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Comment on acp-2021-893

Anonymous Referee #1

Referee comment on "An investigation into the chemistry of HONO in the marine boundary layer at Tudor Hill Marine Atmospheric Observatory in Bermuda" by Yuting Zhu et al., Atmos. Chem. Phys. Discuss., <https://doi.org/10.5194/acp-2021-893-RC1>, 2021

In the manuscript by Zhu et al., the chemistry of HONO at a marine measurement site on Bermuda island was investigated. Different HONO sources were discussed for which NO_x related reactions were considered important under polluted island influenced conditions, whereas HONO formation by particle nitrate photolysis was found to be more important under clean marine conditions. Furthermore, photolysis of ground surface adsorbed HNO₃ was postulated as main HONO source reaction for low NO_x island influenced conditions. An important observation is the missing night-time formation of HONO under clean marine conditions, which is reasonable considering the alkaline sea surfaces acting as a perfect sink for HONO. This result agrees with another recent paper (Crilley et al., ACP, 2021, not cited), but is in contrast to former observations from China and Kanada.

I have several comments, which should be considered in the revised paper.

Major Comments:

1) Description of the HONO daytime budget:

For the production rate (equation 2) NO_x related HONO formation is not well described. First, HONO formation by the gas phase reaction NO+OH could be easily implemented by assuming a reasonable diurnal OH profile (e.g. by its correlation with J(O¹D), or by any simple box model). Since the homogeneous formation is most probably not too important here, even large uncertainties (e.g. factor of two...) will not matter too much. When OH is calculated, also the (minor) loss of HONO by its reaction with OH could be explicitly considered besides the HONO photolysis (see equation 4, where this reaction is now neglected). Considering OH, the PSS of HONO can be calculated and only excess levels (and not measured HONO...) should be explained by the discussed sources (P_{extra}).

Second and much more important, HONO formation by NO_2 conversion during daytime must be implemented as a photolytic process, which is typically parameterized as a function of the NO_2 concentration and (!) $J(\text{NO}_2)$, see work by Stemmler et al.. In this context, also reaction (R3) must include its photosensitized character! Please add $h\nu$ to the reaction (compare R4). A dark reaction R3 is also known, but since night-time HONO formation was not observed, this is not of importance here. When the photosensitized conversion is correctly included, most probably the diurnal shape of the HONO production (P_{extra}) will be well explained (see below). Thus, the different patterns of HONO (one daytime maximum) and NO_2 (two maxima) (see lines 346-348 and Fig. 4) cannot demonstrate the missing importance of reaction (R3) as long as this reaction is not correctly considered.

2) Proposed extra sources:

To identify potential HONO formation mechanisms during daytime, only the extra HONO sources (besides the known reaction $\text{NO} + \text{OH}$, and the known losses by photolysis and reaction with OH, see above) should be calculated and the diurnal profile of P_{extra} be compared with different postulated sources, e.g. by plotting against different parameters, like $J(\text{NO}_2) \times \text{NO}_2$, $J(\text{HNO}_3) \times \text{HNO}_3(\text{av})$, $J(\text{HNO}_3) \times \text{pNO}_3$ etc. for clean marine and island influenced conditions. I am quite sure that the best correlation will be obtained for $J(\text{NO}_2) \times \text{NO}_2$ for island influenced conditions (see below). This will be in contrast to the statement made simply from the concentration (...) profiles (see lines 346-348), which does not include the photolytic nature of the formation process by NO_2 reactions. In addition, there is always a non-linear connection between the HONO production and its concentration, caused by the variable main loss term (photolysis). In addition, reaction R3 is underestimated and R4 overestimated, see below.

Reasons for a major HONO formation by photosensitized conversion of NO_2 on ground surfaces become obvious from Fig. 4:

- There are clear diurnal profiles for HONO and HONO/NO_2 with near noon maxima, pointing to a photochemical nature of the HONO sources;
- HONO levels for clean marine air masses (A) are factors of 4/7 (summer/spring) lower than for island influenced air masses (B), pointing to a major formation on island surfaces;
- Despite the large HONO differences for (A) and (B), pNO_3 is similar for both air masses (compare pNO_3 for (A) and (B)). Thus, any major HONO formation by particle nitrate photolysis is unlikely, at least for island influenced conditions.
- HONO is similar for spring and summer for clean marine conditions, although the NO_2 levels are very different (compare upper two figures for case (A)). Thus, heterogeneous

HONO formation by any NO_2 reactions on ocean surfaces are most probably negligible. In contrast, for island influenced conditions (B), for which active surfaces for reaction (R3) are present (e.g. humic acid surfaces), HONO and NO_2 are both ca. a factor of two higher in spring than in summer.

All together these observations clearly indicate that HONO is mainly formed by photosensitized conversion of NO_2 on island surfaces.

3) Parameterization of the NO_x related reactions:

Besides the separation of HONO formation by gas phase reaction of $\text{NO}+\text{OH}$ and by photosensitized reaction R3 (see above), for the latter reaction a non-linear correlation of the uptake coefficient with the NO_2 concentration is well known (decreasing gammas with increasing NO_2 , see the cited papers by Stemmler et al.). Thus, besides that HONO production and not simply its concentration should be considered (see above), the non-linear correlation between the HONO and the NO_2 concentrations in Figure 5 is also not well described in the paper. Here the authors concluded a perfect first order kinetics of R3 (gamma independent of the NO_2 concentration) and used only the low conversion efficiency, observed in the high NO_x plumes, which will strongly underestimate this source for the low NO_x island influenced conditions, later discussed. In addition, they simply used this lower limit HONO/ NO_x ratio and constantly applied it to parameterize the HONO production, despite its variable photochemical nature (see above). In conclusion, the used parameterization strongly underestimates the photosensitized NO_2 conversion for low NO_x conditions.

4) Parameterization of HONO formation by p NO_3 photolysis

In contrast to R3 the authors overestimated R4 by p NO_3 photolysis. Here by equation (7), an upper limit EF^* of 30 is determined by assuming that all missing HONO sources besides R3 are by p NO_3 photolysis. First, if a higher contribution of R3 were considered (see above), EF^* would get lower, bringing that closer to the lab values. Second, by using aerosol samples the authors determined a much more reasonable $\text{EF}(\text{m})$ of ca. 4 in the laboratory, which is in good agreement with other recent studies (Romer et al., 2018: "most reasonable range $\text{EF}=1-7$ "; Shi et al., 2021: $\text{EF} = \text{ca. } 1$). I encourage the authors to use their own measured $\text{EF}(\text{m})$, making that source much less important, in agreement with the above discussed general observations in Fig. 4.

5) Proposed HONO formation by photolysis of adsorbed HNO_3 on island surfaces

By the same argument, also the proposed major HONO formation by photolysis of ground surface adsorbed HNO_3 will get lower, if the higher contribution of the NO_2 reaction R3 is considered. Also, the high intercept in Figure 6 (independent of $\text{HNO}_3(\text{av})\dots$) compared to

the $\text{HNO}_3(\text{av})$ dependent HONO, is a strong argument why this ground surface photolysis of HNO_3 is not mainly responsible for the missing HONO sources for island influenced conditions.

Specific Comments:

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

Line 53, R3: either add a new, similar photosensitized reaction, or add "hv" to consider only daytime chemistry.

Line 62: The first study, which proposed significant extra daytime HONO production was by Neftel et al., 1996, please add.

Line 72: Add a reference to the new photosensitized R3.

Lines 87-88: The very recent study by Crilley et al., 2021 (ACP) is missing.

Page 5, HNO_3 and pNO₃ measurement: It is not clear how uptake of nitrate containing particles in the stripping coil was considered for the HNO_3 detection and whether the wetted frit disc sampler measures the sum of pNO₃ and HNO_3 , as expected. How were these interferences considered?

Page 5-6: The separation of the terms pNO₃ and NITs for particle nitrate measurements is confusing when later used for parameterization of the HONO source (pNO₃). I suggest to use for both measurements pNO₃ (particle nitrate...) and index the different instruments, e.g. pNO₃(LPAP) and pNO₃(filter).

Line 149: The explanation of the correction factor of 2.06 (by the way: *2.06 or /2.06?) applied for the LPAP pNO₃ measurements is not reasonable. An uptake of 50 % of the particles in the inlet of the frit sampler is too high (particles typically follow the gas stream, see principle of a denuder...). I expect more general differences between the two methods. For example, is HNO_3 (sticky...) also collected on the filter? If the HNO_3 /pNO₃ ratio is 1:1 the factor of two could be explained. In addition, was the pNO₃ recovery

efficiency of the frit sampler measured in laboratory studies? May be the nitrate collected on the frit is not completely extracted by water?

Line 170: Was the fast reaction of $\text{NO} + \text{O}_3$ considered for in the 30 m long inlet line? At least for the plumes this is expected to change the $\text{NO}/\text{NO}_2/\text{O}_3$ system (quadratic reaction kinetics of $\text{NO} + \text{O}_3$).

Line 181: ...Supplement Information S1.

Line 182: the heading (pNO₃) does not fit to the measurements (NITs), see above.

Lines 196-197: Why was the HONO formation only measured for the short 5 min period? From my experience HONO formation decrease with time. Caused by the long lifetime of particles in the atmosphere longer irradiation times (steady state...) are recommended in the laboratory. Thus, please mention that the EF(m) is an upper limit. Compare also former discussions on initial and steady state uptake coefficients.

Line 198: ...Supplement Information S2...

Table 1: If a correction factor was applied for pNO₃ by comparison with NITs, why are the mean concentrations of pNO₃ and NITs not exactly equal?

Figure 3: the relative patterns of HONO and NO_x are very similar for spring and summer (island/plumes) in contrast to pNO₃, which is another hint for NO₂ as main precursor of HONO.

Lines 346-348: Please reformulate the sentence when P(extra) and not HONO is compared to the NO₂.

Lines 378-381: First, during night-time, aerosol reactions will not play any role (compare S/V of particles and the ground). Second, the HONO concentration alone (higher for island influenced compared to clean marine) is no argument for island surfaces being the main source region, since also the precursor (NO₂) is higher for the island influenced air masses. Here the HONO/NO₂ ratio should be considered! But also this ratio is higher for island influenced compared to clean marine conditions (HONO is factors of 4/7 higher, NO₂ only a factor of 2-3) pointing to the heterogeneous HONO formation only on ground surfaces.

Equation (2): Instead of $P(\text{NO}_x \rightarrow \text{HONO})$, add $P(\text{NO} + \text{OH})$ and $P(\text{NO}_2 + \text{organics} + \text{hv})$.

Equation (4): Add the minor loss term $L(\text{HONO} + \text{OH})$.

Line 410: Please do not use the high NO_x data to parameterize $P(\text{NO}_2 + \text{organics} + \text{hv})$ for low NO_x conditions.

Figure 5: Use only the clean marine and island influenced conditions to parameterize $P(\text{NO}_2 + \text{organic} + \text{hv})$, compare to Fig. 4, where the variable plumes were also not considered. Besides the concentration dependence of the reaction, low HONO/NO_x for high NO_2 could be also explained by different distances/transport times from the NO_x sources to the measurement site, for which for low distance measured HONO/NO_x will approach the HONO/NO_x emission ratio, for which similar values of close below 1 % are known.

Line 449: If HONO is deposited on the alkaline sea surfaces, then $P(\text{NO}_x \rightarrow \text{HONO})$ should be the lower (...) limit. And do not use $P(\text{NO}_x \rightarrow \text{HONO})$ in this way, see above.

Line 476-477: The most reasonable range of EF was 1-7 in Romer et al. In addition, the even lower values of Shi et al., 2021 are missing.

Line 482: Why were the data of NITs and not of pNO_3 used here?

Equation (8): Use the experimental $\text{EF} = 4$, see laboratory studies.

Line 519: Just a comment (out of this study...) to the high published EF values of Ye et al.: Could the increasing values with decreasing $\text{p}(\text{NO}_3)$ levels be an artificial background HONO formation of the reactor/filter set-up, which gets relatively more important for lower particle load?

Lines 521-523: EF^* is by definition (see above) systematically too large and $\text{EF}(\text{m})$ should be used (which may have some statistical uncertainties...).

Figure 7: The high HONO and NO_x levels observed before midnight 5/11 (dark no photolytic sink) may be simply explained by direct emissions, since the HONO/NO_x ratio is only ca. 0.5 %, which is very close/even lower to published emission ratios. In contrast, the increasing HONO levels under similar NO_x levels for the two marked plumes on the

morning of 5/11 indicate again the photosensitized nature of the NO₂ conversion (increasing radiation).

Lines 632-633: Modify that sentence when correctly evaluated, see above.

Line 638: The EF of 30 is not "moderately enhanced" but systematically too high (see EF(m) = ca. 4).

Line 640 – 642: Check after re-evaluation. I expect that the NO₂ reaction will get more important and the HNO₃ photolysis less important.

Supplement:

Equation (S1): I do not understand the double normalization? The first normalization is clear, for which UVmodel is already the modelled clear sky UV radiation (= UV*model...). The modelled J-values are calculated for clear sky only, which may be in reality lower, caused by any clouds etc. To consider that, the ratio of measured and clear sky modelled UV is used. But why is the second normalization (UV*model/UV*measured) done?

Line 35 and 36: are the units in the brackets "moles" or do you mean "molecules" (the latter is normally used in the paper)? For molecules use (molec.).

Line 39: $7 \times 10^{-7} \text{ s}^{-1}$ should be for gaseous HNO₃ (and not nitrate).

Technical corrections:

Line 48: Li et al., 2008a (the first Li et al., 2008 in the text...), the second Li et al., 2008b is referred to in Line 74. Change accordingly in the reference list and the text.

Line 51: Dito for Ye et al., 2017a (is the first Ye et al. 2017 in the text...). In Line 327 it should be Ye et al., 2017b. Change accordingly in the reference list and the text.

Line 57: Acker et al., 2006a

Line 65: Villena et al., 2011a and in Line 165: Villena et al., 2011b. Change accordingly in the reference list and the text.

Line 81: Ye et al., 2017 a, b or both?

Line 123: ... on the platform...

Line 130: Ye et al. (2016, 2018); dito in Line 456: Ye et al., 2016

Line 515: NH_4NO_3

References:

General:

- unify the doi: citation, either doi:... or <https://doi.org>.... (but not: doi:<https://doi.org>.);

- when the Science journal is cited always delete the bracket (80- .).

Line 668: L02809 missing (see pdf of the paper)

Line 673: 336b

Line 689: 130,

Line 692: L02813 is missing

Line 699: D21202 is missing

Line 706: Becker, K. H.

Line 713: L05818 is missing

Line 722: L04803 is missing

Line 757: use 8192 and not the LOP numbers (see pdf of the paper)

Line 763: 4099 is missing

Line 766: 4705 is missing

Line 789: 1326-d

Line 809: L15820 is missing

Line 814: 4590 is missing (delete the ACH numbers, see pdf of the paper)

Line 817: 2217 is missing

Line 820: D08311 is missing

Equation S3: Should be [Salicylic acid]