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Comment on acp-2021-532

Anonymous Referee #1

Referee comment on "Is the ocean surface a source of nitrous acid (HONO) in the marine boundary layer?" by Leigh R. Crilley et al., Atmos. Chem. Phys. Discuss.,
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This is an interesting new contribution aiming at exploring the ocean-surface mediated conversion of NO₂ to HONO in the coastal marine boundary layer at two contrasting coastal locations, namely at Cape Verde (Atlantic Ocean), representative of the clean remote tropical marine boundary layer, and Weybourne (United Kingdom), representative of semi-polluted Northern European coastal waters. By monitoring, among others, NO₂ and HONO, it is shown that the HONO production at these two sites differs significantly from previous reports (a factor of 5 lower). As stated by these authors, these results point to significant geographical variation in the predominant HONO formation mechanisms in marine environments and indicate that caution is required when extrapolating the importance of such mechanisms from individual study locations to assess regional and/or global impacts on oxidizing capacity.

I enjoyed reading this manuscript which is well written and illustrated.

Obviously, the approach used here to detangle whether the NO₂ conversion is a source of oceanic HONO is very (or too?) simple, as illustrated by equations 1 and 2. Maybe the reader should be made more aware that this approach oversimplifies the chemistry potentially involved. NO₂ reacts quite slowly with water, at a rate dependent on the actual NO₂ concentration. Therefore, the first order assumption used to derive equations 1 and 2 may not hold everywhere (even if it is unlikely that the second order term may dominate).

Trusting reported values, in this study but also previous ones, it is surprising that the HONO production rates vary to such an extent, and I do regret that section 4 does not discuss more the potential reasons.

The potential role of the SML is briefly discussed when reporting the data from Yu et al (2021), who observed little uptake of NO_2 on bulk sea water under dark conditions ($\gamma = 1.6 \times 10^{-8}$). Indeed, bulk and surface water could exhibit different compositions. Could the chemistry unraveled by the group of Markus Amman (i.e., charge exchange reactions from dissociated phenols to NO_2 , chemistry occurring at higher pH) be this source of HONO? This could in organic enriched SMLs, which will depend on location and season. And in fact, the fact the seasonality (and therefore the presence or absence of the SML) be one reason of the observed discrepancies between the different studies? Maybe the authors could compare SML maps for the different location and time and sampling to see whether or not such a correlation exists?