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The Editor
Atmospheric Chemistry and Physics

Submission of revision for the Atmospheric Chemistry and Physics Discussions manuscript ‘Role of the dew water on the ground surface in HONO distribution: a case measurement in Melpitz’ (MS No.: acp-2019-1088) by by Yangang Ren, Bastian Stieger, Gerald Spindler, Benoit Grosselin, Abdelwahid Mellouki, Thomas Tuch, Alfred Wiedensohler and Hartmut Herrmann

Dear Editor,

please find attached here our response to the reviewer comments for the manuscript mentioned above together with its revised versions of the manuscript and supplement. We would like to thank both reviewers and the editor for all of their valuable and insightful comments to improve the manuscript. We have carefully considered all the reviewer comments and revised the manuscript accordingly. Below, we provide responses to the comments in blue, with changes made in red in the manuscript.

Sincerely yours,

Prof. Dr. H. Herrmann
Professor of Atmospheric Chemistry
Head of TROPOS Atmospheric Chemistry Department

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.

Hang Su (Editor)
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"In her/his major concern 3) intercomparison, the referee #1 would also like to point the authors to another recent paper in which also a MARGA system was intercompared with a LOPAP: Xu et al., AMT.12, 6737-6748, 2019, with very similar results to the other reference mentioned there (strong overestimation of HONO by the MARGA).

Response: We thank Dr. Su for his comment and this information. Accordingly, Xu et al., 2019 is now referenced and compared with our present result in Line 237-240 "The result is in excellent agreement with the former intercomparison of both instrument types in the Chinese field campaign (Lu et al., 2010;Xu et al., 2019) where the HONO mixing ratio measured with the wet-denuder-ion-chromatography (WD/IC) instrument was affected by a factor of three on average."

References

Lu, K., Zhang, Y., Su, H., Brauers, T., Chou, C. C., Hofzumahaus, A., Liu, S. C., Kita, K., Kondo, Y., Shao, M., Wahner, A., Wang, J., Wang, X., and Zhu, T.: Oxidant ($O3 + NO2$) production processes and formation regimes in Beijing, Journal of Geophysical Research: Atmospheres, 115, 10.1029/2009jd012714, 2010.

Xu, Z., Liu, Y., Nie, W., Sun, P., Chi, X., and Ding, A.: Evaluating the measurement interference of wet rotating-denuder–ion chromatography in measuring atmospheric HONO in a highly polluted area, Atmos. Meas. Tech., 12, 6737-6748, 10.5194/amt-12-6737-2019, 2019.

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 #1

Received and published: 7 February 2020

In the manuscript by Y. Ren et al. HONO was measured at the rural station Melpitz in Germany by two different commercial instruments, which were intercompared showing strong interferences and inlet artefacts for one of the instruments. In addition, the measurement data including dew water analysis were used to demonstrate that HONO deposition during night-time and re-emission during the early morning when the relative humidity decrease are important processes in good agreement with former studies. In addition, HONO formation during night- and daytime is discussed and the contribution of HONO photolysis to the daytime formation of OH radicals is compared with the typically proposed main source of OH radicals by O_3 photolysis, showing a similar contribution of both sources. The study contains some interesting information and may be considered for publication in ACP, after significant concerns have been considered.

Major Concerns:

1) Chemical reactions:

I found the manuscript difficult to read, since all discussed chemical reactions are only summarized in the supplement. At least the important reactions should be shown in the main text.

Response: All the discussed reactions were now moved to the main text.

2) Dew and gas measurements:

In the experimental section, gas phase und dew measurements are explained. However, these measurements were not done in a single field campaign, but the dew measurements were performed more than one year later after the gas phase measurements. Later the average dew nitrite data is used to explain the morning peaks of HONO observed one year earlier. This method will cause large uncertainties, since the gas and dew concentrations, but also other parameters may significantly vary from year to year (apples and oranges: : :). E.g. while the temperature was well above freezing during the gas phase campaign (see Fig. 2), dew water was freezing during the later dew campaign (see line 304). However, if water is freezing, oxidation of nitrite is significantly accelerated (see e.g. Nature, 358, 1992, 736-738). Here parallel gas phase and dew measurements are clearly necessary in the absence of frozen dew water.

Response: As the reviewer mentioned, our gas phase measurement was mainly conducted in April 2018. We agree with the reviewer that large uncertainties may occur by comparing the dew measurements of 2019 with the intercomparison period of 2018. However, it was important for our study to get an idea how many HONO is dissolved in dew and to estimate how much of this evaporated HONO can explain the observed morning peak. To achieve nearly identical conditions (nearly the same temperature and global radiation), we performed the dew measurements approximately one year later. As example, the dew experiments were realized in the same temperature range as it was the case for the second week in our intercomparison campaign of 2018. The gas phase HONO measurement in May 2019 was conducted by MARGA and results are shown in Figure R1. As shown in Figure R1, HONO morning peak was also found in the day of May 8th, May 13th and May 14th 2019, although frozen dew water was found for the day of May 8th and May 14th 2019. We agree with the reviewer that the present results give only an imagination how strong the dew evaporation source to atmospheric HONO is. More exact measurements have to be performed to clearly quantify the role of dew evaporation on found atmospheric HONO concentrations. This has to be done in future studies.

Additionally, we cannot exclude that frozen dew was also present in the intercomparison campaign 2018 as we observed in 2019 that frozen dew was also formed for air temperatures above 0 ℃.

The reviewer is right. We observed frozen dew on May 8th, May 13th and May 14th. We also analyzed the defreezed dew samples but they were not used for further analyses because of the interference with an enhanced oxidation. As mentioned in the text (Line 342-348), the dew water of May 11th 2019 was not frozen and the obtained F_{NO2-} (NO_2^- concentration per m^2 of the sampler surface) was used to discuss the HONO morning distribution.

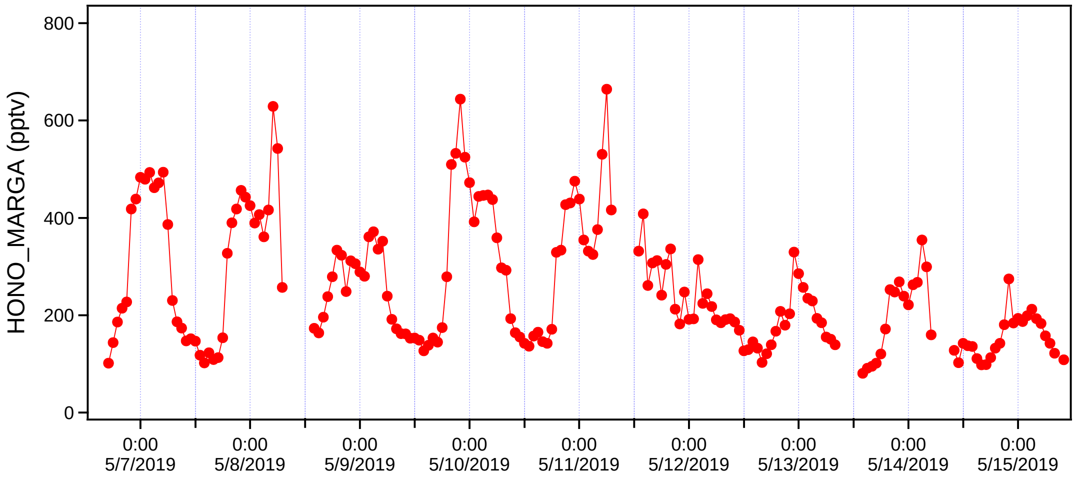

Figure R1. Time series of HONO (MARGA measurement) in Melpitz from May 8th to May

15th 2019. The gap was mainly due to HONO quantification of dew samples and the maintenance of the instrument.

3) Intercomparison:

The intercomparison results should be clearer discussed. Since all known chemical interferences are positive interferences (overestimation of the HONO data) and since I expect that both groups can calibrate their instruments with high accuracy, the results shown in Fig. 1 are quite clear. First, the MARGA instrument overestimates HONO during this field campaign at least (the LOPAP instrument may also have interferences: : :) by ca. 90 % (see data M2, where both instruments are operated in their normal way), and not by 58 % as mentioned in the conclusion (line 619). Second, these _90 % are caused by ca. _60 % chemical interferences inside the MARGA instrument (see data M1, where both instruments used the common MARGA inlet), e.g. by oxidation of SO_2 (see e.g. Spindler et al., 2003) or VOCs by NO_2, which are corrected for by the LOPAP instrument. In addition, ca. 30 % of the HONO MARGA data results from heterogeneous formation of HONO in the inlet of this instrument (PM10 inlet + Teflon line), see the difference between the slopes M2 and M1. So one important conclusion is that MARGA HONO field data should not be used.

This result is in excellent agreement with a former intercomparison of both instrument types in a Chinese field campaign (see J. Geophys. Res., 2010, 115, D07303, doi: 10.1029/2009JD012714) where also a RWAD instrument (similar to the MARGA) overestimated HONO by a factor of three on average. In this context, the statement in line 104 (“first inter-comparison: : :”) is not correct. In addition, the results also show that the use of massive sampling inlets – even if they are coated by Teflon – should not be used for any in-situ HONO instrument.

Response: More discussion has been added for the inter-comparison of MARGA and LOPAP as below in Line 252-262 “The evaporation of dissolved HONO from the off-line sample and heterogeneous reactions of NO_2 and H_2O as well as NO_2 and SO_2 in water as described by Spindler et al. (2003) or VOCs by NO_2 could explain the artefacts in the denuder solution (Kleffmann and Wiesen, 2008), which could account for ca. 58% (M1, where both LOPAP and MARGA used the common MARGA inlet) of these ca. 90% of overestimated HONO measurement from the MARGA. Additional artefacts as heterogeneous formation of HONO due to the long MARGA inlet system should be responsible for another ca. 32% (the difference between slopes M2 and M1). Hence, the results show that the use of massive sampling inlets, even if they are coated by Teflon, should be avoided for any in-situ HONO instrument. As a result, we chose the LOPAP-measured HONO in the following sections because of its high precision."

Line 682, in the conclusion, the overestimation of the HONO data from MARGA than LOPAP was changed as ca. 90 %.

We apologize for this mistake and included the cited study in our manuscript as comparison in Line 237-240. We changed our statement in line 115 as "Our observations provide a direct inter-comparison between LOPAP and MARGA for HONO field measurement".

#4 (1) OH data:

For the discussion of the HONO sources the OH data is necessary (see e.g. reaction 3), which was calculated here by a simple linear correlation with the global radiation. However, this method is highly uncertain since first, short wave UV radiation should at least be used (see similar studies using J(O1D)...), cf. main sources of OH-radicals. Here the ratio between the global radiation and J(O1D) will show strong diurnal and seasonal variability (depends mainly on the SZA: : :). In addition, while the correlation between J(O1D) and OH is indeed often linear, the slope is highly variable and will e.g. depend on the VOC/NOx ratio. Thus, I expect easily a factor of two uncertainties in the calculated OH concentration. Since e.g. half of the HONO daytime levels could be explained by the gas phase reaction (3), see lines 496-497, a factor of two higher OH level could make all discussions about any "unknown HONO sources" obsolete.

Response: As mentioned by the reviewer, [OH] showed a close relationship with the UV solar flux (Rohrer et al. 2006) as generally expected. In addition, the UV solar flux is closely correlated with global solar irradiance (Boy and Kulmala, 2002). On the basis of such a correlation, Gr öß et al., 2018 devised the linear function between global radiation flux (0.3 - 3 μm) measured by a pyranometer and [OH] measured by CIMS for EUCAARI 2008 at Melpitz, the same atmospheric research station as conducted for the present work. Hence, [OH] in the present work was estimated by using this linear function since we did not apply a direct OH measurement, and [OH] could have a factor of two uncertainties. However, regarding on the large uncertainty of [OH] but also large variability of HONO concentration, the "unknown HONO sources" could be not crucial but they could also exist according to the observation of Figure 6. Then the discussion about "unknown HONO sources" has been improved in line 543-550 as below:

"Reaction 3a can continually contribute 50% of the measured HONO from 10:30 to 16:30 (UTC). However, regarding on the large uncertainty of [OH] but also large variability of HONO mixing ratio, the "unknown HONO sources" could be not crucial but it could exist due to the observation of Figure 6. Basically, the additional HONO contribution rate could be estimated from following equation:

$$P_{unknow} = \frac{d[HONO]}{dt} + J_{HONO}[HONO] + k_9[OH][HONO] - k_{3a}[OH][NO] \qquad \text{(Eq. 10)}$$

However, a quite low additional source of 91±41 pptv h^{-1} was derived beside OH reaction with NO…"

#4 (2) In addition, how have the authors calculated the night-time OH levels by this method (ca. 10ˆ4 cmˆ-3, see lines 329-330)? During night-time there is no radiation and calculated OH should be zero: : : Normal OH night-time levels decrease from ca. 10ˆ6 cmˆ-3 in the early night to 10ˆ5 cmˆ-3 in the later night caused by night-time sources of radicals (O3+alkenes, NO3+alkenes: : :). This data and the corresponding sections should be removed.

Response: We agree to the statement of reviewer on the night-time OH radical, and accordingly the night-time OH concentration and corresponding section has been removed in Page 11.

5) Correlation analysis:

In several sections throughout the manuscript correlations were used to identify source processes, which is highly uncertain and which often leads to wrong conclusions. Already in the early 1990 high correlations of Radon with HONO were observed, which are simply caused by the variation of the BLH/vertical mixing for two ground surface sources. Nobody would conclude that Radon is a precursor of HONO. However, for correlations of HONO with different parameters exactly this is done (not only in the present study: : :). E.g. in lines 356-358 correlation of HONO with relative humidity is explained by the heterogeneous reaction 2NO2+H2O, reaction (2). Besides that this reaction is far too slow to explain the night-time formation (gamma for R2 ca. 10ˆ-7 –10ˆ-8, one to two orders of magnitude faster kinetics is necessary, see e.g. line 412), the correlation of HONO with humidity may be artificial! During night-time the ground surface is cooling which leads to a) increasing relative humidity, b) decreasing vertical mixing c) increasing surface to volume ratio of the lower nocturnal boundary layer d) increasing rate for any heterogeneous reactions (which scale with S/V: : :) and increasing levels of ground emitted species, like e.g the proposed HONO-precursor NO2 or the particle surface area of freshly emitted particles. All these changes lead to artificial correlations (e.g. HONO with r.h., with particles,: : :) from which one should not necessarily conclude source processes. All the correlation analysis should be much more carefully discussed and results should be checked for plausibility, see below.

Response: As mentioned by the reviewer, the correlation analysis is a general method used in the literature (Su et al., 2008; Kukui et al., 2014; Michoud et al., 2014; …) which can provide a first insight of relationships between different species. In the present study, the correlation of HONO with NO_2 (previous Figure 6, has been removed) and the correlation of HONO with particle (Figure S6) have been analysed. As shown in Figure S4 and described in the text, the nighttime HONO formation may cause by Reaction 2 (heterogeneous conversion of NO_2 to HONO). This resulting gamma ($\gamma_{NO2 \rightarrow HONO\_g}$) for Reaction 2 varied from 2.4×10^{-7} to 3.5×10^{-6} with a mean value of $2.3 \pm 1.9 \times 10^{-6}$ in line 439 but not ca. 10^{-7} - 10^{-8} of γ for R2 mentioned above. This gamma value is in good agreement with literatures (Kurtenbach et al., 2001;Kleffmann et al., 1998;VandenBoer et al., 2013). The RH dependence of HONO formation has been suggested by numerous lab studies (Finlayson-Pitts, 2009; Finlayson-Pitts et al., 2003; Miller et al., 2009; Ramazan et al., 2006) and also in the field (Stutz et al., 2004). Exactly, Stutz et al. (2004) found a likelihood of increased $HONO/NO_2$ at high RH, in particular, suggesting that HONO formation from heterogeneous conversion of NO_2 was often enhanced at RH above 60% in the field by taking into account of some parameters e.g. S/V ratio. However, regarding the weak correlation between HONO and RH in the previous Figure 6 (now removed) and as discussed by the reviewer, we would like to remove the description of previous Figure 6 and discussion of the HONO formation dependence on RH in the section 4.2.1.

Other correlation analyses, e.g. the HONO/NO2 with particle surface density was also checked and is discussed in the following parts of this response letter.

6) Heterogeneous kinetics

Response: In present work, we would like to derive the uptake coefficient of NO_2 and HONO using Eq.3, Eq.4 and Eq.7. Here we improved our calculation by following the reviewer's comments and suggestion, and also a simple resistance model is now applied.

#6 (1) While equation (5) for the calculation of the heterogeneous conversion of NO2 to HONO is correct for small uptake coefficients, at least when a 100 % HONO yield is assumed (not explained here; only valid for fresh soot, a minor constituent of particles: : :), the calculated uptake coefficients (ca. 10ˆ-15: : :) to explain the missing night-time formation of HONO on particles (as a limiting case) are completely unreasonable! As the authors later correctly mention, the S/V ratio of particles is typically orders of magnitude lower than for ground surfaces. Thus, a higher (!) gamma is necessary for particles compared to the ground. Typically, formation of HONO by NO2 conversion on particles can be only explained, if gamma values in the range 10ˆ-3 to 10ˆ-4 are used. Otherwise this low number would mean that HONO formation could be easily explained by a reasonable uptake kinetics on particles (ca. 10ˆ-6; see lab studies on several heterogeneous NO2 reactions: : :)!? Here the authors should check their calculation – I expect some large order of magnitude errors, e.g. by using a wrong unit of the S/V ratio.

Response: To calculate the uptake coefficient of NO_2 on the particle surface ($\gamma_{NO2\rightarrow HONO\_a}$) in the present study, we assumed that the entire HONO formation was taking place on the particle surface (Line 412-414). Particle surface density S_a was calculated from the particle size distribution of APSS and D-MPSS data as shown in Figure S5 and ranged from 9×10^{-4} to 9×10^{-3} m^2 m^{-3}. In addition, a hygroscopic factor f(RH) following the method of Li et al. (2012) was applied to correct S_a to the aerosol surface density in the real atmosphere. However, the calculation of f(RH) (Line 404) was wrong in our previous version and lead to a very low $\gamma_{NO2\rightarrow HONO\_a}$. We excuse for this error and thank the reviewer for his insight leading to the correction of this error. Finally, an uptake coefficient $\gamma_{NO2\rightarrow HONO\_a}$ of $(8.8\pm5.0)\times10^{-6}$ ranged from 1.5×10^{-6} to 1.9×10^{-5} was obtained and, correspondingly, corrected in the text (line 413).

#6 (2) Besides this, the use of an uptake coefficient is not recommended when a ground surface conversion is considered (see equation 6), at least for large geometric uptake coefficients and for low night-time vertical mixing (see present study). If a leave area index of 10 is used (see line 409) the obtained "true uptake coefficient" of ca. 10ˆ-5 converts into a "geometric uptake coefficient" of ca. 10ˆ-4. For such high values the transport gets rate limiting for a stable night-time atmosphere!

In this case better a flux concept including resistances for convective mixing and molecular diffusion (R_a and R_b) and a surface resistance (R_c) should be used. Only R_c can be converted into an uptake coefficient and vice versa. The inverse of all resistances leads to the deposition velocity from which a surface uptake flux can be derived by multiplying with the concentration. In many cases this deposition velocity is only depending on the transport resistances, which depend e.g. on the wind speed (R_a and R_b can be estimated by parameterizations, see e.g. VDI 3782). Using constant uptake kinetics makes no sense here.

Response: We appreciate this comment of the reviewer and followed his suggestion to use a simple resistance model according to the description of Seinfeld and Pandis (2006) which had been proposed by Huff and Abbatt (2002). This part has been then been added to the SI as follows:

"Investigating resistance limitations in transport of HONO and NO_2 to the ground surface during the Melpitz measurement

In order to assess limitations of NO_2 conversion and HONO deposition in the surface parameterizations derived for the Melpitz dataset, a simple resistance model according to the description provided by Seinfeld and Pandis (2006), which has been proposed by Huff and Abbatt (2002) (Equation S1) was set up.

$$v_d = \frac{1}{R_a+R_b+R_c} \quad \text{(S1)}$$

Here, υ_d is the observed deposition velocity (cm s^{-1}), R_a is the aerodynamic transport resistance (Equation S2), R_b is the molecular diffusion resistance (Equation S3) and R_c is the reactive loss resistance (Equation S4). Each term can be calculated as follows

$$R_a = (\frac{1}{\mu\,\kappa^2})[\ln(\frac{z}{z_0})]^2 \tag{S2}$$

$$R_b = \frac{z_0}{D} \tag{S3}$$

$$R_c = \frac{4}{\gamma\, c} \tag{S4}$$

Where κ is the von Kármán constant (0.4) (VandenBoer et al., 2013), μ is the wind speed as 0.1 - 6 m s^{-1} in the pesent study, z_0 is an estimate of the roughness length of the surface (~ 0.03 m according to a 0.3 m grass height), z represents the surface layer height and is set to 15 m as example for nighttime values in Melpitz. Values for the local surface roughness length and surface layer height were approximated for atmospheric conditions with wind speeds less than 6 m s^{-1} (Huff and Abbatt, 2002;Seinfeld and Pandis, 2006). D is the molecular diffusivity of HONO and NO_2 as 7.2 ×10^{-5} and 1.5 ×10^{-5} m^2 s^{-1}, respectively, at 760 Torr (Hirokawa et al., 2008;Langenberg et al., 2019), γ is the reactive uptake coefficient and c is the mean molecular speed (~ 367 m s^{-1} for HONO and NO_2). These values were derived assuming that the upper limit to the observed HONO reactive uptake was limited equally by molecular diffusion and aerodynamic transport (Equation S1).

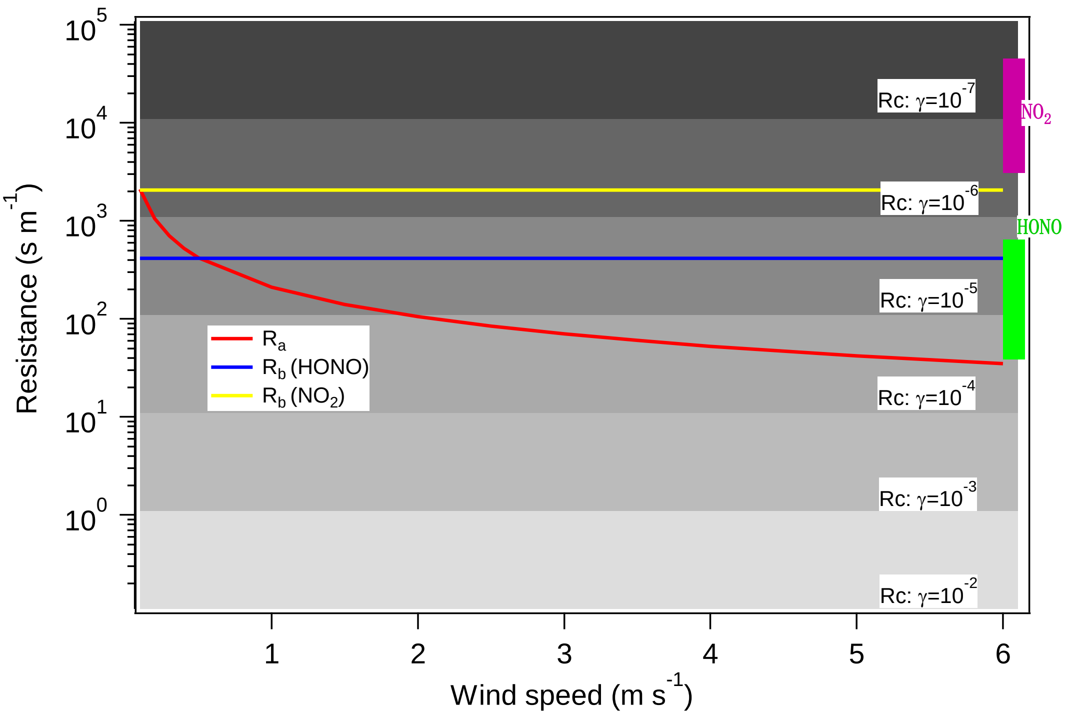

Figure S9. Estimated contributions of resistance parameters to the observable ground surface processes for the HONO and NO_2 uptake values derived from Melpitz station. A series of grey shaded regions define the borders of the reactive uptake resistance (R_c), the R_c values calculated from upper and lower limit uptake values of HONO and NO_2 in this work are shown in green and pink column, respectively. The aerodynamic transport resistance (R_a, red line) and diffusion resistance (R_b, blue line for HONO and yellow for NO_2) are shown in the Figure."

Figure S9 shows the results of the calculated resistances using data limitations from the observation data set and compared to the observed range for HONO and NO_2 in Melpitz. This result presents that the aerodynamic transport resistance increases with decreasing windspeed and could play the main role for the HONO deposition when the wind speed was less than 0.5 m s^{-1}. Regarding on the calculated R_c range (region indicated by green bar) using the reactive uptake values observed for HONO (1.7×10^{-5} to 2.8×10^{-4}), limitation of the observed uptake of HONO was potentially significant from the molecular diffusion resistance term in the data range at wind speeds larger than ~1m s^{-1}. Therefore, the range of HONO uptake coeffcient values calculated in this investigation are potentially limited by a combination of both transport and diffusion to the ground surface. Since such limitations are realistic for the atmosphere, the γ-coefficients calculated here could have a broad scale applicability used for simulation of HONO production and loss at night when constrained by the observations. As shown in Figure S9, the R_c range (region indicated by pink bar) calculated based on the reactive uptake values observed for NO_2 (2.4×10^{-7} to 3.5×10^{-6}) indicate limitation by the reactive uptake process, which may play the main role rather than aerodynamic transport limitations and molecular diffusion limitations.

#6 (3) Also the factor 1/8 in equation 6 (compared to the 1/4 in equation (5)) should be explained, where the authors obviously propose the (too slow, see above) reaction of 2 NO2+H2O (R2) as the main HONO source, for which a formal HONO yield of 50 % is used. In contrast, several former gradient studies (e.g. J. Geophys. Res., 2002, 107 (D22), 8192, and Atmos. Chem. Phys, 2017, 17, 6907-6923, doi: 10.5194/acp-2016-1030) found experimental HONO yields from the NO2 uptake on the ground in the very low % range (2-4%...), i.e. only ca. 3% of the deposited NO2 is converted into HONO on the ground during night-time and not 50 %: : :

Response: While night time concentrations of HONO can be reasonably explained by the heterogeneous conversion of NO_2 surfaces on humid surface (Kleffmann, 2007), Eq. 4 (previously Eq.6) as $k_{het} = \frac{1}{8}\gamma_{NO2\rightarrow HONO\_g} \times \upsilon_{NO2} \times \frac{S_g}{V}$ was used in present study to derive the uptake coefficient of NO_2 on the ground surface as suggested in the literatures (Li et al., 2010;Kurtenbach et al., 2001;VandenBoer et al., 2013;VandenBoer et al., 2014). As defined in Reaction 2, $2NO_2 + H_2O \rightarrow HONO + HNO_3$, two deposited NO_2 would form 1 molecule of HONO. Hence a formal yield of 50% (1/8) was used in this equation. In addition, certain field studies also found relatively high NO_2-to-HONO ground conversion ratio (Lu et al., 2018;Yu et al., 2009;Li et al., 2012;Su et al., 2008) from ca. 10% to ca. 34% (5.5-16.3% obtained in this work) and even higher. However, precisely lab work should be conducted to observe a more reliable NO_2-to-HONO ground conversion ratio.

#6 (4) Furthermore the HONO deposition on the ground and the derived necessary uptake coefficients (see section 4.2.3) are impossible! Besides the same argument as for the NO2 uptake on ground surfaces (see above, the use of uptake coefficients for fast ground uptake makes no sense, better use the flux concept and a variable deposition velocity: : :), the values for the HONO uptake coefficient in the range 5.6-19.5 are impossible!? When I was reading the abstract (line 25), I first expected that the authors simply missed the order of magnitude after the given numbers (e.g. x10ˆ-6: : :). Even if one considers a LAI of 6 (see line 410, for the HONO uptake this is not specified: : :?) the maximum calculated value could be only 6 but never 19.5, which would imply a real uptake coefficient using the true surface area larger the unity. Please check for the definition of the uptake coefficient, e.g. by IUPAC, with a maximum value of one. Reason for the order of magnitude errors is equation (9), where the concept of the deposition velocity is mixed with the concept of the uptake coefficient. To calculate L(HONO) (=dc/dt) a first order rate coefficient k (s-1) is multiplied by the concentration (dc/dt = – k × c). The first order rate coefficient for a heterogeneous reaction is calculated from the uptake coefficient by:

k= 1/4 x gamma x average molecular velocity of HONO x S/V.

S/V can be exchanged by 1/H, as done by the authors. So instead of using the deposition velocity (3.35 cm/s, line 450) in equation (9) the mean molecular velocity of HONO (ca. 3.7x10ˆ4 cm/s) should be used, leading to four orders of magnitude lower values: : : And for these high values (>10ˆ-4) the HONO uptake is definitely transport limited, see above.

Response: For the calculation of HONO uptake coefficient, the HONO deposition velocity of 3.35 cm s^{-1} was used and the HONO uptake coefficient ranged from 5.6 to 19.5 was obtained and we are sorry for this mistake. As suggested by the reviewer, the mean molecular velocity of HONO as 3.67×10^{4} cm s^{-1} was used in Eq. 7:

$$L_{HONO} = \frac{1}{4}\gamma_{HONO,ground} \times [HONO] \times \frac{\upsilon_{HONO,ground}}{H} \qquad \text{(Eq. 7)}$$

In addition, the value of *H* was calculated from the backward trajectory based on GDAS data and ranged between 20 m and 300 m from 22:00 until around 04:00 UTC in April 2018 during the present study. Then we obtained a value ranged from 1.7×10^{-5} to 2.8×10^{-4} for HONO uptake coefficient (Line 481-482).

#6 (5) And finally, I do not understand the concept used for the quantification of the deposited

HONO, which is later compared to the dew water nitrite. Here the total deposited HONO is given in the unit ppt (see e.g. line 428) but should be given at the end in molecules/cm2 to compare that with the dew nitrite (similar unit). To what S/V or boundary layer height does that "deposited mixing ratio" relate? Do the authors expect that the concentration change for the deposited HONO (dc/dt) is constant in whole boundary layer? Here a surface density (molecules/cmˆ2) should be derived by integrating the product of the variable (turbulence depending, see above) deposition velocity with the concentration.

Response: We are sorry for the mistake. Exactly, the total deposited HONO (in pptv) on the ground surface was assumed same as the total night-time HONO loss of 970±730 pptv (6 h), calculated by integrating L_{HONO} from 22:00 to 4:00 (UTC) from the nighttime measurement. Hence, we removed this description in section 4.2.3. However, the HONO deposition flux (F in molecule cm^{-2}) was not proposed in this study since the calculation of $F = v_d*C$ is also a function of surface layer height (z) and must be related to a reference height at which C is specified. In the present study we just obtained the HONO concentration at the sampling point (3.5 meters from the ground).

Finally, the description and discussion about the uptake coefficient in the text was improved Line 495-510 in the manuscript – this text now reads: "A simple resistance model based on the concept of aerodynamic transport, molecular diffusion and uptake at the surface (presented in SI) as proposed by Huff and Abbatt (2002) was used to evaluate the factor(s) controlling the potential applicability of the γ-coefficients calculated here for the uptake of NO_2 and deposition of HONO. As shown in Figure S9, the deposition loss of HONO is potentially limited by a combination of aerodynamic transport, molecular diffusion and reaction processes. However, the HONO uptake will be transport-limited if the real uptake coefficients are $\geq 2.8\times10^{-4}$ and wind speed was less than 0.5 m s^{-1}. In addition, molecular diffusion could play an important role for HONO uptake on the surface, especially when the winds speed is larger than ~1 m s^{-1}. Regarding the uptake of NO_2 on the ground surface, the range of NO_2 uptake coefficients as 2.4×10^{-7} to 3.5×10^{-6} obtained in the present work indicates limitation only by the reactive uptake process. The consistency between our findings and the values of these parameters in models (Wong et al., 2011;Zhang et al., 2016) suggest that the broad scale applicability of these field-derived terms for surface conversion of NO_2 should therefore be possible. However, those value of γ found for HONO ($\gamma_{HONO, ground}=1.7\times10^{-5}$ to 2.8×10^{-4}) require further exploration from various field environments and controlled lab studies."

Specific Concerns:

The following concerns are listed in the order how they appear in the manuscript.

Lines 22-23: Specify the deposited HONO in the same unit as the dew nitrite surface density (e.g. molecules /cmˆ2).
Response: Here we would like to present a measured nighttime loss of HONO with strength sink of $L_{HONO}=0.16\pm0.12$ ppbv h^{-1}. Hence, the "nighttime ground surface deposition" was changed to "nighttime loss" in Line 21.

Line 25: correct the gamma values (see main concerns).
Response: The ground uptake coefficients for HONO and NO_2 were corrected as followed: $\gamma_{NO2\rightarrow HONO} = 2.4\times10^{-7}$ to 3.5×10^{-6}, $\gamma_{HONO,ground} = 1.7\times10^{-5}$ to 2.8×10^{-4} in line 25.

Line 47: The paper by Gutzwiller et al. is not on the NO2+soot reaction but on the reaction of NO2 with semi-volatile hydrocarbons (see line 49). Better use the study by Arens et al. from the same group or the first studies from 1998 by Ammann et al., or Gerecke et al.
Response: Line 48-49, the references of Ammann et al., 1998;Arens et al., 2001;Gerecke et al., 1998 were used to replace the paper of Gutzwiller et al. 2002.

Line 50 and table S1: The authors should distinguish between the oxidation of phenols etc. in the dark (reaction 2b) and the photosensitized conversion of NO2 (see Stemmler et al.) by adding a new reaction for the daytime HONO formation (e.g. new reaction 3).

Response: Line 69, a new reaction 3b as $HA \xrightarrow{h\nu} A^{red} + X$; $A^{red} + X \rightarrow A'$; $A^{red} + NO_2 \rightarrow A'' + HONO$ was added in the text.

Line 59-60, the heterogeneous reaction NO+NO2+H2O is completely unimportant and not state of the art. In addition it should be "Andrés-Hernández et al.".
Response: We removed the reaction as $NO+NO_2+H_2O$ from the text.

Line 61: There is only one study by Zhang and Tao (delete the a) und the same reference is listed twice in the references (lines 899-904).
Response: Line 62, the reference of Zhang and Tao., 2010 has been corrected.

Line 61: the reaction NO2*+H2O was studied by Li et al. and not by Finlayson-Pitts. In addition, also this source is completely unimportant (see Carr et al. and Amedro et al.) and was simply an Excimer laser two-photon artefact: : :.
Response: We removed the reaction $NO_2^*+H_2O$ from the text.

Line 63: The heterogeneous reaction of NO with adsorbed HNO3 is also completely unimportant at atmospheric conditions (gamma <10ˆ-9, see J. Phys. Chem. A, 2004, 108, 5793-5799).
Response: We removed the heterogeneous reaction of NO with adsorbed HNO_3 from the text.

Line 64: delete the “a” for Zhou et al. and delete again one of the double references at the end (lines 908-913).

Response: The reference of Zhou et al., 2011 has been corrected in Line 65.

Line 74: either use R1 or reaction 1 (unify).

Response: Line 82, R1 has been corrected to “reaction 1”

Lines 77-78: delete the last sentence; that describes already the results.

Response: The sentence “However, this is not the case in this work.” has been deleted from the text.

Line 85: the instrument can measure down to 0.2 ppt, see Atmos. Chem. Phys., 2008, 8, 6813-6822, doi: 10.5194/acp-8-6813-2008.

Response: Line 93, the detection limit of LOPAP has been corrected to 0.2 pptv and the reference Kleffmann and Wiesen, 2008 was referred.

Line 95-97: Stieger et al. also intercompared HONO, which should be mentioned here (HNO3 is not the topic of this manuscript: : :).

Response: The description of HNO_3 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 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.

Line 104-105. The statement is not correct, see major concerns.

Response: The statement was corrected “Our observations provide a direct intercomparison between LOPAP and MARGA for HONO field measurement” in Line 115.

Line 121: The used SJAC uses 100 _C hot water steam forming hot steam droplets on which different reactions of NO2 form nitrite (e.g. NO2 + organics, see Gutzwiller et al.) which show positive temperature dependencies. Thus also the aerosol nitrite MARGA data should be used with caution. This interference can be easily tested by spiking HONO free NO2 to the instrument during a field measurement (=> % NO2 interferences for nitrite...).

Response: We agree with the reviewer, the particulate nitrite data of the MARGA system could be interfered by the different reactions of NO_2 in the SJAC system, hence uncorrected aerosol NO_2^- data were not used by the authors.

Line 165: At what temperature were the nitrite solutions stored in the fridge? Should not be below freezing temperature, see above.

Response: The dew samples were stored in a fridge with approximately 6 ℃ (was added in line 193). We avoided long storage times between sampling and analysis.

Line 195 ff: Were the clear sky J-values from the TUV model scaled by the measured global radiation for short fluctuations by local cloud cover (see figure 2) or was that really done by data from the NASA web page (see line 201)? Normally this is done by scaling the clear sky TUV values with measured radiation (e.g. from a J(NO2) filter radiometer: : :).

Response: The J-values from the TUV model was scaled by the measured global radiation.

Lines 213-215: I do not understand that statement. While the surface pH of a dry batch Na2CO3 denuder should be very high (pH=10?) the pH of the MARGA is close to neutral (5.7, see line 121), so they are different!?

Response: We improved our explanation in Line 247-251. It now reads "Genfa et al. (2003) reported that they found a discrepancy between two denuder systems working with Na_2CO_3 and H_2O_2 resulting in different pH. However, in the comparison by Stieger et al. (2018), the MARGA system and the off-line batch denuder had the same pH and the found differences (scattering) cannot be explained by pH differences."

Lines 262-264: No that statement is not corrcet, the trend of HONO (strongly decreasing during daytime) is different to HNO3 (almost constant), see Figure 4. Reasons are the decreasing HONO precursor concentration NO2 (increase of the BLH; both are ground emitted or formed species), while HNO3 is formed by NO2+OH homogeneously in the gas phase and decreasing NO2 is compensated by increasing levels of OH during daytime: : :

Response: We are sorry for the wrong statement and appreciate the explanation; we deleted the statement for the "HNO_3".

Line 271-273 and figure 4: Please also show the HONO/NOx ratio in figure 4.

Response: The HONO/NOx ratio was added in Figure 4.

Lines 274-276: A formation or loss reflects dc/dt while a frequency (s-1) is a first order rate coefficient (apples and oranges), reformulate the sentence.

Response: The sentence was reformulated as "This decrease during nighttime indicates the HONO loss process (dry and wet deposition, trapped in the boundary layer or dew etc.) surpassing the HONO formation from the NO_2-to-HONO convention" in Line 317-319.

Line 286-289: Under acidic conditions HONO is not highly soluble, cf. the pKa. In addition the dew water was neutral during the dew campaign, see line 297.

Response: The sentence "might be slightly acidic due to acid contribution from acidic aerosols (such as NH_4HSO_4)" has been removed from the text.

Line 326ff: delete that section on NO+OH during night-time, see major concern.

Response: The section of NO+OH was deleted.

Lines 350-353 and equation 4: This equation (="two point fit") was not used, but the slope from all data, see sentence before, which is the correct procedure. Delete the equation.

Response: The previous equation 4 was deleted.

Line 354: Should be correlation and not covariance.

Response: This part has been deleted.

Line 355 and Figure 6: A plot of HONO against NO2 during night-time makes no sense as discussed in many former studies (e.g. by J. Stutz's group), as the HONO to NO2 ratio typically increase during night-time (see equation 4 to determine the "NO2 conversion frequency"). Thus typically the higher data points are those from the later night (with higher r.h: : :.) while the lower slope data reflect the early night (with lower r.h., see artificial correlation).

Response: Previous Figure 6 has been removed from the paper.

Line 359: I do not understand the high value of the HONO/NO2 ratio of 11.3% while a HONO/NOx ratio of 4-5 % was also obtained (see table 1). Since NO is much lower than NO2 (see figure 2), the HONO/NO2 ratio should be only slightly higher than HONO/NOx ratio. Check the numbers for consistency.

Response: The HONO/NOx ratio presented in Table 1 was calculated for the daytime and nighttime using the time period 04:00-18:00, UTC and 18:00-04:00, UTC, respectively. However, the HONO/NO2 ratio was calculated for the early evening 17:30-00:00 UTC. That made the difference between the value HONO/NOx and HONO/NO2.

Lines 363-364: Reason for the higher conversion frequency is the different time period used. While here only the initial increase of the HONO/NO2 ratio during the early evening was used (later this is decreasing caused by more efficient HONO uptake on dew surfaces in Melpitz) in most other studies the almost entire night-time increase was evaluated, where formation and deposition overlaps leading to lower conversion frequencies.

Response: We agree to the statement by the reviewer. However, the calculation of HONO/NO2 followed the criteria as already mentioned in the text:

(a) only the nighttime data in the absence of sunlight (i.e., 17:30-06:00 UTC) were used;

(b) both HONO concentrations and [HONO]/[NO_2] ratios increased steadily during the target case;

(c) the meteorological conditions, especially surface winds, should be stable.

In addition, some literatures also calculated the HONO/NO_2 by only using the initial increase of the HONO/NO2 ratio during the early evening. e.g. Alicke et al. (2002), Wang et al. (2017), (Alicke et al., 2003)…

Lines 379-380: Here again an artificial correlation is studied (see major concerns). HONO and particles are both formed or emitted near to the ground and variation of the BLH causes the correlation. The question ground vs. particles can be only answered if parallel gradient measurements of HONO, NO2/NOx and particle surface area are performed (see discussion in Atmos. Environ, 2003, 37, 2949-2955).

Response: We agree to the statement from the reviewer. Accordingly, we reformulated the sentences as "Moreover, given the weak correlation between HONO (R^2=0.566), [HONO]/[NO_2] (R^2=0.208) and S_a (Figure S6), this work concludes that, as previously reported (Wong et al., 2011;Sörgel et al., 2011;Kalberer et al., 1999), the HONO formation through heterogeneous NO_2 conversion on particle surfaces needs to be regarded as unimportant." in Line 417-421.

Line 407: Since the data between 17:30 and 22:00 is considered here, any measured BLH between midnight and 7:00 is meaningless?

Response: We corrected our description and terms as "Where H is the mixing layer height calculated from the backward trajectory based on GDAS data and a range of 20 m to 300 m from 17:00 until around 00:00 UTC in April 2018 was used in present study (Figure S7)" in Line 433-435.

408-410: Was a LAI of 6 used (than exchange "we add" by "we used": : :) or did you add the value of 6 to the LAI of 4-10? Reformulate: : :

Response: Line 438, "we add" was changed to "we used".

Lines 415-418: Also reformulate: ": : :the NO2 uptake coefficient: : : is larger than the reactive surface: : :". What you mean here is that the S/V of aerosols is much smaller than the S/V of the ground and thus the heterogeneous formation takes place on ground surfaces: : :

Response: Line 443-447, the sentence was reformulated as "However, it should be noted that the obtained NO_2 uptake coefficient on the ground surface is closely to the reactive surface provided by aerosols, but as the S/V ratio of particles is typically orders of magnitude lower than for ground surfaces, it is suggested that the heterogeneous reactions of NO_2 on ground surface may play a dominant role for the nighttime HONO formation."

Lines 436-437 and Fig. 7b: Since the HONO/NO2 ratio is time depending (see above) better plot the average first order rate coefficient for NO2 conversion against the inverse of the WS. You also would not plot the ratio product/reactant in a smog chamber experiment against any variable, but the rate coefficient. Since the WS is a marker for the vertical turbulent mixing the observed anti-correlation is a strong argument for the proposed ground source region of HONO.

Response: The Figure 7b was moved to SI as Figure S8. The relationship of NO_2-HONO conversion frequency (k_{het}) with the inverse of wind speed during nighttime (18:00-04:00) is illustrated in Figure S8b. In addition, the resistance model as shown in Figure S9 could indicate that the uptake of NO_2 on the ground surface would mainly be caused by its reaction process rather than aerodynamic transport and diffusion.

Line 474: Delete reaction (6) but add the new reaction 3 (photosensitized conversion of NO2, see major concerns).

Response: The former reaction (6) was replaced by a new reaction 3b (photosensitized conversion of NO_2) in Line 521.

Lines 500-501: If NO+OH contributes to ca. 50 % to the daytime HONO levels (see lines 496-497 => significant source!) than its sources strength should be some hundred ppt per hour. Check for the low number!

Response: Line 549-550, an additional source of 91 ±41 pptv h^{-1} was derived beside OH reaction with NO for the daytime HONO after carefully checking, according to a HONO mixing ratio 98 ±15 pptv for the time period of 10:30-16:30 UTC.

Lines 504-505, hypotheses (1): Why should HONO formation in the morning be caused only by HNO3/NO3- photolysis and not by a more reasonable photosensitized conversion of NO2 (new reaction 3)? In the morning NO2 levels are still high while HNO3 is high only later during the day (cf. Fig. 4)! Please plot the “unknown source” against a) the product (HNO3/NO3- x J(HNO3)) and b) (NO2 x J(NO2)). I expect the latter correlation is much better: : :

Response: Line 588-598, we followed the reviewer’s comments, photosensitized conversion of NO_2 was also applied in the model as:

“To investigate the contribution of photosensitized conversion of NO_2 (reaction 3b) on the diurnal HONO based on the second hypothesis, the following model calculation (Model 5) was performed:

$$\frac{d[HONO]}{dt} = k_3[OH][NO] + k_{het}[NO_2] + \frac{1}{4}(\gamma_a\frac{S_a}{V} + \gamma_g\frac{S_g}{V})\upsilon_{NO2}J_{NO2}[NO_2] - J_{HONO}[HONO] - k_{10}[HONO][OH] - \frac{1}{4}\gamma_{HONO,ground}[HONO]\frac{\upsilon_{HONO,ground}}{H} \quad \text{(Eq. 13)}$$

Here the γ_a and γ_g are the light-enhanced NO_2 uptake coefficient of 2.5×10^{-4} and 2.0×10^{-5} (Stemmler et al., 2006) on the aerosol surface and ground surface, respectively. And J_{NO2} was multiplied with $\frac{light\ intensity}{400}$ when the light intensity ≥ 400 W m^{-2}. As shown in Figure 6 (Model 5, cyan line), the photosensitized NO_2 on the aerosol and ground surface could not reproduce the HONO morning peak. This favors the third hypothesis that dew evaporation processes release HONO resulting in the sudden morning peak.” This may due to a relative low NO_2 concentration around 2-5 ppbv.

In addition, the plots of "unknown source" vs a) the product (HNO_3/NO_3^- x $J_{(HNO3)}$) and b) (NO_2 x $J_{(NO2)}$) show that the latter correlation is better but both of these reactions could not explain a HONO morning peak as below.

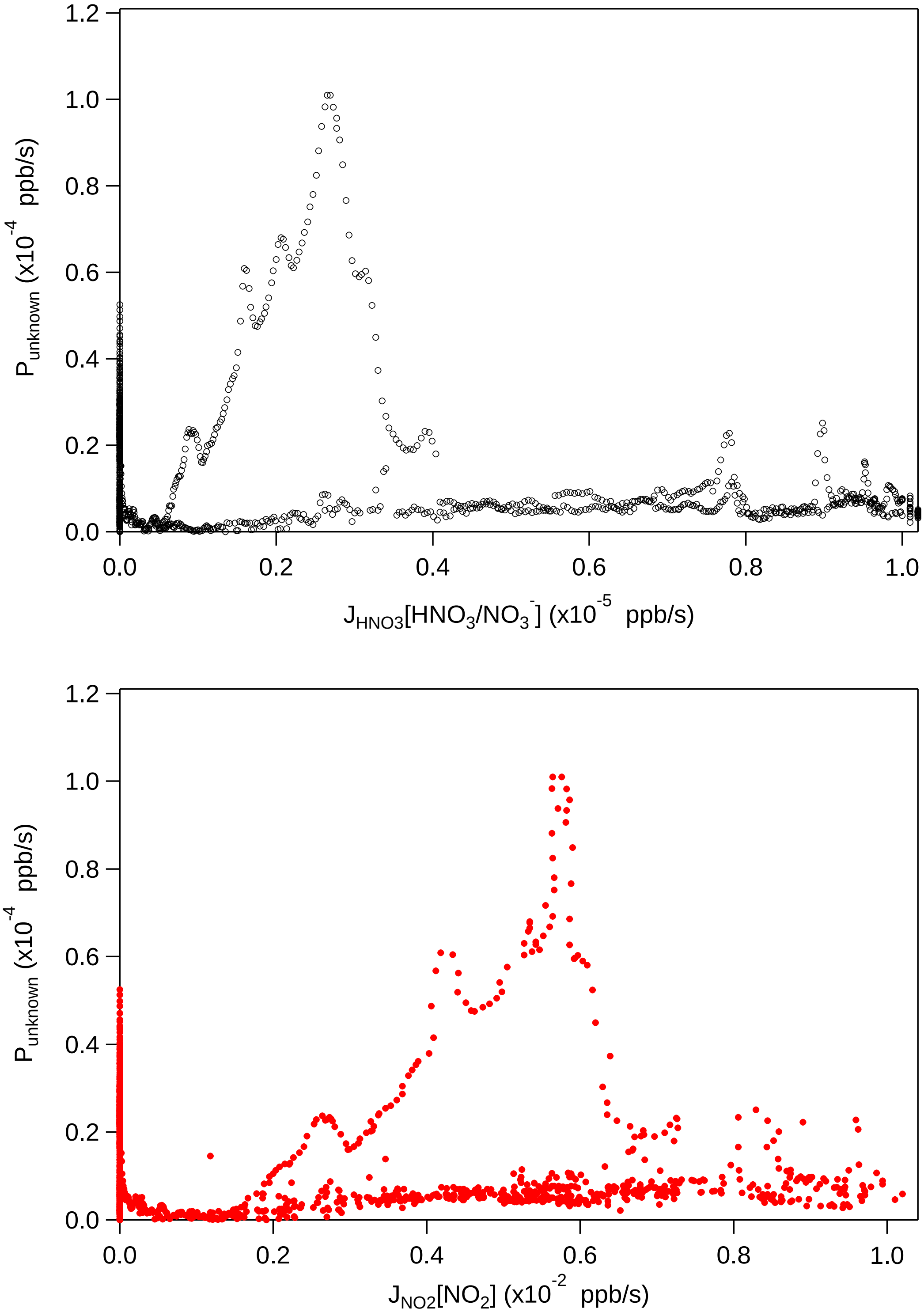

Figure R2: Plots of "unknown source" vs a) the product (HNO_3/NO_3^- x $J_{(HNO3)}$) and b) (NO_2 x $J_{(NO2)}$). Both of this correlation cannot explain the observed HONO morning peak.

Line 507: Should be equation 11.

Equations 13, 14, 15: the last term in the equations is again not correct (the deposition velocity should be exchange by the mean molecular velocity of HONO). And again, the concept of the uptake coefficient does not work for ground surfaces and fast uptake (transport limited uptake at gamma > 10ˆ-5 - 10ˆ-4, depending on Ra and Rb).

Response: Line 559, "previous equation 10" was corrected to "equation 9".

In the Equation 11, 12, 13, 15 the mean molecular velocity of HONO, updated mixing height H of 70 m from the backward trajectory and recalculated average uptake coefficient of $(1.0\pm0.4)\times10^{-4}$ were applied in the model as presented above. As discussed above #6 (2), the HONO uptake on the ground surface could be limited by the combination of aerodynamic transport and molecular diffusion regarding on the derived HONO uptake coefficient of 1.7×10^{-5} to 2.8×10^{-4} in the present study. Since such limitations are realistic for the atmosphere, the γ-coefficients calculated here could be broad scale applicability used for simulation of HONO production and loss at night when constrained by the observations. In addition, the equation 7 of $\frac{1}{4}\gamma_{\mathrm{HONO,ground}} \times [\mathrm{HONO}] \times \frac{\upsilon_{\mathrm{HONO,ground}}}{H}$ was used to reproduce the nighttime loss of HONO in the Equation 11, 12, 13, 15.

Line 530: The used value for J(HNO3) for the photolysis of surface HNO3/NO3- is too low, here "enhancement factors" (ratio surface photolysis/gas phase photolysis, see e.g. Environ Sci. Technol., 2018, 52, 13738-13746 and references therein) between 7 and 1000 have been proposed in recent studies for this reaction.

Response: Line 582-584, we followed the reviewer and "the photolysis frequency J_{HNO3} was derived from the TUV model by multiplying an enhanced factor 30 due to a faster photolysis of particle-phase HNO_3 (Romer et al., 2018).", As a result, the photolysis of HNO_3/NO_3^- (Model 4, pink line) still could not reproduce the HONO morning peak shown in Figure 6. However, this could well reproduce the HONO for the time period of 10:30 to 16:30 (UTC).

Line 546-547: Why are there two values (max/min) of k(emission) for each emission peak?

Response: To precise the k_{emission} calculation, as shown in Figure 7, max/min of k_{emission} were obtained in two more line parts in the plot of $\frac{HONO_{unknown}}{99.5-RH}$ vs. the internal time.

Lines 556-559: Again I do not understand the units of the integrated emission/deposition. Is that a concentration from a layer of 1 m or of 500 m? The numbers of released HONO molecules would be different by more than two orders of magnitude: : :

Response: We are sorry for the confusion. Exactly the quantity of HONO emission from the dew water was calculated by integrating the HONO morning peak in Model 6, and which was compared with the measured total HONO nighttime loss in the same sampling level. They are not exactly the emission/deposition rate, and we did not measure a HONO flux in our study. Finally, we decided to remove this part.

Section 4.3.3: If I understand the concept used (equation 17) correctly (?) than the authors take all dew nitrite and mix that after hypothetical evaporation as HONO homogeneously into a layer of variable height. Then they plot the resulting average (homogeneous) layer concentration against the height (see Figure S9). But in this case the resulting gradient does not reflect a real gradient in the atmosphere. If the concentration is calculated e.g. for a lower layer of 20 m, than all nitrite is already consumed and there is nothing left for any higher layers. Thus, the real concentrations would be much lower! But maybe I did not understand that correctly: : :

Response: We agree with the reviewer that previous Figure S9 cannot represent a HONO gradient, hence we removed the previous Figure S9. Then we applied the Equation 16 to calculate the HONO morning mixing ratio by assuming a homogeneous mixing. We corrected our description in Section 4.3.3 as following

"4.3.3 HONO emission from dew water evaporation in the morning

The hypothetical morning HONO mixing ratio (pptv) due to the complete dew water evaporation could be estimated from the following equation by taking the measured dew nitrite and the mixing layer height […] Hence, the morning HONO mixing ratio could be estimated as: 2264.1±612.3, 1132.1±306.2, 452.8±122.5, 226.4±61.2 and 75.5±20.4 pptv, respectively, for a mixing height of 20, 40, 100, 200 and 600 m using the mean F_{NO2-} from May 11th 2019 for the calculation."

Line 577: delete phenol, nitrophenol and HCHO, that is not the topic here.

Response: We deleted "phenol, nitrophenol and HCHO".

Lines 578-579: While emission of NH3 during evaporation might be reasonable, reemission of the highly sticky HNO3 is not expected. While HONO evaporates already e.g. at 80 % r.h., where you still find many formal monolayers of adsorbed water, HNO3 will still strongly stick to such humid surfaces: : : In addition, if you have acids (HNO3, H2SO4) and ammonia in the dew water, low volatile ammonium salts will be formed (e.g. ammonium sulphate) which will also not evaporate when the dew water has gone.

Response: We agree with the reviewer. Hence, we removed discussion of NO_3 in section 4.3.3.

Line 619: should be 90 % and not 58 %.

Response: Line 682, we corrected it as 90%.

Lines 623-625: If my interpretation of the gradient data is correct (see above) delete that section.

Response: we corrected and give a description in Line 687-689 as follow: “the morning HONO mixing ratio depending on dew water evaporation […], assuming a homogeneous mixing of evaporated HONO”

Lines 631-633: Correct for the numbers, see above.

Response: Line 697, we corrected the ground uptake coefficients for HONO and NO_2 at night as: $\gamma_{NO2\rightarrow HONO\_g} = 2.4\times10^{-7}$ to 3.5×10^{-6}, $\gamma_{HONO,ground} = 1.7\times10^{-5}$ to 2.8×10^{-4}.

References: Line 677: Brüggemann

Line 682: 107, D22, 8196,: : :

Line 683: Pätz H.-W.

Line 685: 108, D4, 8247,: : :

Line 691: 157-160

Line 692: Rössler

Line 695: Andrés-Hernández

I stopped here, there are numerous errors in the reference list.

Response: We corrected the author name and other information as mentioned by the reviewer and we took a carefully check for all the reference.

Table 1: What is the difference between HONO and HNO2 (unify: : :)? In addition, which HONO data is shown here (LOPAP or MARGA)? Specify, should be the LOPAP data, see intercomparison results.

Response: We removed HNO_2 data in the Table 1 since it is the value from MARGA.

Figure caption 2: “The gaps were: : :” You find at least three gaps in the HONO data: : :

Response: We corrected the “The gap was” as “The gaps were” in Figure 2 caption.

Figure 3: The nitrite MARGA data should be used with caution, because of high interferences by different NO2 reactions, see above. In addition, I would not use the artificial HONO data by the MARGA, see intercomparison results.

Response: We agree with the reviewer and we did not use the HONO and nitrite data from MARGA, Figure 3 only to show the measurement by MARGA.

Figure 4: add the HONO/NO2 or HONO/NOx ratio.

Response: We added HONO/NOx in Figure 4.

Supplement:

Table S1: Reaction 2 and 2a are similar only with different complexity. And reaction 2a only works at ppm levels of NO2, otherwise uptake coefficient of N2O4(g) higher than one are necessary: : :

Add a new photosensitized conversion of NO2 on organic substrates. Here I would use a new number (e.g. 3a), since reaction 2a is a disproportionation reaction (red + ox of NO2) while in reaction 2b (dark) and in the new photosensitized reaction (e.g. 3b) NO2 is an oxidant.

Also use a new reaction (4) for 2c, also different mechanism.

You may remove reaction (4), (6) and (7), they are definitely unimportant.

Response: We removed the Table S1 and moved all the reactions to the main text. We added the photosensitized reaction as 3b, and renumbered other reactions following the suggestion of reviewer. We also removed the previous "reaction 4, 6 and 7".

Figure S3: delete the 20 in the lower y-axis

Response: The Figure S3 was improved.

Figure S5: specify the unit of the colour code. Is that the particle surface density Sa? Specify in the caption.

Response: The color code is the particle number density and added in the caption.

Figure S8: Are the two fits (blue lines) used for the data from both days? Why isn't all shown data fitted (than the slopes should be similar)? See also my question above to table 4.

Response: Now the previous Figure S8 was moved to the main text as Figure 7. These two fits show a slower (min $k_{emission}$) and faster (max $k_{emission}$) HONO emission from the dew water regarding on the different time process of HONO morning peak (Figure 2).

Figure S9: Please integrate HONO over 600 m (unit should be HONO/area). Is that number similar to the dew nitrite surface density used? I expect it is much larger, see above. If yes remove that figure and the corresponding section.

Response: We agree with the reviewer and removed the previous Figure S9. We also improved our concern to the corresponding section 4.3.3. as shown in above.

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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 NO2-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 ℃ 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_2^- 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^{-3} (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^{-1} 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 NO2-SO2 and NO2-H2O corrections very small (VandenBoer et al., 2014) and cannot possibly explain this discrepancy. Further to this, the same work also demonstrates that in high NH3 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 we 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 NO_2^- due to the oxidation of SO_2 with NO_2. However, the mentioned study also summarized that the influence of the reaction of SO_2 with NO_2 on the resulting MARGA HONO concentration is low for a pH below 6. The reason is the competition of the SO_2 reactions between H_2O_2 and NO_2. Latter reaction is more effective for higher pH. Thus, at a denuder pH of 5.7, the influence of the reaction between SO_2 and 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 SO_2 and 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 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 NO2 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 NO2 conversion to HONO on surfaces is minimized) be used to determine whether a relationship between measured HONO and NO2 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_2 and H_2O as well as NO_2 and SO_2 in water described by Spindler et al. (2003) or VOCs by NO_2 in Line 252-258.

In addition, to proposed by Stemmler et al. (2006), the photosensitized NO_2 could contribute the daytime HONO formation, hence NO_2 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_2 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_{10} 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^3. Using the air flow of the MARGA with 16.7 $l\ min^{-1}$, 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 $l\ min^{-1}$. 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 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 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 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.

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 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.

However, particulate nitrite ranged from 0.012 to 0.11 μg 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 NO_2^- concentrations with caution because of positively correlated temperature dependencies of the NO_2^- formation by 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 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 NH3 and HNO3 are released from dew similarly in the morning, as their mixing ratios also increase shortly after sunset. However, the observed particulate NH4NO3 also increases, which is likely more consistent with aerosol aloft being mixed down into the nocturnal boundary layer and repartitioning to release NH3 and HNO3. Volatilization of HNO3 from surfaces containing water does not seem plausible given the strong acid nature of this species. If this were the case, deposition of HNO3 would not be represented as a terminal sink in atmospheric models. While NH3 may be released from dew, 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.

Response: All the discussion about the dew water emission of NH_3 and 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 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.

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.

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).

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’

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 HNO3 artefact matter? Should this be HONO? Given the subsequent lack of clarity in discussing the intercomparison issues below, additional details 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_3 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 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 of : : : '

Response: Line 128-129, the sentence was corrected to "An inlet flow of 1 m^3 hr^{-1} …"

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: : :'

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.

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".

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 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 NO_2^- concentration to Table 2 as suggested by the reviewer and more information in lines 333-334. However, we do not have such data about the recovered 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).

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 NO_2^- concentrations with caution because of positively correlated temperature dependencies of the NO_2^- formation by 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 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".

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 peak might possibly be caused by the photolysis of particle-phase HNO_3/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".

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: 'NO2-to-HONO conversion frequency'

Response: Line 319, we corrected this sentence as "… surpassing the HONO formation from the NO_2-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 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 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 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 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_4HSO_4)" 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 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(NO2-) be observed 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(NO2-) is included in the averaging over the other dew F(NO2-) 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 ℃. This was also the case in May 2019. No temperature below 0 ℃ 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(NO_2^-) was observed on May 11th where dew water was not frozen. Frozen dew water was observed for the other days (May 8th, May 13th and May 14th) with lower F(NO_2-). These samples were discarded because of possible interferences in the HONO partitioning. Finally, F(NO_2^-) obtained on May 11th was used for the following sections. We revised our description as below: "higher F_{NO2-} was obtained on May 11th, where dew water was not frozen. On other days (May 8th, May 13th and May 14th) frozen dew water was observed, which likely inhibited HONO to dissolve. Hence, these frozen samples were not considered in this paper. On May 11th, the final F_{NO2}^- …".
On May 11th, 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 NO_2^- concentration in the third sample is lower. However, the total value of F(NO_2-) for this morning would be the sum of the first (8.0 μg m^{-2}) and the third sample (1.43 μg 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 (HONO/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 NO_2-to-HONO conversion. As a result, a lower [HONO]/[NO_2] ratio was obtained than before. However, this has no change on k_{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'

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

Line 362: High HONO/NO2 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?

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^2/m^2) compared to an urban which might have enhanced heterogeneous NO_2-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.

Response: As reported by Li et al. (2012), the uptake coefficient of NO_2 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_2 to HONO. In this work, we corrected our uptake coefficient of NO_2 which was wrong because of the bad RH correction. Then this obtained uptake coefficient of NO_2 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 changed to "If the entire HONO formation was taking place on the particle surface, the calculated $\gamma_{NO2\rightarrow HONO\_a}$ varied from 1.5×10^{-6} to 1.9×10^{-5} with a mean value of $(8.8\pm5.0)\times10^{-6}$, 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 1×10^{-6} to 1×10^{-5} (Kleffmann et al., 1998;Kurtenbach et al., 2001).".

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.

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 H2O and this sentence should be rephrased carefully.

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 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 HONO and mixing layer height H from backward trajectory and then $\gamma_{HONO,ground}$ uptake coefficient was obtained from 1.7×10^{-5} to 2.8×10^{-4} with average of $(1.0\pm0.4)\times10^{-4}$ (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.

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 part of the discussion. Remove.

Response: “with the maximum mixing ratio of 1400±100 pptv” was deleted.

Lines 469-471: See Major comment on NH4NO3 thermodynamic partitioning and mixing. Remove this argument.

Response: “It should be noted that gaseous NH_3, HNO_3 and particulate NH_4^+, NO_3^- also 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, 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?

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 $\gamma_{HONO,ground}$ value.

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’

Lines 529-531: There is a lot of literature stating that particulate NO3- photolyzes 10-1000 times faster than gaseous HNO3. 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_{HNO3} due to a faster photolysis of particle-phase HNO_3 as mentioned in Line 583-584.

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 23th.

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”.

Lines 577-579: Remove NH4NO3 discussion.

Response: Section 4.3.3, the discussion of NH_4NO_3 was removed.

Line 581: ‘consistently’ should be ‘previously’

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

Line 583: ‘these’ should be ‘our’

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.

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.

Table 1: Clearly indicate the MARGA measurements.

Response: The obtained data of MARGA was noted as ^{b} 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.

Response: “pH was measured by a pH meter (mod. Lab 850, Schott Instruments) on a subsample of the total volume” has been noted as ^{b} 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.

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.

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 descripted in Line 294-296 to discuss the hypothesis of morning peak could be caused by the photolysis of particle-phase HNO_3/NO_3^-. Hence the 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 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/NO2 with x and y error bars corresponding to standard deviations of HONO and NO2 of all data collected in that RH bin (e.g. 0-20 %)?

Response: The previous Figure 6 about the "Correlation between HONO and NO_2 at night" was removed since the unconvinced discussion as the HONO to NO_2 ratio typically increase during night-time and could be artificial correlation between RH with HONO/NO_2.

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 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 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.

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 $k_{emission}$ = 0.006 pptv $\%^{-1}$ s^{-1} and maximum dew HONO emission $k_{emission}$ = 0.026 pptv $\%^{-1}$ 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 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.

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.

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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