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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 #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.

2. 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?

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.

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?

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. 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?

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.

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.

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.

Detailed Comments

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

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

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.

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).

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

Line 82: ‘detect’ should be ‘detects’

Line 90: should be ‘found excellent agreement’

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.

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

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. . .’

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.

Line 139: ‘air zero’ should be ‘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.

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).

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.

Line 262: ‘concentrated’ should be ‘concentration’

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

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

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)

Line 276: ‘NO2-to-HONO conversion frequency’

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.

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 favourable 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.

Line 295: ‘concern’ should be ‘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.

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

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.

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

Line 341: ‘cases’ should be ‘conditions’

Line 362: High HONO/NO2 values were also reported in (VandenBoer et al., 2013).

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

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.

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.

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.

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?

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

Line 465: 'above…' should be 'to reach an average minimum…'

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

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

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.

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?

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

Line 522: 'would be' should be 'was'

Line 526: 'preceded' should be '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?

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

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

Lines 577-579: Remove NH4NO3 discussion.

Line 581: 'consistently' should be 'previously'

Line 583: 'these' should be '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.

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

Table 1: Clearly indicate the MARGA measurements.

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.

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.

Figure 3: Change ‘HONO_MARGA’ to ‘HONO’

Figure 4: Remove panels e) and f)

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

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 %)?

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.

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.

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.

Figure S2: What is the trough material made of?

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

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

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