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

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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

35 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

40 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

45 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

50 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

55 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 ℃.

60 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.
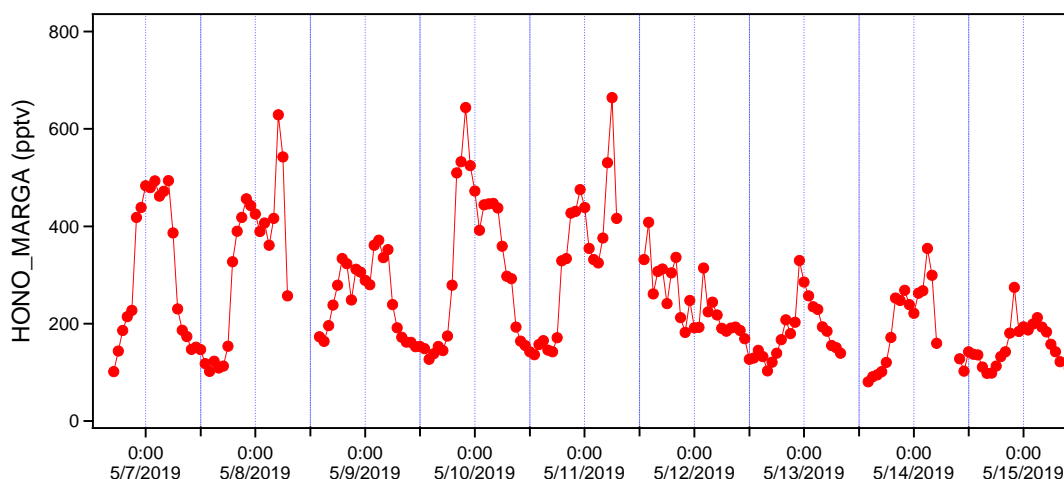
Figure R1. Time series of HONO (MARGA measurement) in Melpitz from May 8th to May 15th 2019. The gap was mainly due to HONO quantification of dew samples and the maintenance of the instrument.

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, Größ 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:

$$P_{unknow} = \frac{d[HONO]}{dt} + J_{HONO}\,[HONO] + k_9[OH][HONO] - k_{3a}[OH][NO] \hspace{2em} (Eq.\ 10)$$

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. 10^{-7} – 10^{-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. 10^{-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 10^{-3} to 10^{-4} are used. Otherwise this low number would mean that HONO formation could be easily explained by a reasonable uptake kinetics on particles (ca. 10^{-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 $(8.8 \pm 5.0) \times 10^{-6}$ 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. 10^{-5} converts into a "geometric uptake coefficient" of ca. 10^{-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

230 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:

235 "**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

240 (2002) (Equation S1) was set up.

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

Here, v_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

245 $$R_a = \left(\frac{1}{\mu \, \kappa^2}\right)\left[\ln\left(\frac{z}{z_0}\right)\right]^2 \quad (S2)$$

$$R_b = \frac{z_0}{D} \quad (S3)$$

$$R_c = \frac{4}{\gamma \, c} \quad (S4)$$

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

250 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} m² s⁻¹, respectively, at 760 Torr (Hirokawa et al., 2008;Langenberg

255 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).
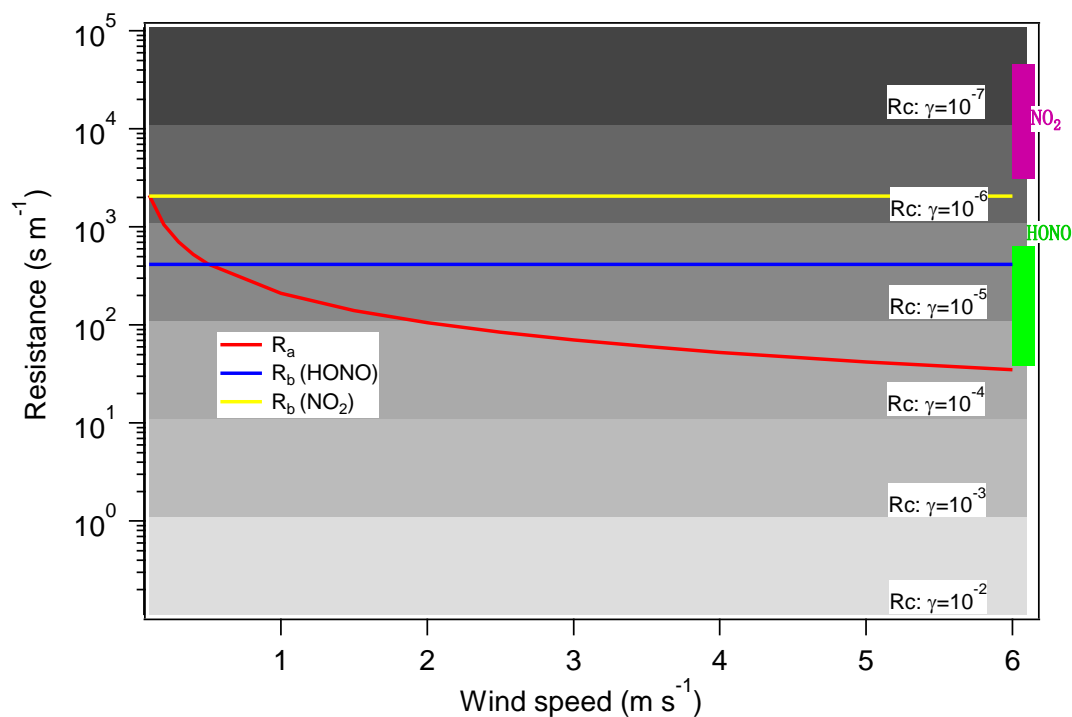
260

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

265 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

270 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

275 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

280 (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 $\geq 2.8 \times 10^{-4}$ 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 ($\gamma_{HONO, ground} = 1.7 \times 10^{-5}$ 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 /cm^2).

Response: Here we would like to present a measured nighttime loss of HONO with strength sink of $L_{HONO} = 0.16 \pm 0.12$ 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: $\gamma_{NO2 \rightarrow HONO} = 2.4 \times 10^{-7}$ to 3.5×10^{-6}, $\gamma_{HONO,ground} = 1.7 \times 10^{-5}$ 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 $\overset{h\nu}{\rightarrow}$ A$^{\text{red}}$ + X;   A$^{\text{red}}$ + X → A´; A$^{\text{red}}$ + NO$_2$ → 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.".

390   *Response:* We removed the reaction as NO+NO$_2$+H$_2$O 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
395   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$_2$O 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,
400   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.

405   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.

410   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
415   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.

13

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: : :

455   *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
460   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
465   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.

470   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.

475   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
480   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
485   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.

490   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.

495   *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;

500   (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
505   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
510   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.

515   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
520   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:

$$\frac{d[HONO]}{dt} = k_3[OH][NO] + k_{het}[NO_2] + \frac{1}{4}(\gamma_a\frac{S_a}{V} + \gamma_g\frac{S_g}{V})\upsilon_{NO2}J_{NO2}[NO_2] - J_{HONO}[HONO] -$$

$$k_{10}[HONO][OH] - \frac{1}{4}\gamma_{HONO,ground}[HONO]\frac{\upsilon_{HONO,ground}}{H} \qquad (Eq. 13)$$

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 (HNO₃/NO₃⁻ x J(HNO3)) and b) (NO₂ x J(NO2)) show that the latter correlation is better but both of these reactions could not explain a HONO morning peak as below.
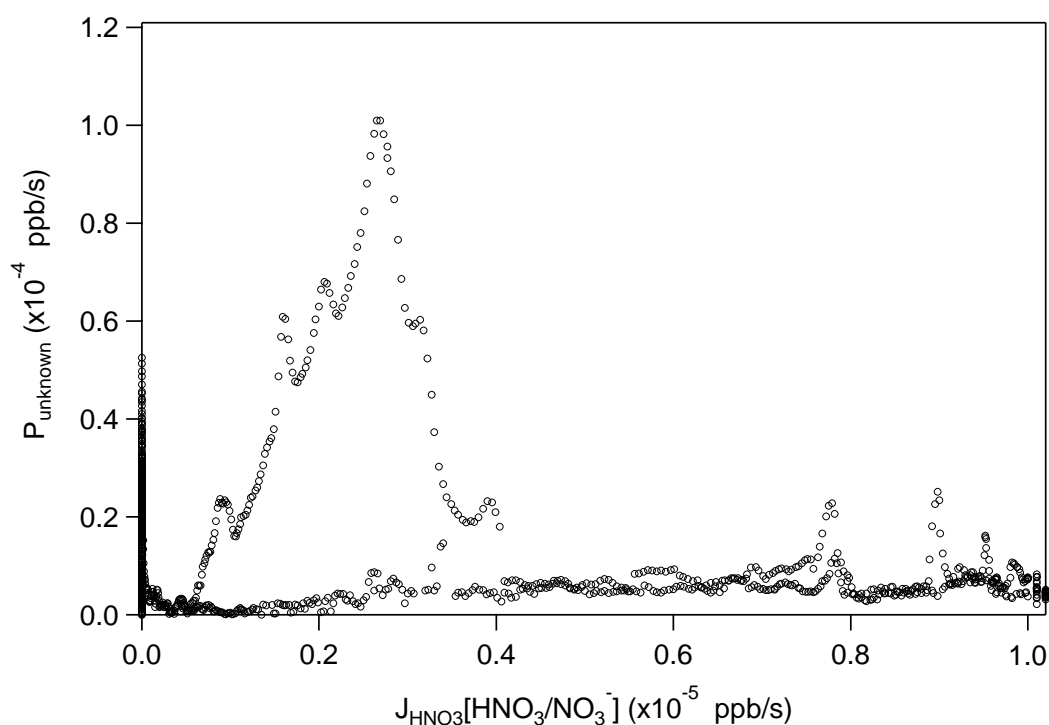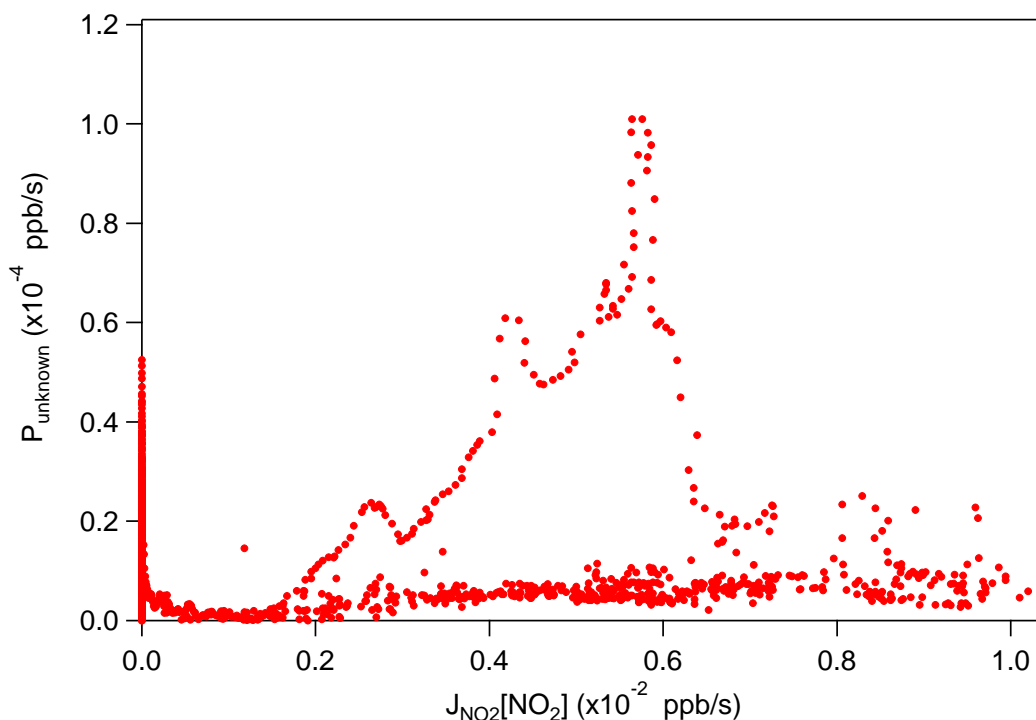
Figure R2: Plots of "unknown source" vs a) the product (HNO$_3$/NO$_3^-$ x J$_{(HNO3)}$) and b) (NO$_2$ x J$_{(NO2)}$). Both of this correlation cannot explain the observed HONO morning peak.

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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 > 10^-5 - 10^-4, depending on Ra and Rb).

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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

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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

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addition, the equation 7 of $\frac{1}{4}\gamma_{HONO,ground} \times [HONO] \times \frac{\upsilon_{HONO,ground}}{H}$ 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: $\gamma_{NO2 \rightarrow HONO\_g}$ = 2.4×10^{-7} to 3.5×10^{-6}, $\gamma_{HONO,ground}$ = 1.7×10^{-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

695 *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
700 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
705 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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