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Interactive Comment

Interactive comment on "Pseudo steady states of HONO measured in the nocturnal marine boundary layer: a conceptual model for HONO formation on aqueous surfaces" *by* P. Wojtal et al.

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We thank the referees for their comments. Both favor publication after some minor corrections, which we will attend to as outlined below.

Anonymous Referee #1 This MS presents some interesting observations, showing a pseudo-steady state (PSS) in HONO overnight in the lower marine boundary layer over a polluted area. This observation may have broader reach and certainly calls for an examination of existing data. I do think the discussion could be improved by reference to some of the recent work from the groups of Christian George, Markus Ammann and others, who have demonstrated heterogeneous HONO production being stimulated by sunlight. Their basic mechanism could, in principal, be operating under moonlight as well (assuming there are photoactive chromophores present in the sea-surface microlayer (SSM) which ab- sorb the requisite wavelengths.

Author Response - Our view is that the source of HONO we observe at night is generated by a dark mechanism. The referee suggests that heterogeneous HONO production during the day stimulated by sunlight, could be operating under moonlight. This is easy to dismiss in several ways: i) there has never been a single report suggesting that night time concentrations of HONO are related to the well know lunar cycle; and nor is there a correlation in this study ii) a new moon (no light) was observed on July 3/4 2005; and yet we had some of our highest HONO levels on July 4 iii) The flux of photons under a full moon are 5-6 orders of magnitude less than the flux of photons from the sun at solar noon; clearly too low for the same photostimulated mechanism to be operating.

Referee - I do have a problem with the proposed mechanism. It is very vague just what is meant by the "nanolayer" - how is this different from the top of the microlayer? Given the low solubility on NO2 in water, and its low attraction for water in general (as displayed in quantum chemical calculations, for example) the needed concentrations seem unbelievable. Could not NO2 be present in the organic fraction of the microlayer for example? (It should be more soluble in this fraction than in the water.) In summary, while the observations are interesting and certainly worthy of reporting, I believe that the suggested model need more thought.

Author Response - Our mechanism right now is somewhat speculative, but consistent with the observations we have made and consistent with observations made in other studies in non-marine areas. Our goal here was to propose a potential model for HONO production in aqueous environments that occur everywhere, not just in marine areas. Our observations in marine areas though help to simplify the possibilities. It is clear from many many other studies that a dark mechanism for HONO production occurs on surfaces, and that water is needed on that surface. It is clear from most of those studies

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that the mechanism is not a homogeneous aqueous phase mechanism. Thus, we have proposed a mechanism that is not only consistent with just our own observations in this simplified marine environment (simplified only with respect to water coverage), but also consistent with observations in urban areas at night and on laboratory surfaces in the dark. While I agree with the reviewer that the organics in the microlayer somewhat complicate the issue, the SSM microlayer is still predominantly aqueous (>99%), not organic.

Anonymous Referee #2 General comments - This paper presents nighttime HONO measurements in a polluted marine boundary layer. The authors presented a conceptual model to further analyze the observed data to improve a better understand of HONO formation. My only concern is that the processes regarding HONO formation in the conceptual model is rather simple and as the authors have pointed out in Conclusions, more analysis and relevant measurements are needed in order to better understand the HONO formation in the atmosphere. In general I think the paper is well written and reports some reasonably important results. I would recommend it be published in ACP after revision and ask the authors to consider the following special comments in their revision.

Special Comments 1. In Introduction, in the literature review of HONO formation: NO2 reduction on organic surface and the photolysis of surface-deposited HNO3/nitrate (Zhou et al.) should be also included.

Author Response- As we are predominantly discussing observations at night, we felt that discussions of photolytic mechanisms might complicate the issue. Clearly we are looking to add insight to HONO formation mechanisms that are non-photolytic. Nonetheless, we will add such reference to photolytic mechanisms to round out the introduction.

2. Detection limits (3 sigma) were 0.30 ppb for HONO, 0.45 ppb for SO2, and 0.20 ppb for NO2, determined by repetitive determination of a low concentration sample.

âĂŸAĂĞTHONO detection limit is not very significantly different from its nighttime levels (_0.5 ppbv), which causes a large uncertainty in the measurements and may affect some of the conclusions.

Author Response- It is truce that we are working close to the detection limit for a single measurement point. But we have statistics on our side. The standard error of a 1 hour bin mean for example (~n=7 points) reduces the detection limit for the mean to ~ 0.1ppm for HONO.

3. Were there any measurements for marine boundary layer heights? This important information needs to be discusses somewhere if there was no direct measurement.

Author Response- There were not any measurements of MBL heights. We have discussed MBL height, hMBL . It is included in Section 3.3, Equation 5 and Equation 6. In section 3.3 we refer to measurements in the marine boundary layer at night in a different study (Brown 2004), where they measured Hmbl=100m. We have assumed this for discussions that occur subsequently although the results, conclusions, logic presented will not change significantly if the boundary layer is different. Since it can definitely be different in our location, we will add a short discussion of the implications for our arguments.

4. Section 3.6, 1st paragraph, add Yi et al. (Importance of dew in controlling the air-surface exchange of HONO in rural forested environments, Geophys. Res. Lett., 33, L02813, 2006) about the dew evaporation to release HONO and other nitrogen species.

Author Response- This is very relevant. We will add this reference.

5. Fig.2, there was large variability in the observed HONO mixing ratios from day to day. It would be great to explain a little bit for the reasons.

Author Response- A short discussion of this variability can be added. Our results seem to suggest that temperature differences can account for some of the variability, but no

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all of it.

6. Fig. 7 is relatively scatter, maybe should plot HONO/NO2 vs. RH

Author Response- What we have said in the paper and tried to get across is that plotting HONO/NO2 is only relevant if you KNOW that the formation of HONO is first order in NO2. That is the implicit assumption in making such a plot. We have clearly shown that at night in this aqueous environment, the formation of HONO is frequently not first order in NO2. And as we have argued, the HONO formation it is not directly related to the relative humidity either. The fact that we see just a weak correlation with HONO is consistent with this.

Interactive comment on Atmos. Chem. Phys. Discuss., 10, 25153, 2010.