

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

Chris Reed et al.

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The authors would like to thank the reviewer for taking the time to assess our manuscript. We have answered their queries and suggestions point by point below.

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

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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 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 (modelled 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.

>While we agree with the reviewer that in their cited example N₂O₅ chemistry forming ClNO₂ is a source of radicals and NO_x at the Scripps pier (Kim et al., 2014), at Cape Verde NO₂ is two to three orders of magnitude lower than in California thus the equilibrium concentration of N₂O₅ is negligible. Furthermore the study of Savarino et al., (2013) specifically on the isotopic composition of nitrate at Cape Verde found isotope ratios which were incompatible with high production rates of HNO₃ from N₂O₅ hydroly-

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sis, and concluded that N₂O₅ and nitryl compound (ClNO₂ BrNO₂) levels in this region are very low. This is consistent with other studies modelling the pristine MBL at Cape Verde i.e. Sommariva and Von Glasow, (2012).<

Discussion of this has been added to discussion of figure 10. This now reads.

“In all cases N₂O₅ (in black) is effectively zero at all times due to very low NO_x mixing ratios in this pristine environment and the relatively high ambient temperatures (24.5 oC) where the N₂O₅ lifetime is ~ 3 s⁻¹. This precludes N₂O₅ channels to NO_x (and ultimately nitrate), consistent with the experimental findings of Savarino et al., (2013) at Cape Verde who found isotope ratios which were incompatible with high production rates of HNO₃ from N₂O₅ hydrolysis, and concluded that N₂O₅ and nitryl compound (ClNO₂, BrNO₂) levels in this region are very low. This is consistent with our own and other studies modelling the pristine marine boundary layer at Cape Verde of Sommariva and Von Glasow, (2012). This is in contrast with more polluted regions where N₂O₅ has been shown to be a route to NO_x and ClNO₂ (Kim et al., 2014).”<

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.

> As stated in the text surface nitrate photolysis rates are scaled to that of gas phase nitric acid, which is consistent with the results and approach of Ye et al., (2016) who found a correlation between the required in situ HONO source and the product of the bulk nitrate concentration and the photolysis frequency of gaseous HNO₃. All surface nitrate was parameterized similarly as bulk ‘NIT’ in our model study. This parameterisa-

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tion in fact represents a convolution of what could be many different surfaces or phases with many different quantum yields of which there are poor constraints, thus we use the well-defined rate of gaseous HNO₃ photolysis as a proxy.<

Specific Comments

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

>‘Peroxy acetyl nitrate’ added<

P2: L17 – Remove the word “through”

>Removed<

P3: L10 – Remove the first “global”

>Removed<

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?

>Correct, standard addition to ambient air is done for calibration. Line now reads: “Calibration for NO sensitivity and NO₂ converter efficiency occurs every 73 hours by standard addition to ambient air as described by Lee et al., (2009); in this way correction for humidity affecting sensitivity, and O₃ affecting NO₂ conversion efficiency are unnecessary.”<

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?

>See our response to the reviewers first point regarding N₂O₅ hydrolysis as a major

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source of HNO₃<

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

>Added<

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).

>This figure is now changed<

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?

>This refers to purely gas phase photolysis of HNO₃ and is not scaled. It does use photolysis quantum yields and corrections from JPL<

References

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