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Atmospheric Chemistry and Physics
Discussions

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 O3 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.

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.

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 SO2 (see e.g. Spindler et al., 2003) or VOCs by NO2, 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.

4) 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.

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.

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.

5) Heterogeneous kinetics

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.

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 (Ra and Rb) and a surface resistance (Rc) should be used. Only Rc 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 (Ra and Rb can be estimated by parameterizations, see e.g. VDI 3782). Using constant uptake kinetics makes no sense here.

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, doi:10.1029/2001JD000390 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 %. . .

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 x 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.

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.

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).

Line 25: correct the gamma values (see main concerns).

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.

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).

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.".

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).

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....

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).

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

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

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

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.

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

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

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...).

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

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. . .).

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!?

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. . .

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

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.

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

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.

Line 354: Should be correlation and not covariance.

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).

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.

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.

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).

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

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. . .

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…

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.

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

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!

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…

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).

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.

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

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…

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…

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

Lines 578-579: While emission of NH3 during evaporation might be reasonable, re-emission 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.

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

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

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

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.

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.

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

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.

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

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.

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

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

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.

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