

Comment on acp-2021-893

Anonymous Referee #2

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-RC2>, 2022

General comments:

The paper titled "An investigation into the chemistry of HONO in the marine boundary layer at Tudor Hill Marine Atmospheric Observatory in Bermuda" by Zhu et al. present measurement results of temporal distributions of nitrous acid (HONO) and its budget analysis in background marine environments at Bermuda. Laboratory study examining the importance of particle nitrate as photolytic HONO source was also conducted along with the field campaigns. The photolytic of Pno3 and HNO3 were found to dominate HONO production in Bermuda, largely different from those reported in urban and polluted areas, which may suggest the unique chemistry of HONO as well as other reactive nitrogen species in the observation site, although these novel results are still needed confirmed or further discussed. The manuscript was well written and presented, but some issues needed to be clarified. Therefore I recommend the publication of Zhu et al. work after replying the following comments clearly.

Specific and technical comments:

- Line 25-26, As discussed in section 3.4, NO_x-related reactions contributed minorly in daytime formation of HONO, while the photolytic of Pno3 and HNO3 dominate HONO production in marine and island influenced air, respectively. Please confirm it and revised it properly.
- Table 1. The statistical result of pNO₃ and NITs are better present in ug/m³, which was in particle phase. In addition, as bld values were obtained for HONO and NO_x during the campaigns, the calculation for the mean values should be provided.
- Figure 2, it is interesting to note that the highest ratio of HONO/NO_x appeared in the southeast direction, while both HONO and NO_x showed highest values in the northeast direction, where the city of Hamilton located. Can you explain it?
- Line 255-260. The spikes that associated with the ship emissions should be carefully checked.
- Line 260-265 I do not think the contribution from direct emissions would be higher during night than during the day, as human activities were much reduced during the night, which supported by the diurnal pattern of NO₂ in Fig.4. Higher NO₂ concentrations were observed during the day. I agree that the transport times (1.4h in 2m/s wind speed) may longer than the photolytic lifetime of HONO in the daytime. However, one should note that the higher NO₂ appeared in the early morning that the radiation in relative low levels, thus the photolytic lifetime of HONO expected to be much longer.

Please clarify it.

- Line 440-445. The using of equations (5) and (5) would introduce large uncertainty in estimating the P NO_x-HONO, as the heterogeneous production from nitrogen dioxide (NO₂) on serval surface is non-linear. Thus, the estimated missing source for HONO by equation (6) is questionable. In addtion, direct emission was not include in equation (6) which may overestimate the Pmissing as mentioned above. In addition, I would expect the authors considered and evaluated thecontributions of photosensitized heterogeneous conversion on island surfaces and aerosol surface that reported to be contributed importantly to HONO formation (ie. Liu et al., 2021).
- Line 515. HN_4NO_3 or NH_4NO_3 ? In addition, as the water-soluble ions were also analyzed, the existence of NO₃⁻ in particles should be discussed, which would further support the comaprable of low EF values from this study with that reported by Shi et al., 2021.
- Line 521-523, I note that an upper limit EF* of 30 was used, not the measured EF(m) of much lower value (about 4) determined in the laboratory of this study, if it is ture claimed by the author that using the store aerosol samples caused large discrepancy, how about the results of Pno₃ photolysis rate conducted by previous laboratory studis using similar method? I do not think the using of high EF*that result in a high contribution of Pno₃ photolysis on HONO production is reasonable. At least, the authors should evaluate the results using the high and low EF values.
- Line 545-549. HONO production rate of 0.016 pptv/s from photolystic of HNO₃ was suggested, which contributed 84% of the HONO photolytis loss rate. How this value is calculated, and is it possible for such high contribution of HNO₃ photolystic on HONO which rarely reported? In addition, how about its contribution in marine influenced air? I note that this value was not provide in Table 2.