

Interactive comment on “Evidence for renoxification in the tropical marine boundary layer” by Chris Reed et al.

Anonymous Referee #2

Received and published: 1 March 2017

Overall Assessment

The manuscript by Reed et al. presents 2-years of results on a unique diurnal cycle of NO, NO₂ and O₃ concentrations in the marine boundary layer from measurements at a coastal site in Cape Verde Atmospheric Observatory (CVO). Of particular interest is a noon-time high in NO_x concentrations. A box model approach was used to model this diurnal profile, which is explained as arising from particulate nitrate photolysis and reactions of reactions of halogen nitrates (products of nitrate radical and halogen hydroxide chemistry during the nighttime). The authors argue that field observations could not be explained by dissociation of PAN that is transported to the site from anthropogenic sources over long distances. The methodology associated with measurements of NO_x, HONO, O₃ etc. are appropriately chosen and carefully executed. I think there is a potentially interesting data set here and a nice opportunity to explore the role of nitrate

C1

aerosol photochemistry as a daytime NO_x source. However, for completeness I would like to see an analysis of the relative importance of ClNO₂ as a daytime NO_x source vs. the other potential daytime NO_x sources that were postulated.

The authors mention that the diurnal pattern in the CVO NO_x concentrations was historically attributed to thermal decomposition of NO_y species (see p. 6, L6). By NO_y, the authors refer mostly to PAN, but what about N₂O₅ heterogeneous chemistry? Consideration of N₂O₅ heterogeneous chemistry appears to be limited to hydrolysis (modeled using $\text{N}_2\text{O}_5 \rightleftharpoons 2 \text{NO}_3^-$, with an uptake coefficient of 0.02). This likely explains why in Fig. 10 the model shows non-existent N₂O₅ concentrations at this site over a 24 hour period. However, previous studies of N₂O₅ in coastal regions show that steady-state concentrations of 20-100 ppt can exist, with peaks during the nighttime. Those studies also demonstrate that aside from hydrolysis to form particulate nitrate, a major fate for N₂O₅ is conversion to ClNO₂ on sea salt aerosol and the ocean surface. (e.g. PNAS, 2014, 111, 3943). Other studies show that photolysis of ClNO₂ during the daytime can lead to a significant source of radicals and NO_x. There is no mention of ClNO₂ throughout the manuscript, nor its potential impact on the diurnal profile. I recommend looking closely at these reactions in the model. Sufficient experimental data exists by now to parameterize N₂O₅ + Cl⁻ chemistry on sea salt aerosol in the model.

Lastly, I feel the authors should clarify what parameters they are using to derive the nitrate photolysis rates. Are the absorption cross sections and quantum yields for gas phase nitric acid or aqueous nitrate used? I do not think it would be correct to use gas phase nitric acid parameters to derive photolysis rate constants when the focus is on aqueous (particulate) nitrate as the daytime renoxification source. After all, HNO₃ is a strong acid and will be present as nitrate on aerosol surfaces or in bulk aqueous droplets under atmospherically relevant conditions found in the field. Aqueous nitrate photochemical parameters are therefore most accurate and applicable to this study.

Specific Comments

C2

Abstract and P2: L10 – I suggest defining the acronym “PAN” when it is first mentioned in the abstract and in the main manuscript.

P2: L17 – Remove the word “through”

P3: L10 – Remove the first “global”

P3: L23-25 – Request for clarification: If the calibration is done in ambient air (rather than in zero air) how can one be sure what the exact concentration is. Are standard additions of NO and NO₂ done for calibration?

P4: L21 – Do the authors mean: “so as not to sample from the main lab manifold”.

P9: L2: delete “is.” L13: the authors state, the major net sink for NO_x is the formation of nitric acid by reaction of NO₂ and OH. What about N₂O₅ deposition to aerosols as a major source of HNO₃?

P12: L3 – add “cycle” or “profile” after diurnal.

Figure 2. Shaded area indicating standard deviation of the measurements does not show up on my copy. Consider using a different color (e.g., black and grey).

Figure 6: HNO₃ photolysis is listed as a source of NO₃ or OH and NO₂. Is this formation rate considering a 10 fold enhancement of the HNO₃ (or aq. nitrate) photolysis rate, or is this just un-scaled HNO₃ photolysis using quantum yields and x-sections from JPL evaluations?

Interactive comment on Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2016-1111, 2017.