrect. Prior studies with similar wet denuder systems have shown that the NO<sub>2</sub>-SO<sub>2</sub> and NO<sub>2</sub>-H<sub>2</sub>O corrections very small (VandenBoer et al., 2014) and cannot possibly explain this discrepancy. Further to this, the same work also demonstrates that in high NH<sub>3</sub> atmospheres, similar to those observed in this work, that the denuder pH is sufficient alkalinity and buffer capacity to collect the observed HONO quantitatively as nitrite. This prior work also makes a comparison with a home-made version of the LOPAP with inlets separated vertically by several meters, where intercomparison was only made when both instruments were calibrated with the same sodium nitrite solution. A strong capability to accurately measure HONO by both instruments was demonstrated. Similar attention to measurement quality must be made by the Authors here to improve the quality of their intercomparison.

**Response:** Xu et al. (2019) found significant contributions of  $\text{NO}_2^-$  due to the oxidation of  $\text{SO}_2$  with  $\text{NO}_2$ . However, the mentioned study also summarized that the influence of the reaction of  $\text{SO}_2$  with  $\text{NO}_2$  on the resulting MARGA HONO concentration is low for a pH below 6. The reason is the competition of the  $\text{SO}_2$  reactions between  $\text{H}_2\text{O}_2$  and  $\text{NO}_2$ . Latter reaction is more effective for higher pH. Thus, at a denuder pH of 5.7, the influence of the reaction between  $\text{SO}_2$  and  $\text{NO}_2$  on the higher MARGA HONO concentrations should be low.

However, Xu et al. (2019) found in their comparison between MARGA and LOPAP also a large scattering between both instruments and identified influences of  $\text{SO}_2$  and  $\text{NH}_3$ . They suggested that the sampling of the acidifying and alkalic compounds, respectively, are the main reason for the deviations as both compounds influence the pH of the MARGA absorbance solution and, thus, the formation of potential HONO artefacts within the MARGA analysis. Additionally, high  $\text{NH}_3$  concentrations could favor the sampling of HONO with the MARGA.

The calibration information of LOPAP was added in Line 164-168. The MARGA instrument used in this campaign was also well calibrated (Line 142-150), all of these procedures can ensure us a high quality of HONO measurement.

2.3 The results presented in the intercomparison (Section 3.1) are challenging to follow. The Authors mention ‘batch denuder’ (Line 215) and ‘offline batch denuder’ (Line 217) but this is not explained clearly anywhere. What are these batch denuders? How were they prepared and why are they relevant to measurements being compared between the MARGA (an online instrument) and the LOPAP?

**Response:** We excuse for the confusion. We unified “batch denuder” and “offline batch denuder” to “off-line batch denuder”. The off-line batch denuder setup is similar to the MARGA WRD. It consists of a rotating annular denuder in an open system without inlet tubes to avoid interactions of sampled air and walls. The liquid is collected after one-hour sampling and is analyzed off-line with ion chromatography (Stieger et al. 2018). This information are provided in Line 243-247.

Both MARGA and off-line batch denuder used an absorption solution with a pH of approximately 5.7. Thus, the found scattering between both instruments presented in Stieger et al. (2018) cannot be explained by different pH. This comparison is only given as additional information to exclude pH artefacts.

2.4 The Authors conclude their intercomparison to say that a long inlet on the MARGA could explain the higher HONO they are measuring. Is this hypothesized to be from  $\text{NO}_2$  hydrolysis on the inlet? The mechanism of interference on the inlet is assumed. It must be made clearly. If yes, can all MARGA daytime HONO data below 500 pptv (e.g. two to three hours from every minimum in the afternoons when  $\text{NO}_2$  conversion to HONO on surfaces is minimized)

be used to determine whether a relationship between measured HONO and NO<sub>2</sub> due to an inlet effect is likely? It should also be possible to determine whether the magnitude of this effect is really as high as the 58-90% enhancement observed here.

**Response:** We cannot specify the reactions that occur in the MARGA inlet system. However, heterogeneous formation of HONO within the inlet might explain approximately 30 % of the HONO artefact as we mentioned in Line 257-259. And other ca. 58% of the HONO artefacts could be caused by artefacts in the denuder solution as the by heterogeneous reactions of NO<sub>2</sub> and H<sub>2</sub>O as well as NO<sub>2</sub> and SO<sub>2</sub> in water described by Spindler et al. (2003) or VOCs by NO<sub>2</sub> in Line 252-258.

In addition, to proposed by Stemmler et al. (2006), the photosensitized NO<sub>2</sub> could contribute the daytime HONO formation, hence NO<sub>2</sub> conversion to HONO on surfaces could not exactly been minimized in the afternoon. Thus, it was hard to derive a relationship between measured HONO and NO<sub>2</sub> due to an inlet effect.

2.5 The photos of the inlet configurations (Figure S1a-b) do not make it very easy to understand what the sampling flows, line volumes, and therefore residence times, of the sampled gases were in M1 versus M2. The red text on Figure S1b is not possible to read. Was the sample residence time in M1 much smaller than in M2 due to a change in the inlet flow rate?

**Response:** The quality of Figure S1 was improved and more detailed information (e.g. sampling follow, line volume etc.) was added in the SI.

To improve the understanding of the chosen intercomparison setup, we refer to the Figure S1. In Figure S1b, the MARGA PM<sub>10</sub> inlet is shown. This inlet was used for both instruments in the first measurement period M1 to identify the inlet artefact. Therefore, the inlet tube was extended with a Y-connector (Figure S1a) within the measurement container. The tube from the inlet to the connector had a length of approximately 2 m.

For the second intercomparison period M2, the LOPAP inlet was set next to the MARGA inlet on the roof of the container. No interactions between LOPAP and MARGA inlet occurred.

A simple calculation of the MARGA inlet residence time was performed. Including a 2 m long inlet tube with a diameter of approximately 1 cm result in a volume of 157 cm<sup>3</sup>. Using the air flow of the MARGA with 16.7 l min<sup>-1</sup>, the resulting residence time of the air within the tube is approximately 0.57 seconds in the second intercomparison method. The flow rate for the LOPAP was 1.035 l min<sup>-1</sup>. Combined with the flow of the MARGA, the residence time in the first intercomparison period was 0.532 seconds, which is only marginally shorter and a potential influence of stronger interaction between walls and sampled air can be neglected. This information is in SI.

In Figure 1, the Authors present the findings from their intercomparison and the systematic  
145 offset between the two techniques (i.e. the uncertainty in the slope seems small) suggests that  
the poor comparison is due a calibration or blank-correction issue rather than significant  
sources of interferences. The plot of the intercomparison regressions does not include the  
1-sigma error evaluated in either the slopes or the intercepts and should be added. Looking  
150 closely at the measurements in Figure 1, there seem to be a number of observations of much  
higher HONO by the 5 min LOPAP measurements over the MARGA. Previously, (Sörgel et  
al., 2011) demonstrated that the LOPAP could sample fog droplets to result in such a positive  
bias, drawing off of prior work by (Bröske et al., 2003; Kleffmann et al., 2006). Were any fog  
events observed during the field campaign and was particulate nitrite observed by the  
MARGA and in the LOPAP HONO channel? Presumably, with so much dew, the  
155 meteorological conditions were also favourable for fog formation? This could further support  
the uptake and deposition of HONO into dew at the surface, as the MARGA nitrite  
measurements would observed this directly.

**Response:** The 1-sigma error evaluated in the slopes and the intercepts for the  
intercomparison plot was added in Figure 1.

160 As the reviewer mentioned, a number of observations have shown that 30 seconds averaged  
HONO data of LOPAP were higher than that of MARGA (Figure 1a) in the morning and  
middle-noon, which is not represented well when comparing 1 hour averaged HONO data  
from both instruments (Figure 1b). That indicates that the MARGA was not sensitive enough  
for the short time of HONO variation. We agree with the reviewer, that the meteorological  
165 conditions of dew formation were also favorable for fog formation. But unfortunately, no  
obvious fog events were observed. However, we cannot exclude that occasional ground fog  
events in the early morning were present but these ground fog events would probably not  
have affected the inlet in approximately 4 m above the ground.

170 However, particulate nitrite ranged from 0.012 to 0.11  $\mu\text{g m}^{-3}$  was also measured by MARGA  
and shown in Figure 3. However, it is really important to notice here that we used the  
particle-phase  $\text{NO}_2^-$  concentrations with caution because of positively correlated temperature  
dependencies of the  $\text{NO}_2^-$  formation by  $\text{NO}_2$  reactions (Gutzwiller et al., 2002).

3. The reactions from Table S1 are referenced regularly throughout the manuscript and  
should be moved, either as a table or as separated reactions corresponding to their first  
175 presentation throughout the introduction.

**Response:** All the reactions referenced have been moved from previous Table S1 to the  
manuscript corresponding to their first presentation throughout the introduction and text.

4. The Authors suggest that  $\text{NH}_3$  and  $\text{HNO}_3$  are released from dew similarly in the  
morning, as their mixing ratios also increase shortly after sunset. However, the observed

180 particulate  $\text{NH}_4\text{NO}_3$  also increases, which is likely more consistent with aerosol aloft being  
mixed down into the nocturnal boundary layer and repartitioning to release  $\text{NH}_3$  and  $\text{HNO}_3$ .  
Volatilization of  $\text{HNO}_3$  from surfaces containing water does not seem plausible given the  
strong acid nature of this species. If this were the case, deposition of  $\text{HNO}_3$  would not be  
represented as a terminal sink in atmospheric models. While  $\text{NH}_3$  may be released from dew,  
185 this would be challenging to discern from the data presented here. The several instances  
where this justification is made to bolster the release of HONO from dew should be removed  
from the manuscript and SI, along with the associated figures. The direct dew observations,  
model rate parameterizations, and subsequent model-measurement comparison are  
sufficiently strong to make this case.

190 **Response:** All the discussion about the dew water emission of  $\text{NH}_3$  and  $\text{HNO}_3$  has been  
removed from the manuscript, e.g. in sections 4.3.3 and 5.

### Detailed Comments

Line 37: ‘were’ should be ‘are’. This correction is needed frequently throughout the  
195 manuscript and should be made where appropriate throughout.

**Response:** This part has been deleted from the text since we deleted the Table S1. We also  
checked all the text for this mistake.

Line 45: ‘induced’ should be ‘activated’. The Authors should also cite the work of (Aubin and  
Abbatt, 2007) on this topic.

200 **Response:** Line 49, the “induced” was corrected to “activated”; and the reference of Aubin  
and Abbatt, 2007, is cited.

Lines 56-65: This is an extremely long list of reactions that need to be broken down into  
organized categories. Typically, where lists have entries that contain commas, the list items  
are separated using ‘;’ so they can be easily distinguished.

205 **Response:** Line 55-65, this part has been reformulated and the reaction list items are  
separated using “;”.

Lines 65-67: The potential role of dew releasing HONO was also discussed in (Lammel and  
Cape, 1996; Lammel and Perner, 1988; VandenBoer et al., 2014).

210 **Response:** References of (Lammel and Perner, 1988; Lammel and Cape, 1996; VandenBoer et  
al., 2014) are cited in Line 75.

Lines 81, 88, and 90: Instrument full names should be given first, followed by their  
abbreviations.

**Response:** Done by following the comments in Line 89, 96 and 99.

Line 82: ‘detect’ should be ‘detects’

215 **Response:** “detect” was corrected to “detects” in Line 90.

Line 90: should be ‘found excellent agreement’

**Response:** “the” was deleted in Line 98.

Lines 94-97: Why does an HNO<sub>3</sub> artefact matter? Should this be HONO? Given the subsequent lack of clarity in discussing the intercomparison issues below, additional details  
220 about the artefact between the MARGA and batch and coated denuders with shorter inlet lines should be very clearly outlined here.

**Response:** We are sorry for the mistake, the description of HNO<sub>3</sub> has been removed here and the description of HONO intercomparison was added “The cited group found a large scattering ( $R^2 = 0.41$ ) for the HONO comparison between MARGA and an off-line batch  
225 denuder without an inlet system. The probable reason was the off-line analysis of the batch denuder sample as the resulting longer interaction of gas and liquid phase during the transport led to further heterogenous reactions.” in Line 104-107. In addition, more detailed information of the batch denuder and possible artefacts have been added in Line 243-252.

Line 117: Sentences should not start with numbers. Consider rephrasing to ‘An inlet flow  
230 of : : : ‘

**Response:** Line 128-129, the sentence was corrected to “An inlet flow of  $1 \text{ m}^3 \text{ hr}^{-1} \dots$ ”

Lines 127-129: Was LiBr used in both the gas and particulate channels? It seems unlikely that this is easily done in the SJAC. Please clarify. Also, the second sentence should read ‘: : : both collected over the course: : :’

235 **Response:** LiBr was used in both gas and particulate channel added during the sample injection to the IC and was added in Line 138-140; “in” was corrected to “over” in Line 140.

Lines 136-137: Two reactions for the derivatization of nitrite to the azo dye are mentioned here but not presented anywhere. The reaction notation conflicts with the reaction numbers presented in Table S1. Please clarify and add the reactions, if desired.

240 **Response:** We clarified the reactions by presenting other reactions as “reaction 1...” as shown in text, also we referenced the publications (Kleffmann et al., 2006; Heland et al., 2001) for the derivatization reactions R1 and R2 in Line 160-161.

Line 139: ‘air zero’ should be ‘zero air’

**Response:** Line 162, “air zero” was corrected to “zero air”.

245 Lines 153-155: The methodology for cleaning the glass plates and collecting samples is presented, but no blank collections are presented where deionised water applied to the glass plates was measured. This should be included in Table 2 to increase the strength of these findings. It would also be valuable, if the Authors have such data, to present the nitrite

recovered from washing these glass plates after nights when no dew formation occurred to  
250 compare the deposited quantities. This would strongly support the magnitude of calculated  
uptake of HONO into the bulk water on these surfaces during dew formation events.

**Response:** The blank values were already subtracted in Table 2 but we added the blank  $\text{NO}_2^-$   
concentration to Table 2 as suggested by the reviewer and more information in lines 333-334.  
255 However, we do not have such data about the recovered  $\text{NO}_2^-$  from washing these glass plates  
after nights when no dew formation occurred, an issue which should be addressed in the  
future.

Line 224: Why was PM10 nitrite not measured? If there was fog, or reactive coarse  
particulate matter as observed by (He et al., 2006; VandenBoer et al., 2015), then you may  
observe the partitioned HONO directly with the MARGA as in (VandenBoer et al., 2014).

260 **Response:** The PM10 nitrite was also measured and shown in Figure 3 in right Y axis.  
However, as mentioned above, we used the particle-phase  $\text{NO}_2^-$  concentrations with caution  
because of positively correlated temperature dependencies of the  $\text{NO}_2^-$  formation by  $\text{NO}_2$   
reactions (Gutzwiller et al., 2002) within the SJAC.

Line 249 onward: The discussion from here on is vague about which measurement is being  
265 used for each section. This needs to be clearly denoted. Presumably the LOPAP measurement  
is being taken as having the best accuracy for measuring HONO, but this needs to be clearly  
stated.

**Response:** We clarified this in Line 261-262, it now reads: “As a result, we chose the  
LOPAP-measured HONO in the following sections because of its high precision”.

270 Line 262: ‘concentrated’ should be ‘concentration’

**Response:** Line 306, ‘concentrated’ was corrected to ‘concentration’.

Lines 264-266: This sentence is unclear and hard to follow. Rephrase.

**Response:** Line 297-298, We agree and the sentence was corrected as “The HONO morning  
275 peak might possibly be caused by the photolysis of particle-phase  $\text{HNO}_3/\text{NO}_3^-$  (Zhou et al.,  
2003;Ye et al., 2016;Zhou et al., 2011).”.

Line 267: ‘during the campaign’ is referring to the prior campaigns just cited in the preceding  
sentence or in this work? Please clarify.

**Response:** Line 309, we clarified it as “during our campaign in Melpitz”.

280 Line 268: ‘HONO would be reemitted in the atmosphere’, also here ‘lead’ should be ‘led’  
(there are many instances of this throughout the manuscript that need to be corrected)

**Response:** Line 310-311, “is” was changed to “would be”; “lead” was corrected to “led” and  
was checked all over the text.

Line 276: 'NO<sub>2</sub>-to-HONO conversion frequency'

285 **Response:** Line 319, we corrected this sentence as "... surpassing the HONO formation from the NO<sub>2</sub>-to-HONO conversion".

Lines 279-284: These are two sets of observations, not cases. Please indicate why these are nicely categorized for further exploration by clarifying their utility. At Line 282 the Authors indicate that HONO increased with wind speed, but usually this corresponds to a decrease in concentration due to dilution. Is this increase related to wind direction? This section then ends  
290 without further exploration of the two cases and needs to be completed.

**Response:** Since these two sets of observations have been described in Line 291-292 and also Section 4.2.3, we decided to remove this paragraph. We agree with the reviewer, HONO mixing ratios could have decreased by enhanced dilution through stronger wind. As shown in Figure 2 and 5, this increase did not relate to the wind direction. However, we assume the  
295 increasing wind speed enhanced the dew water evaporation and the decrease of RH leading to the morning peak.

Lines 286-289: These two sentences are misleading and contradict an accurate discussion that follows regarding the pH-dependent effective partitioning of HONO between the gas phase and aqueous solution. Acidic water would readily volatilize HONO. Revise this for  
300 consistency with the following discussion. In particular, the work of (He et al., 2006) demonstrated that leaf surface washings were alkaline, which drove favorable HONO partitioning to the surface. Were any grass washings collected here to investigate the effective pH of the vegetated surface? What about the glass plates after exposure over nights where no dew formed? Either of these, but ideally both, would make a stronger case for effective dew  
305 uptake of HONO.

**Response:** We are sorry for the mistake. The wrong statement "might be slightly acidic due to acid contribution from acidic aerosols (such as NH<sub>4</sub>HSO<sub>4</sub>)" has been removed from the text. In addition, as shown in Table 2, the pH of dew water collected from the glass plate is neutral. However, we did not collect the grass washings and glass plates washing after exposure over  
310 nights where no dew formed. These valuable applications will be done in the future.

Line 295: 'concern' should be 'focuses'

**Response:** We agree, in Line 331, the "concern" was corrected to "focuses".

Lines 303-307: This needs to be clarified. I see no temperatures where dew water would be frozen in April. Did this actually occur in May? And why would higher F(NO<sub>2</sub>-) be observed  
315 on frozen dew? As the Authors state, the phase transition would act to inhibit HONO partitioning. This section needs to be revisited and revised for clarity. It is also surprising that this high F(NO<sub>2</sub>-) is included in the averaging over the other dew F(NO<sub>2</sub>-) observations. This

would deliberately bias the use of this value later. A better approach would be to statistically exclude the outlier using the Grubb's test or, better yet, include all of the observations in the average since the number of dew samples is very limited.

**Response:** Yes, frozen dew occurred also when the measured air temperature (in 5 m above the ground) was above 0 °C. This was also the case in May 2019. No temperature below 0 °C was observed in a height of 5 m, but colder temperature near the surface resulted in freezing dew.

We are sorry for the misunderstanding. Exactly the higher  $F(\text{NO}_2^-)$  was observed on May 11<sup>th</sup> where dew water was not frozen. Frozen dew water was observed for the other days (May 8<sup>th</sup>, May 13<sup>th</sup> and May 14<sup>th</sup>) with lower  $F(\text{NO}_2^-)$ . These samples were discarded because of possible interferences in the HONO partitioning. Finally,  $F(\text{NO}_2^-)$  obtained on May 11<sup>th</sup> was used for the following sections. We revised our description as below: "higher  $F_{\text{NO}_2^-}$  was obtained on May 11<sup>th</sup>, where dew water was not frozen. On other days (May 8<sup>th</sup>, May 13<sup>th</sup> and May 14<sup>th</sup>) frozen dew water was observed, which likely inhibited HONO to dissolve. Hence, these frozen samples were not considered in this paper. On May 11<sup>th</sup>, the final  $F_{\text{NO}_2^-}$  ...".

On May 11<sup>th</sup>, a third dew water sample was collected from 3:30 to 5:20 (UTC) after collecting the first sample (18:00 – 3:20 UTC) as shown in Table 2. The  $\text{NO}_2^-$  concentration in the third sample is lower. However, the total value of  $F(\text{NO}_2^-)$  for this morning would be the sum of the first ( $8.0 \mu\text{g m}^{-2}$ ) and the third sample ( $1.43 \mu\text{g m}^{-2}$ ), which was used in our study for following calculations. We also clarified this in Line 335-336 and Line 342-345 and Table 2.

Line 312: End first sentence after 'evaluated'. Start next sentence with 'Generally'

**Response:** We agree and changed in Line 353.

Lines 315-319: If the Authors have no data that meet these criteria, then why bother listing them. Simply state that a direct emission number could not be quantified here and then apply one that has been widely used, such as the study by (Kurtenbach et al., 2001) cited on Line 314. This can then be applied to correct the HONO formation and loss rates at night, when the correction can be accurately used. This cannot be simply ignored.

**Response:** We removed the "criteria" from the section 4.1. Since (Kurtenbach et al., 2001) reported the emission factor ( $\text{HONO}/\text{NO}_x$ ) as 0.3-0.8% in Wuppertal Germany and regarding on the condition (low HONO direct emission) of field campaign, a low emission factor of 0.3% obtained by (Kurtenbach et al., 2001) was used to correct the HONO emission from HONO formation of  $\text{NO}_2$ -to-HONO conversion. As a result, a lower  $[\text{HONO}]/[\text{NO}_2]$  ratio was obtained than before. However, this has no change on  $k_{\text{het}}$  within large uncertainty (Table 3).

Lines 331-334: This is a most unusual exercise. This pathway has been long ignored as it is well known to be negligible.

**Response:** This part about the nighttime OH has been removed.

Line 341: 'cases' should be 'conditions'

355 **Response:** Line 371, 'cases' was corrected to 'conditions'.

Line 362: High HONO/NO<sub>2</sub> values were also reported in (VandenBoer et al., 2013).

**Response:** The reference (VandenBoer et al., 2013) was added in Line 388.

Line 370: This discussion is incomplete. What chemistry is happening here and why?

360 **Response:** Line 397-399, we conclude this section by "This could be ascribed to the higher S/V surface in the rural site because of the higher leaf area index (LAI, m<sup>2</sup>/m<sup>2</sup>) compared to an urban which might have enhanced heterogeneous NO<sub>2</sub>-HONO conversion."

Lines 388-392: This needs to be revised. This logic is very hard to follow and is the inverse approach from what is typically presented to make such a comparison between a modeled rate and observations. The uptake coefficient comparison does not seem to follow logically from the prior calculation. The Authors should revisit this. It would be better to show that typical aerosol uptake coefficients used by (Tsai et al., 2018; Wong et al., 2012) fail to produce the observed quantities of HONO and to quantify the fraction that aerosol conversion represents so it is clear that aerosol conversion is trivial.

370 **Response:** As reported by Li et al. (2012), the uptake coefficient of NO<sub>2</sub> to HONO could be calculated if the entire HONO formation were taking place on aerosol surfaces. VandenBoer et al. (2013) also applied the same method to obtain an uptake coefficient of NO<sub>2</sub> to HONO. In this work, we corrected our uptake coefficient of NO<sub>2</sub> which was wrong because of the bad RH correction. Then this obtained uptake coefficient of NO<sub>2</sub> was used in the following model in section 4.3.2. We revised our description in Line 412-417 to make it clearer. The text was

375 changed to "If the entire HONO formation was taking place on the particle surface, the calculated  $\gamma_{\text{NO}_2 \rightarrow \text{HONO}_a}$  varied from  $1.5 \times 10^{-6}$  to  $1.9 \times 10^{-5}$  with a mean value of  $(8.8 \pm 5.0) \times 10^{-6}$ , which is lower than the reported values from VandenBoer et al. (2013) as  $10^{-4}$  but it is in the good agreement with those observed in studies on relevant surfaces, which ranged between  $1 \times 10^{-6}$  to  $1 \times 10^{-5}$  (Kleffmann et al., 1998; Kurtenbach et al., 2001)."

380 Line 414: These references are not for ground proxies, but atmospheric aerosols. Remove and add studies that use real soils and soil proxies, such as (Donaldson et al., 2014; VandenBoer et al., 2015). These are both consistent with the observations made in this work and are more representative.

385 **Response:** (Donaldson et al., 2014; VandenBoer et al., 2015) was used to replace the earlier references in Line 442.

Lines 430-431: The trends discussed are not plotted on Figure 7a and need to be added. It seems unlikely that these trends are very robust. The kinetics of reaction 2 are not well constrained for increasing surface availability of H<sub>2</sub>O and this sentence should be rephrased

carefully.

390 **Response:** The trend has been added in Figure 7a. The statement about the kinetics of reaction 2 has been removed.

Line 453: The Authors should expand on why the difference between their observations and those from Boulder are so dramatic. The observations constraining HONO uptake on the ground surface presented in (VandenBoer et al., 2013) are all for nights where dew did not  
395 form, but deposition was observed to increase with RH (see equation 3 in Section 3.1 of that paper). Perhaps it is possible to estimate an effective HONO uptake coefficient from the flow tube work of (He et al., 2006) to compare to?

**Response:** We are sorry for the wrong value of HONO uptake coefficient in the previous version, we recalculated the HONO uptake coefficient by using mean molecular velocity of  
400 HONO and mixing layer height H from backward trajectory and then  $\gamma_{\text{HONO,ground}}$  uptake coefficient was obtained from  $1.7 \times 10^{-5}$  to  $2.8 \times 10^{-4}$  with average of  $(1.0 \pm 0.4) \times 10^{-4}$  (Line 481-482). This value is in the good agreement with the value of VandenBoer et al., 2013.

Line 461: Discussion is incomplete (see Major comment on this). Summarize the importance of your findings.

405 **Response:** We now used the Resistance Model and the according results are discussed in Line 495-510.

Line 465: ‘above: :’ should be ‘to reach an average minimum: :’

**Response:** Line 514, “above” was corrected to “to reach”.

Line 466: Why is the daytime maximum presented here? It is distracting from the point of this  
410 part of the discussion. Remove.

**Response:** “with the maximum mixing ratio of  $1400 \pm 100$  pptv” was deleted.

Lines 469-471: See Major comment on  $\text{NH}_4\text{NO}_3$  thermodynamic partitioning and mixing. Remove this argument.

**Response:** “It should be noted that gaseous  $\text{NH}_3$ ,  $\text{HNO}_3$  and particulate  $\text{NH}_4^+$ ,  $\text{NO}_3^-$  also  
415 present the same trend like HONO as shown in Figure 4.” was deleted.

Lines 499-501: Fix subscript typo on ‘unknown’ in the equation. The final sentence is hard to follow and this section does not end very clearly. What is the ‘additional source’? P(unknown)? Revise for clarity.

**Response:** Line 548, subscript typo ‘unknow’ was corrected to be ‘unknown’. Additionally,  
420 we added our explanation as “This could be well explained by the photochemical processes such as reactions 3b and 6 and would be discussed deeply in the next section.” in Line 551-552.

Lines 514-515: The parameterization of boundary layer height used in the box model has not been explained and needs to be added somewhere. Were static or dynamic conditions of boundary layer height used? What measurements were used to set these boundary layer conditions and how are they justified to be suitable for use in this model?

425  
430 **Response:** The mixing layer height  $H$  was calculated from the backward trajectory based on GDAS data as shown in Figure S7 and dynamic conditions of boundary layer height were used in the present study. We mentioned this parameter in Line 568-570 “The mixing layer height  $H$  was calculated from the backward trajectory based on GDAS data as shown in Figure S7 and a dynamic conditions of boundary layer height was used.”

Line 518: Following ‘12.5’ the authors should add ‘that we calculated from our observations’

**Response:** Line 571, ‘that we calculated from our observations’ was added after  $\gamma_{\text{HONO,ground}}$  value.

435 Line 522: ‘would be’ should be ‘was’

**Response:** Line 576, ‘would be’ was corrected to ‘was’

Line 526: ‘preceded’ should be ‘made’

**Response:** Line 579, ‘preceded’ was corrected to ‘made’

440 Lines 529-531: There is a lot of literature stating that particulate  $\text{NO}_3^-$  photolyzes 10-1000 times faster than gaseous  $\text{HNO}_3$ . How do the Authors justify why this was not included in the model?

**Response:** We agree with the reviewer, hence a factor of 30 from the recently publication (Romer et al., 2018) was multiplied to  $J_{\text{HNO}_3}$  due to a faster photolysis of particle-phase  $\text{HNO}_3$  as mentioned in Line 583-584.

445 Lines 539-540: Was it dry ground or rain that was observed on the night of 23 April? Please specify.

**Response:** Line 604, we clarified that it was dry ground surface on the night of April 23<sup>th</sup>.

Line 548: What is ‘this value’? Is it the average? Or is it one of the maximum or minimum?

**Response:** Line 613, “this value” was corrected to “the average value”.

450 Lines 577-579: Remove  $\text{NH}_4\text{NO}_3$  discussion.

**Response:** Section 4.3.3, the discussion of  $\text{NH}_4\text{NO}_3$  was removed.

Line 581: ‘consistently’ should be ‘previously’

**Response:** Line 642, ‘consistently’ was corrected to ‘previously’.

Line 583: ‘these’ should be ‘our’

455 **Response:** Line 644, ‘these’ was corrected to ‘our’.

Line 613: ‘are rich of ground surface (forest and grass)’ is inaccurate. Consider rephrasing to ‘experience frequent dew formation’. The type of surface likely does not matter much when bulk water is available. If this were the case, the glass dew collectors would not have done a representative job of collecting the dew composition.

460 **Response:** Line 676, ‘are rich of ground surface (forest and grass)’ was corrected to ‘experience frequent dew formation’.

Line 616: Conclusions and Atmospheric Implications: Rewrite fully to reflect manuscript changes made.

**Response:** These parts have been strongly rewritten.

465 Table 1: Clearly indicate the MARGA measurements.

**Response:** The obtained data of MARGA was noted as <sup>b</sup> in Table 1.

Table 2: The methods are unclear whether the pH of the dew was measured on a subsample of the total volume. Add some details on this to the caption and to the method section. It could be possible that direct measurement of the dew sample could lead to ion contamination from the salt bridge of the pH meter being in contact with the sample. Add blank sample values of collected nitrite here (i.e. deionised water passed over clean glass plates and trough into sampling vessel) for comparison. It would also be useful to see what nitrite deposition occurs to these surfaces at night in the absence of dew, so as to contrast the magnitude of change that the presence of dew makes.

470 **Response:** “pH was measured by a pH meter (mod. Lab 850, Schott Instruments) on a subsample of the total volume” has been noted as <sup>b</sup> in the Table 2 and method section 2.4.

The blank sample value was also added in Table 2. However, we do not have the data of “nitrite deposition occurs to these surfaces at night in the absence of dew” but we would like to apply it in the future.

480 Figure 1: The panel order in this figure is unusual. Typically, panels are lettered from a, starting at the top, with the letters located outside of the axes. The top panel intercomparison is not easy to read. The slopes should be positive on the plot, with HONO\_LOPAP (pptv) on the bottom axis, not the top.

**Response:** The Figure 1 was improved by following the Reviewer’s suggestion.

485 Figure 3: Change ‘HONO\_MARGA’ to ‘HONO’

**Response:** The ‘HONO\_MARGA’ was corrected to ‘HONO’ in Y axis of Figure 3.

Figure 4: Remove panels e) and f)

**Response:** The panel e and f were described in Line 294-296 to discuss the hypothesis of morning peak could be caused by the photolysis of particle-phase  $\text{HNO}_3/\text{NO}_3^-$ . Hence the

490 panel e and f were kept here.

Figure 5: Are these measurements from the LOPAP? How was the error determined? This was not presented in the methods and should be added.

**Response:** We mentioned that it is the HONO data of LOPAP in the caption and the method of error calculation was added in Line 167-168 as “and then the error of HONO mixing ratio  
495 was estimated based on the detection limit and a relative error as 10%.”

Figure 6: This is not very convincing as there is a lot of overlapping data. Maybe create RH bins for each 20 % increment. Each bin would be centred at the average HONO/NO<sub>2</sub> with x and y error bars corresponding to standard deviations of HONO and NO<sub>2</sub> of all data collected in that RH bin (e.g. 0-20 %)?

500 **Response:** The previous Figure 6 about the “Correlation between HONO and NO<sub>2</sub> at night” was removed since the unconvinced discussion as the HONO to NO<sub>2</sub> ratio typically increase during night-time and could be artificial correlation between RH with HONO/NO<sub>2</sub>.

Figure 7: Lettered labels on the panels are different from others above. Please make these consistent across all figures. It is very hard to take anything away from 7b. Consider moving  
505 to the SI. Trend lines need to be added to 7a to address comments above.

**Response:** The lettered labels were made consistent with others Figures. The “previous Figure 7” was moved to SI as Figure S8. And trend line was added in Figure S8a.

Figure 8: I would like to see a third panel here that depicts the OH radical concentration, measured HONO, and HONO from Model 5 that includes upper and lower limits on the  
510 model output according to the minimum and maximum k(emission) rates observed. This would provide a better comparison to the range of observations and would likely package the argument of dew partitioning even better.

Again, move the panel letters outside of the axes and keep them consistent with prior figure formatting.

515 **Response:** We agree with the Reviewer that a third panel with measured HONO and HONO from the model output according to the observed minimum and maximum k(emission) rates could provide a better comparison to the range of observations. However, since the Figure 6 (previous Figure 8) is already compact, we created a Figure S11 in the SI, which was explained in Line 619-623 as “In Figure S11, the observed HONO atmospheric mixing ratio and the calculated HONO mixing ratio by model 6 using a minimum dew HONO emission  
520  $k_{\text{emission}} = 0.006 \text{ pptv } \%^{-1} \text{ s}^{-1}$  and maximum dew HONO emission  $k_{\text{emission}} = 0.026 \text{ pptv } \%^{-1} \text{ s}^{-1}$ , respectively, show that HONO emission from the dew water evaporation... ”.

Figure S1: Why are both sets of photos separately labeled? Add schematics to depict tubing diameters, lengths, and flows for each sampling configuration. The schematic needs to be

525 consistent with the requested revisions to the sampling methods section. Fix caption to be accurate.

**Response:** Figure S1 was improved to indicate the sampling flow of LOPAP and MARGA, the length and diameter of the sampling line. The sampling strategy was also described in the SI.

530 Figure S2: What is the trough material made of?

**Response:** The trough is made of polyvinyl chloride.

Figure S8: This should be in the main manuscript. It is a great figure for this paper.

**Response:** The previous Figure S8 was moved to the main manuscript as Figure 7.

535 Figure S9: Should 'evolution' be 'structure'? Evolution implies time dependence which is not what is described in the text of the manuscript.

**Response:** The previous Figure S9 was removed because of the wrong defined concert.

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