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

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The authors would like to thank the reviewer for their careful review and positive comments on the significance and robustness of this manuscript and for taking the time to review our work. Our responses to their points are detailed point-by-point below.

General comments:

The Authors present a compelling set of model results to explain the chemistry underpinning commonly observed daytime maxima in NOx at the Cape Verde Atmospheric Observatory. The impact of condensed phase nitrate photolysis in improving understanding of the NOx cycle in the marine boundary layer from long-term datasets, which capture diurnal features, has not been presented to date. This manuscript provides a robust method with which to test the findings of intensive field and lab observations

of this phenomenon. The authors also find that the role of halogens is important in describing several features in the temporal nature of the NOx diurnal patterns, building on recent findings that such chemistry may be important in controlling the cycling of reactive nitrogen in remote marine regions. The presented manuscript is well-written and most of the data in the figures is presented clearly. Overall, this work is acceptable for publication in Atmospheric Chemistry and Physics after a number of minor revisions and technical corrections have been made, which are presented in detail below.

Minor comments:

1) The title of the manuscript does not convey two of the major topics of this paper, nitrous acid and halogen hydroxides. The authors should consider modifying their title to reflect the important roles of HONO and halogens on renoxification processes in this work.

»> Incorporating all the major aspects of the paper would make for a very long title. We prefer to leave it as it – the information on key aspects is in the abstract. «<

2) The authors cite a number of real-world surface (Baergen and Donaldson, 2013; Ye et al., 2016a), laboratory substrate studies (Handley et al., 2007; Scharko et al., 2014; Zhou et al., 2003), a model estimate (Cohan et al., 2008) and two works on aerosol nitrate catalytic degradation (Ndour et al., 2009) and photolysis (Ye et al., 2016b) as the basis for parameterizing the particulate nitrate conversion rates in their model (e.g Pages 7-8). The majority of the cited work is for nitrate photolysis on proxy surfaces at the atmospheric interface and this is not clearly stated throughout the manuscript, which makes the focus on aerosol nitrate photolysis throughout the manuscript somewhat confusing. The connection and implications of linking nitrate photolysis on/in these other condensed phases is not clear in its applicability or in its limitations and this would be worth expanding on in the manuscript. This photochemistry is obviously important in this environment, but if studies of surface media and bulk aqueous solution (Scharko et al., 2014) are used to constrain the rates in the model and contribute to

the discussion (e.g. effects of pH and RH), then the discussion should be expanded to include the expected role of surfaces versus aerosols in the MBL or how the parameterization of aerosol photolysis encompasses all of these sources.

»> We agree, and have expanded this discussion as follows:

Changed (pg 9): "There have been a number of papers which have identified much faster photolysis of nitrate within and on aerosol, than for gas phase nitric acid (Baergen and Donaldson, 2013; Cohan et al., 2008; Handley et al., 2007; Ndour et al., 2009; Scharko et al., 2014; Ye et al., 2016a, 2016b; Zhou et al., 2003).

To: "There have been a number of studies that have identified much faster photolysis of nitrate within and on aerosol, than for gas phase nitric acid. These include studies using real-world natural and artificial surfaces (Baergen and Donaldson, 2013; Ye et al., 2016a), laboratory substrates such as organic films and aqueous acidic solutions (Handley et al., 2007; Scharko et al., 2014; Zhou et al., 2003), aerosol nitrate (Ndour et al., 2009; Ye et al., 2016b), and a model estimate (Cohan et al., 2008). "

"The product ratio appears dependent on aerosol pH (Scharko et al., 2014)" to "The product ratio appears dependent on aerosol pH, with HONO production occurring only at low pH (Scharko et al., 2014)."'

After "In order to explore the implications for Cape Verde NOx chemistry, we re-ran the base model removing the PAN source but including particulate nitrate (p-NO3) photolysis (R6) leading to HONO and NO2 production, scaled to the gas phase photolysis of HNO3." We have added "This parameterisation nominally represents photolysis of nitrate within and on aerosol, however conceptually includes any additional surface production of HONO and NO2." «<

3) The rapid photolysis of aerosol nitrate suggests that the lifetime of the reservoir may be quite short during the day (âĹ́ijhours, (Ye et al., 2016b)), but this may be dependent on the chosen photolysis rate. It would be worthwhile to discuss this and present the

diurnal trend from the model (or indicate that this term is held constant) to compare to these previous findings. Clarifying whether the aerosol nitrate photolysis mechanism can operate on the ambient aerosol observed without depleting it and discussing how the reservoir is maintained would improve the argument that this is a reasonable HONO and NOx source.

»> All model parameters are unconstrained, that is they are initialised at the stated values and allowed to reach equilibrium which occurs within 3 days of starting the model (with a 1 second step size). This is stated in the model description. Because nitrate is in large excess to the NOx formed, our model simulations show no significant depletion of the aerosol nitrate. We have added particulate nitrate to figure 10 (of model simulations of the diurnal behaviour of NOy) to demonstrate the conservation of particulate nitrate through the model simulations. «<

4) The (Crilley et al., 2016) manuscript only cites a (Heland et al., 2001) paper on the LOPAP, without any operational details on how such low detection limits were achieved for the instrument used in this work. The majority of the data in Figure 2 are below the stated LOD of the LOPAP (< 1pptv), suggesting that this data has an associated high uncertainty, which is not depicted. What is the exact LOD of the instrument and what data can be reliably reported in this figure? It would also be helpful to present the methods for calibration, background correction, and determining the precision and accuracy of the measurements, as those achieved here are non-trivial.

»> We have updated Section 2.2 to include more details on the operation of the LOPAP at Cape Verde. At CVO, the sampling conditions were set in order to maximise the sensitivity of the LOPAP, using a gas sampling flow rate of 2 lpm. A 2 point calibration was performed using a standard solution of nitrite (NO2-) at concentrations of 0.8 and 10 μg L-1. To account for instrument drift, baseline measurements using an overflow of high-purity N2 were performed at regular intervals (8 hours). The detection limit (2σ) of the LOPAP was calculated by the variability during a typical baseline measurement under N2 and was found to be 0.2 pptV. The relative error of the LOPAP was conservatively

set to 10% of the measured concentration.

We have included the details of how we performed the calibration, baseline corrections and calculation of the detection limit at Cape Verde, so that Section 2.2 now reads:

"Between 24th November and 3rd December 2015 a Long Path Absorption Photometer (LOPAP) (Heland et al., 2001) was employed at CVO to provide an in-situÂň measurement of nitrous acid. The LOPAP has its own thermostated inlet system with reactive HONO stripping to minimise losses so did not sample from the main lab manifold. The LOPAP inlet was installed on the roof of a container lab ∼ 2.5 m above ground level, unobstructed from the prevailing wind. Calibration and operation of the LOPAP was carried out in line with the standard procedures described by Kleffmann and Wiesen, (2008). Specifically at CVO, the sampling conditions were set in order to maximise the sensitivity of the LOPAP, using a gas sampling flow rate of 2 lpm. A two point calibration was performed using a standard solution of nitrite (NO2-) at concentrations of 0.8 and 10 μg L-1. To account for instrument drift, baseline measurements using an overflow of high-purity N2 were performed at regular intervals (8 hours). The detection limit of the LOPAP (2σ) was calculated by the variability during a typical baseline measurement under N2 and was found to be 0.2 pptV. The relative error of the LOPAP was conservatively set to 10% of the measured concentration."

In addition, with regards to Figure 2, in reviewing the data we noticed an error in the baseline corrections applied, with the updated figure shown below. From the new Figure 2, the majority of the data is now above the detection limit (0.2 pptV) for the LOPAP, and so will have the associated uncertainty previously stated (10%). The net effect is a small, but appreciable improvement in model/observation comparison. «<

5) The Authors focus their model on the 'summer season' (Page 5, Line 3) as this is the period of greatest data density from CVO. Is this dataset also filtered for clear-sky days to reduce comparison bias between the model and measurements? This season is most likely to be affected by cloudy days according to CVO observations reported in

(Carpenter et al., 2010). Also, the model compares to HONO measurements from the winter period, when ambient NOx measurements do not exhibit the same diurnal pattern (i.e. the mid-day maximum) that the majority of this manuscript seeks to explain. It would be useful to present why the authors expect that winter HONO mixing ratiosand diurnal structure are representative of summer HONO.

»> Data has not been filtered for cloud cover due to the rapid nature of the chemistry involved and the low time resolution (twice per day) cloud cover data provided by the Mindelo weather station which is ∼15 km away over hilly terrain. The average cloud cover for the summer period was 45%, consisting of predominantly broken cumulus clouds moving at speed. We focus on the summer season as it has the greatest data coverage and is out of the dust season which runs through winter and spring (Carpenter et al., 2010; Fomba et al., 2014). The period of HONO measurements occurs in a dust free period, while the majority of the winter NOx measurements are heavily influenced by dust which has a greater effect on photolysis rates and cloud cover. The more or less constant nitrate concentrations over the entire year and the relatively small seasonal changes in solar radiation at this tropical location (and in fact temperature, wind speed and direction etc) (Carpenter et al., 2010) lead us to believe that it is reasonable to expect HONO abundances and behaviour to be similar in winter and summer. A midday maximum in NOx is observed across all seasons at the CVO (although some data are noisier), so we have evidence that the process is occurring year-round. We have added greater explanation and detail to this effect. «<

6) Finally, how have the authors included or reasonably excluded boundary layer and transport dynamics in their 0D model? The report from (Carpenter et al., 2010) states that the limited information available in this regard indicates no diel modulation of the boundary layer height, but that it can change substantially from day to day at a site 200 km away. The work cited for DSMACC (Emmerson and Evans, 2009) does not suggest how the boundary layer is represented in the model and it could be that some of the mismatch in early morning and evening NOx levels is due to mixing and entrainment

or local transport phenomena instead of the model chemistry. It would be useful for the authors to discuss such processes as being accounted for, or as limitations, in the methods and at the appropriate points in the manuscript discussion (e.g. (Wolfe et al., 2016)).

»> The boundary layer is fixed in the DSMACC model at the average cloud base height as reported in Carpenter et al., (2010) which is expected to approximate boundary layer height. This is a reasonable approximation at a site receiving maritime air as the sea surface temperature doesn't change much over the course of a day due to the large thermal mass. This is in contrast to the study cited (Wolfe et al., 2016) by the reviewer which concentrates on measurements over land with large daily variability which does indeed result a mismatch between model and observation due to averaging. It is conceivable that very rapid mixing between a layer with halogens and a layer without halogens could result in the mismatch between model and observed NOx, however, a mechanism to remove the halogens as quickly as mixing occurred would also be needed. We agree with the reviewer that it would be useful to include this discussion – and have added the following to Section 2.3 describing the box model. "The meteorological parameters pressure, temperature, relative humidity, and boundary layer height are set to median values reported by Carpenter et al., (2010). Boundary layer height is fixed at 713m as no overall seasonal or diel pattern is evident in boundary layer height at Cape Verde (Carpenter et al., 2010). This is entirely expected at a site representative of the marine boundary layer, which has almost no island effects (except for very rare instances of wind outside the northwesterly sector, which are excluded). Thus – we discount any influence from boundary layer height changes on the diurnal cycles presented" «<

Technical corrections:

Page 1, Line 26: 'the box model simulation' of what? Everything?

»> "of NOx" added «<

Page 2, Line 3: provide a range of typical values for NOx observations in the remote MBL

»> Range added (10 to <100 pptV) with references. (Carsey et al., 1997; Lee et al., 2009; Monks et al., 1998) «<

Page 2, Lines 13-16: This is an example where the authors specify only particulate nitrate, yet cite work probing a variety of condensed phase nitrate proxies, ranging from surface-adsorbed nitrate to bulk aqueous solutions. The authors should be more specific here regarding the media and interfaces (e.g. particle-gas, surface-gas, aqueous gas) these works have described and that they have all found an enhancement in nitrate photolysis in the condensed phase although the mechanisms are not well understood.

»> Agreed, as with point 2 above we have clarified this section to be more specific about which surface/phase each study refers to. Changed to:

"However, more recently the possibility of 'renoxification' by rapid nitrate photolysis on a variety of surfaces has garnered attention. Photolytic rate enhancements have been reported on aerosol nitrate (Ndour et al., 2009; Ye et al., 2016b), urban grime (Baergen and Donaldson, 2013, 2016), natural and artificial surfaces (Ye et al., 2016a), and in laboratory prepared organic films and aqueous solutions (Handley et al., 2007; Scharko et al., 2014; Zhou et al., 2003)." «<

Page 2, Line 17: Delete 'through'

»> Done «<

Page 2, Lines 17-21: Specify that these reactions are all taking place in the gas phase.

»> Done «<

Page 3, Line 17: 'for a short period in Nov/Dec 2015' should be restated to the number of days in the winter of 2015, with the observational period explicitly given in the HONO

measurement section.

»> Done – the observational period was already explicitly given in the first line of the measurement section. "for 10 days in Winter 2015" added «<

Page 3, Line 23 - Page 4, Line 4: Is assessment of RH and O3 effects on NO sensitivity and NO2 converter efficiency at a period of 71 hours assuming that there is little change in sample RH and O3 over time or that the 1 hour offset in performing this calibration, spread over 2 years, corrects for these diurnal variations over the long term? Also, the measurements reported by (Lee et al., 2009) indicate that this period was 37 hours long. The authors describe in detail how RH of the sample flow is minimized, but do not present information as to the range or relative proportion of RH that sample flows are reduced to/by. O3 has a clear diurnal cycle presented throughout the manuscript, so it would be expected that corrections are necessary on an hourly timescale, not once every three days. While many other interferences are clearly detailed for the approach to correction in (Lee et al., 2009; Reed et al., 2016a, 2016b) this particular modification and approach could be more clearly demonstrated to have little variation, with an example of the variability that would be required to have significant systematic bias in the measurement due to RH and O3 changes within a 71 hour period. Also, the authors do not present any information about whether aerosols are removed from the sample flow, which could lead to artifact NOx signals in the system, similarly to other adsorbed species in the photolysis cell. A greater description of the main lab manifold at the beginning of this section would be sufficient to clarify.

»> A description of the lab manifold has been added, as well as including details of the sample filtration (0.22 micron filter) used.

"Air is sampled from a common 40 mm glass manifold (QVF) which draws ambient air from a height of 10m above ground level. The manifold is downward facing into the prevailing wind at the inlet and fitted with a hood. The manifold is shielded from sunlight outside, and thermostated within the lab to 30oC to prevent condensation. Air

is drawn down by centrifugal pump at $\sim$ 750 L/min-1 resulting in a sample flow speed of 10 m/s-1 and a residence time to the NOx instrument of 2.3 seconds. Humidity and aerosol are reduced by two dead-end traps at the lowest points of the manifold inside and outside the lab which are drained off regularly. Manifold sample flow, humidity and temperature are recorded and logged continuously. Air is sampled a 90o to the manifold flow through $\frac{1}{4}$ inch PFA tubing at 1 standard L per minute, being filtered through a 47mm, 0.22 μm mesh filter before entering the NOx analyser."

Regarding changing O3 biasing the converter efficiency, the high photolysis power converter reduces conversion efficiency by 0.013% per ppb O3. The seasonal range in this study is $\sim$ 11ppb ozone resulting in a 0.14% variation over the year, whereas the maximum daily variation in O3 reported by (Read et al., 2008) is 5 ppb, so 0.065% change in NO2 conversion efficiency due to ozone change. This is well within the accuracy of the overall measurement uncertainty.

Regarding sample drying and variability, the Rh% at Cape Verde can vary between $\sim$60 to 90% (Carpenter et al., 2010) which would have a dramatic effect on sensitivity through quenching of the chemiluminescent reaction and necessitate frequent calibration. The exact reduction in sample humidity that the Nafion dryer provides is unknown, only in so much that sensitivity drift is between calibrations is <2% between maintenance periods. This point has been added after the description of the Nafion dryer.

"The humidity of the sample gas is further reduced by a Nafion dryer (PD-50T-12-MKR, Permapure), fed by a constant sheath flow of zero air (PAG 003, Eco Physics AG) which is also filtered through a Sofnofil (Molecular Products) and activated carbon (Sigma Aldrich) trap. This reduces sample humidity variability which affected NO sensitivity through chemiluminescent quenching (Clough and Thrush, 1967) where sample humidity can vary from 60 to 90% (Carpenter et al., 2010). Calibration for NO sensitivity and NO2 converter efficiency occurs every 73 hours in ambient air as described by Lee et al., (2009); in this way correction for humidity affecting sensitivity, and O3 affect-

ing NO2 conversion efficiency are unnecessary. Sensitivity drift between calibration is <2%, within the overall uncertainty of the measurement."

A correction; NOx calibration was every 73 hours, rather than 71 as originally stated. Regarding the change from 37 hours (Lee et al., 2009), in that work the sample was not dried and the instrument sampled from an external inlet housing the NO2 and an NOy converter which were subject to heating during the day. For these reasons calibration was required more frequently. Later upgrades improved the stability greatly through better temperature control and gas handling requiring less frequent (lengthy) calibration. «<

Page 4, Line 15: Should 'period' be 'range'? 'being' should be 'are' and since much of this section is reporting data to two significant digits, shouldn't the detection limit for NO of 0.3 be 0.30?

»> Period is correct, LOD of NO has been corrected to 0.30. «<

Page 4, Line 21: The 'main lab manifold' is not described above. It would be very useful to have this presented above to know how external air is being delivered to the NOx instrumentation.

»> A description of the lab manifold, its flow rate, diameter, material etc has been added to the description of NO and NO2 measurements as per a previous point. «<

Page 4, Lines 25-26: Do the PM measurements at the site ever indicate the presence of nitrite? Given the prevalence of dust impacting the site, nitrite could be formed on these surfaces. The LOPAP has been shown to effectively sample large aerosols, such as fog droplets, and the authors state dust and sea salt as dominating the mass transport of condensed nitrate to CVO. This could bias the HONO measurement as LOPAP instrumentation does not typically exclude such coarse particles (e.g. (Sörgel et al., 2011)) and the dual-channel scrubbing coils used to quantify background and interference signals only effectively transmit particles less than 1 micrometer in diameter.

»> Neither the long term study of Fomba et al., (2014) nor the short term study of Muller et al., (2010) at the Cape Verde site report the presence of nitrite in aerosol. «<

Page 6, Line 6: should this sentence finish 'in the instrument inlet'? From (Reed et al., 2016a, 2016b) the thermal decomposition of PAN seems to occur in the photolysis cell?

»> No, the Lee et al., (2009) paper attributes the level of NOx to NOy species decomposing in the atmosphere. The word "atmospheric" has been added to clarify this. «<

Page 6, Lines 10-11: This sentence is describing nocturnal processes, yet photolysis and OH losses are listed. Please correct this error. Also, there is evidence in the presented data that the HONO buildup at night is still occurring (data below 0 pptV at 18:00, and above at 06:00) as would be expected, from the measured precursor NO2 being present at night and able to undergo heterogeneous hydrolysis. This may not be statistically significant, depending on the uncertainty in the HONO measurement, or the data may only be an estimate based on the exact instrument detection limits, so some clarification here should be given by considering those two limits. Previous work has also shown a rapid approach to steady state in nocturnal HONO in marineenvironments due to reversible thermodynamic partitioning in marine boundary layer surface waters, which is not mentioned here (Wojtal et al., 2011).

»> In response to the reviewers 4th point we have specified the measurement uncertainty and LOD for HONO. We have added discussion of the nocturnal steady state concentration of HONO with reference to the reviewers suggested reference. This paragraph now reads:

"Figure 2 shows the average diurnal cycle at CVO of measured HONO concentrations. The data exhibits a strong daytime maximum peaking at noon local time (Solar noon ~13:20) and reaching near zero at night, indicating a photolytic source. HONO is lost through deposition, photolysis and reaction with OH, whilst night time build-up often

observed (Ren et al., 2010; VandenBoer et al., 2014; Zhou et al., 2002), here HONO appears to reach a steady state concentration of ~0.65 pptV throughout the night. This pseudo steady state behaviour of nocturnal HONO has previously been reported in the polluted marine boundary layer by Wojtal et al., (2011), albeit reporting much higher HONO mixing ratios." »>

Page 6, Line 17: 'daytime' should be placed between 'additional' and 'source'

»> Added «<

Page 6, Lines 19-20: 'are difficult to explain' should be 'cannot be explained'

»> Corrected «<

Page 6, Line 21: 'either of NOx or HONO'. Shouldn't this be 'NOx and HONO'?

»> Corrected «<

Page 7, Lines 22-23: The authors should replace 'would appear' with 'is'. Also, it would seem that the intrusion of ship emissions, if stochastic, would be normalized from the mean through the consideration of 2 years of summer data. This is supported by therange versus the mean of the NOx data presented in many figures.

»> Agreed, change made. «<

Page 8, Lines 14-17: It would be expected that the aerosol nitrate would be distributed across both fine and coarse mode aerosol and photolyze differently based on their optical and chemical properties. The authors state in lines 26-28 that this is the case. It would be useful to clarify that the best match of nitrate photolysis enhancement that reproduces observed HONO is a rate integrated across all surface nitrate photolysis sources at CVO since only bulk aerosol composition has been measured in (Fomba et al., 2014).

»> Agreed. We have added in the paragraph immediately below on page 9 lines 4,5 that we parameterize all aerosol nitrate and aerosol surface area. The uptake of HNO3

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or XONO2 aerosol surface forms 'NIT' + some other species which is then photolysable at a single faster rate which is a multiple of the gas phase HNO3 jvalue.

"This parameterisation nominally represents photolysis of nitrate within and on aerosol, however conceptually includes any additional surface production of HONO and NO2." «<

Page 8, Lines 26-28: It is confusing why the authors cite the (Laufs and Kleffmann, 2016) work here as they state in the abstract of their work, a conclusion counter to the thesis of this work: 'If these results can be translated to atmospheric surfaces, HNO3 photolysis cannot explain the significant HONO levels in the daytime atmosphere. In addition, it is demonstrated that even the small measured yields of HONO did not result from the direct photolysis of HNO3 but rather from the consecutive heterogeneous conversion of the primary photolysis product NO2 on the humid surfaces. Thesecondary NO2 conversion was not photoenhanced on pure quartz glass surfaces in good agreement with former studies. A photolysis frequency for the primary reaction product NO2 of J(HNO3 - NO2) = 1.1x10^{-6} s^{-1} has been calculated (0 SZA, 50% r.h.), which indicates that renoxification by photolysis of adsorbed HNO3 on non-reactive surfaces is also a minor process in the atmosphere.' The work described by the cited works of (Baergen and Donaldson, 2013, 2016; Scharko et al., 2014; Ye et al., 2016a, 2016b; Zhou et al., 2003) are all in disagreement with (Laufs and Kleffmann, 2016) and the photolysis rates from these measurements are used to constrain this model. They also clearly discuss the wide range of photolysis values without such contradictory statements. The authors should consider revising the works cited in this location.

»> Agreed. Laufs and Kleffmann, (2016) was cited as a low end estimate of HNO3 photolysis frequency on surfaces, rather than for its overarching conclusion. The reference has been removed. «<

Page 9, Line 1: Figure 5 includes PAN transport. Remove the reference to it here.

Page 9, Lines 5-8: The ability to reproduce the NOx profile is based on a large loss

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of NO2 and production of NO, the former of which is not observationally consistent. Stating this and the need to explore further chemical mechanistic constraints would improve the transition to the next section of the manuscript.

»> Agreed, the following paragraph has been added immediately before section 3.3

"Introduction of an additional source of NOx is able to roughly produce a flat diurnal cycle, though is not able to simulate a definite peak of NOx during daytime. With the addition of a source and no change in sinks for NOx this is unsurprising and leads to over estimation of NOx. This is therefore likely that one or more NOx sinks are absent from the base simulation which must be explored further." «<

Page 9, Line 9: It would be useful to include some reference to halogen chemistry in this section header

»> A short introduction to halogen nitrate formation has been added.

"Aside from loss to HNO3 directly through reaction with OH (R1) NOx is also lost to nitrate by reaction with halogen oxides (XO) forming a halogen nitrates (R7) (Keene et al., 2009). Read et al., (2008) showed how halogen oxides mediate ozone formation and loss at Cape Verde thus their indirect effect on NOx. Their direct effect on NOx loss was included in studying NOx sinks. XO + NO2 + M → XONO2 + M (R7)" «<

Page 9, Line 12: '(NIT)' this is the only instance of this shorthand in the manuscript. Delete.

»> Done «<

Page 9, Lines 13-15: This would be much easier to follow if broken into 2-3 sentences.

»> Agreed, reworded for clarity «<

Page 10, Lines 5-6: Dust and sea salt are stated to be the 'predominant aerosol' at CVO. Is this by number, mass, or surface area? Please specify, with reference to (Carpenter et al., 2010; Fomba et al., 2014), so there is greater clarity in understanding

if the majority of the nitrate is expected to be in the coarse mode.

»> By mass, in coarse mode added with reference to Fomba et al., (2014) and Carpenter et al., (2010) «<

Page 10, Line 14: Delete 'e.g. JPL' and change the citation format to 'Burkholder et al., (2015)'

»> Done «<

Page 10, Lines 15-16: It would seem that the heterogeneous chemistry on fine mode aerosol may be what is poorly constrained. Would it be possible to speculate on this?

»> Indeed, as noted by Abbatt et al., (2012) uptake coefficients of many reactive uptake processes are very poorly constrained, in addition to gaps in our understanding of gas phase halogen chemistry highlighted by Simpson et al., (2015). «<

Page 10, Line 19: 'NO3' should be 'HNO3'. Also, is the static reactive uptake coefficient of 0.15 used in the model for HNO3 partitioning reasonable given the likely need for this value to increase mid-day to sustain the reservoir of particulate nitrate?

»> Corrected to HNO3. A static uptake coefficient is a reasonable assumption (without information to the contrary) in this case as nitrate is minimally depleted compared to the total amount during daytime as shown in response to a previous comment. «<

Page 12, Lines 8-9: This seems like a transition to an 'Atmospheric Implications' section

Page 12, Line 18: Update this to include the role of other surfaces.

»> This paragraph has been reworded to be less specific about aerosol nitrate and included other possible surface sources. "From these simulations it would appear that the photolysis of surface adsorbed nitrate may be the dominant source of NOx into the marine boundary layer around Cape Verde. Photolysis of aerosol nitrate, or nitrate in solution would be capable of producing a diurnal cycle in NOx which was consistent

with the observations when HOX + NO3 chemistry is considered also." «<

References: Chemical subscripts and capitalization issues need to be corrected in: Burkholder et al (2015), Evans and Jacob (2005), Handley et al (2007), Laufs and Kleffmann (2016), Li et al (2014), Moxim et al (1996), Nakamura et al (2003), Pollack et al (2011), Ryerson et al (2000), Saiz-Lopez et al (2008), Sander et al (1999), Scharko et al (2014), Ye et al (2016a), and Zhou et al (2003)

»> Corrected «<

Figure 1: Why is the NOx axis red, when the NOx trace is black? The color scheme here is generally not suitable for red-green color blind individuals and also does not print well in grayscale. Consider a scheme for figures, to use throughout, that is more easily discerned. Standard error is weighted by the number of samples considered, but those values are not presented anywhere. It would be worthwhile to do so, especially for the summer period. The rest of the manuscript only considers the summer observations. Thus, only 'summer' requires a definition of the months considered. Labels in the figure could just be the months considered and would remove the need to cross-reference.

»> The number or samples for the summer period was 153 for each hourly average data point. We have changed the colour of the NOx axis in this and all other figures to black and changed the figure labels to define the months in each season. «<

Figure 2: Add the cumulative accuracy and precision error and depict the instrument detection limit.

»> In reviewing the data we noticed an error in the baseline corrections applied which we have now corrected. From the new Figure 2, the majority of the data is now above the detection limit (0.2 pptV) for the LOPAP, and so will have the associated uncertainty previously stated (10%). The LOD has been indicated also. «<

Figure 3: (left) For all plots like this, would it be more informative to present the values

of the difference between the model and the measurement? The color and formatting challenges noted in Figure 1 apply here too. (right) The reaction text is difficult to read and the scale breaks are confusing. Would a log scale work and still emphasize the necessary rates?

»> Agreed, we have added, rather that substituted a panel showing the difference between model and measurement for NOx and HONO. Additionally, the ROPA panel has been changed to be friendlier to any colour-blind reader and the reaction text has been emboldened. «<

Figure 4: This figure could be simplified if the difference between NOx, NO2, and NO relative to the observations were depicted in three separate panels for the photolysis factors considered. It would also be a more quantitative representation of which factor is most suitable.

»> Agreed, the figure has been simplified into a single panned showing the difference between model and observation for NOx for the six different photolysis rates. (NO and NO2 disagree by the same factor given the same oxidant concentration). The original figure is moved to supplementary information. «<

Figure 6: Can the magnitude of the particulate nitrate photolysis be presented here? It would be nice to compare it to the other NOx source mechanisms. Also, it is surprising that HONO photolysis isn't presented as the manuscript suggests that its intermediate nature is key in reNOxification at CVO. (right) Same comments as Fig 3. (caption) Insert 'for NOx' after 'loss analysis'

»> The figure has been updated with new colours and bolder text. With regards to the reviewers first point the magnitude of nitrate photolysis (p-NO3 → NO2/HONO) is presented in the right panel and constitutes the top two major sources of NOx. We have now made this more clear in the text. «<

Figure 7: There is no PAN on this figure, but it is listed in the caption. The difference

notation, again, may be more informative for presenting the comparisons.

»> Agreed, the difference notation has been used to show model-observation disagreement for NOx, HONO, IO and BrO in place of the original figure which is moved to supplementary material. Reference to PAN has been removed. «<

Figure 8: Could the dips in the early morning NOx in the model be mismatching the observations because of NOx transport or dilution that isn't accounted for in the 0D model?

»> As in answer to the reviewers 6th point regarding boundary layer height and mixing in the 0-D model used: The boundary layer is fixed in the DSMACC model at the average cloud base height as reported in Carpenter et al., (2010) which is expected to approximate boundary layer height. This is a reasonable approximation at a site receiving maritime air as the sea surface temperature doesn't change much over the course of a day due to the large thermal mass. «<

Figure 11: What do the dashed lines represent?

»> Dashed lines represent HOx and OH the where dominant source of NOx is particulate nitrate photolysis and HOX + NO3 chemistry is included. The caption has been corrected indicating this. «<

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Fig. 1.

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