Reply to Reviewer Report 2

In the following the comments of the reviewer are presented (black) alongside with our replies (in blue) and changes made to the manuscript (in red).

General statement: The authors have a very interesting data set. I'm not familiar with the chemistry of this region but I assume there are few high quality NOx measurements and perhaps no radical measurements. Analysis is through the use of deviations from the Leighton photostationary state to get peroxy radical concentrations which are then used in conjunction with measured NO to obtain ozone production rates. Observed OH and HO2 are presented only via a color-coded ship track. As far as I can tell, the only use of the observed OH and HO2 is to determine loss rates of ozone which when added to the PSS ozone production rate yields a net ozone production rate. The ratio of HCHO to NOx (both observed quantities) is used as an indicator ratio to predict regions in which O3 production is either NOx or VOC sensitive.

Comparisons are made with a Eulerian model for NOx, ozone, and RO2 mixing ratios as well as for net O3 production rate. This article contains the quantum of information to warrant publication. I can only guess that either they want to write up the radical and HCHO measurements in a separate study or that they are uninterruptable for one reason or another.

I found the article difficult to follow in places. It is my belief that the authors have underestimated the uncertainty of the instruments used to determine peroxy radicals. The authors need to re-examine their error propagation formula. I am calling this a major revision as it affects the most prominent results in the paper. In practice it can be done in an afternoon. They could also compare the PSS value of RO2 with measured HO2 (which is stated to be preliminary due to an up to 20% interference by RO2). This is a reality test.
Dear reviewer, thank you very much for reviewing our manuscript and for the insightful comments. Below we provide detailed responses to your comments. Please note that PSS RO_2 has been compared to HO_2 in Sect. 3.2, P 21 L450.

Comment 1: line 124 "UV-induced positive bias in the NO2 measurements due to photolysis of HONO, BrONO2, NO3 and ClNO2 to produce NO was characterized ahead of the campaign to be 7.7 %, 7.2 %, 5.6 % and 1.5 % of the respective ambient concentration of HONO, BrONO2, NO3 and ClNO2 respectively,"
(Italics mine). No where in the paper is it mentioned that these species are measured. Have interferences been determined based on model-calculated or typical concentrations? Or do these figures represent the percent interference if the interferent has the same concentration as NO?
We have used absorption cross sections from the MPI-Mainz UV/VIS Spectral Atlas of Gaseous Molecules (Keller-Rudek et al., 2013) for the estimation of the parallel interference. The particular photolysis rate of NO_2 and the regarded NO_y-compound was calculated by (Eq. 1)

$$j = \int F(\lambda,T)\cdot\sigma(\lambda,T)\cdot\varphi(\lambda)\,\mathrm{d}\lambda, \qquad (1)$$

where $F(\lambda,T)$ is the spectral emission of the UV LEDs, $\sigma(\lambda,T)$ the absorption cross section and $\varphi(\lambda)$ the quantum yield. For the calculation of the photolysis rate of the particular NO_y-compound the respective quantum yield was conservatively estimated to be equal 1, yielding an upper limit for the interference. On Page 5, L 124 now it says: The UV-induced positive bias in the NO_2-measurement due to photolysis of HONO, $BrONO_2$, NO_3 and $ClNO_2$ to produce NO was estimated at 7.7 %, 7.2 %, 5.6 % and 1.5 %, respectively, based on the absorption cross sections from the MPI-Mainz UV/VIS Spectral Atlas of Gaseous Molecules (Keller-Rudek et al., 2013). These values represent upper limits for the interference of the respective NO_y compound as the respective molecular quantum yield was estimated conservatively at 1. Note that the values represent percent interferences if the interferent had the same concentration as NO_2. Due to small daytime concentrations of these molecules in the MBL, a UV-induced bias was neglected for the observations in this study.

Comment 2: line 181 NO2 was further measured by cavity ring-down spectroscopy (Sobanski et al., 2016) and used for correcting the instrumental background of the CLD NO2 data, as described above (the correction was taken as the ultimate absolute measurement uncertainty in the CLD NO2 data).

The uncertainty of the NO2 chemiluminescent measurement is not equal to that of the cavity ring-down instrument. The chemiluminescent NO2 is the difference between two measurements, one of which gets divided by 0.294 to take into account photolysis efficiency. In order to add errors in quadrature, I need to know the NO to NO2 ratio. I'm guessing that the relative uncertainty of NO2 will be at least twice that of NO. The NO2 chemiluminescent measurement is affected adversely by the relatively low photolysis efficiency. That accounts for random errors in NO2. Comparison with the cavity ringdown may take care of the NO2 instrumental background but how does it take care of the random errors?

Random errors are taken up by the calculation of a one-minute average before the instrumental background was estimated from the difference in the two NO_2 measurements. Note that random errors in the data are expected to be reduced as our final data analysis is based on a five minute average. NO_2 is calculated by

$$\mathrm{NO_2} = \frac{\mathrm{NO_c} - \mathrm{NO}}{K_e},$$

where NO_c is the signal of the channel equipped with the photolytic converter, NO the signal of the NO-channel and K_e the NO_2 conversion efficiency. We agree that the relative uncertainty in the NO_2 has to be estimated by means of the largest error possible from the relative uncertainties of NO (6 %), NO_c (6 %) and the conversion efficiency K_e (3 %) rather than only from the uncertainty of the NO_c-signal and the uncertainty of the conversion efficiency. The revised TMU for NO_2 follows as:

$$\Delta\mathrm{NO_2} = \sqrt{\Delta\mathrm{NO}^2 + \Delta\mathrm{NO_c^2} + \Delta K_e^2} = \sqrt{6\%^{\,2} + 6\%^{\,2} + 3\%^{\,2}} = 9\ \%.$$

We also agree that the absolute error of a single NO_2 data point might exceed 9 % when NO_2 is calculated from two high numbers (e.g. if we assume 100 ppb_v NO and 101 ppb_v NO_c, NO2 would be ~ 4 ppb_v), the error in NO_2 would be underestimated by 9 %. However the average and the median relative uncertainty of each data point of the campaign at 5 minute integration time are 13.6 % and 11.8 %, respectively, which is indeed slightly higher than the statistical estimate of 9 %. However the above average of 13.6 % yields a standard deviation of 6.9 %, which yields that both the average and the median relative uncertainty of NO_2 are significantly not different from the statistical estimate of 9 %. As we finally calculate median values for days and regions, it is more practicable to estimate a statistical error for the NO_2 measurement at 9 %. The manuscript has been explicitely revised on Page 7, L 162. Now it says: The TMU in NO_2 has been estimated by means of the largest error possible from error propagation at

$$\Delta\mathrm{NO_2} = \sqrt{\Delta\mathrm{NO}^2 + \Delta\mathrm{NO_c^2} + \Delta K_e^2} = \sqrt{6\%^{\,2} + 6\%^{\,2} + 3\%^{\,2}} = 9\ \%$$

at a confidence level of 1σ and an integration time of five minutes.

Also the TMU of NO_2 in Table 2 has been corrected to 9 %.

Line 205 Total Measurement Uncertainty. All of these numbers appear very optimistic. In a previous comment, I gave my reasons why the TMU of NO2 appeared low. I do not know why the TMU of HO2 is not larger than OH. There are many sources of uncertainty in the conversion of HO2 to OH which is the quantity actually measured. The authors state a 20% bias due to RO2 chemistry. I do not know to what extent quantification of HO2 is made easier than that of OH because there is more HO2 than OH and hence a larger signal.

The 1 sigma accuracy of OH is 20 % and the average precision is $3.4 \cdot 10^5$ molec cm^{-3}. The accuracy of HO_2 is 20 % and the largest uncertainty due to interference by contribution of RO_2 is 7 % or 3 ppt$_v$ whichever is higher. The average precision of HO_2 is 3 ppt$_v$. The uncertainty in OH is estimated as the 1 sigma accuracy whereas the uncertainty in HO_2 is estimated at $\sqrt{(20\,\%)^2 + (7\,\%)^2} \approx 21\,\%$. Note that HO_2 is calculated as the difference from two signals: HO_2 = (HO_2 + OH) – OH, whereas the signal (HO_2+OH) is about two order of magnitude larger than the signal from OH, which means that the uncertainty in OH can be neglected in the determination of the uncertainty in HO_2. On page 8, L 196-200 now it says: HO_2 data used in this study is still preliminary due to not yet corrected interference of organic peroxy radicals RO_2. The largest uncertainty due to interference by contribution of RO_2 is 7 % or 3 ppt$_v$, whichever is higher. The 1 sigma accuracy of both OH and HO_2 is 20 %. The uncertainty in the OH data is here estimated as the 1 sigma accuracy of the data set at 20 %, whereas the uncertainty in HO_2 is estimated at $\sqrt{(20\,\%)^2 + (7\,\%)^2} \approx 21\,\%$. The measurement uncertainty for HO_2 has been corrected to 21 % in Table 2.

Comment 3: Line 272 "In low NOx environments (< 100 pptv) previous studies have indicated that further NO oxidizing trace gases such as peroxy radicals (HO2, RO2) and halogen monoxides (XO) may result in a deviation from unity (Nakamura et al., 2003; Hosaynali Beygi et al., 2011; Reed et al., 2016)."

Deviations from the Leighton relation can also be important at higher NO. Departures of the Leighton ratio from unity depend (primarily) on the competition between HO2+NO and O3+NO. In polluted environments, HO2 concentrations can increase, remain steady, or decrease only slowly as NO is increased.

Several studies address deviations from the Leighton Ratio. However in high NO_x regimes gaps between measurement and estimate can be closed by incorporating higher oxidations (HO_2, halogen monoxides). However, in low NO_x regimes, even addressing these further oxidants does not close the gap between observation and estimate (see for instance Hosaynali Beygi et al., 2011). We have added the following sentence Page 10, L 245: Deviations from expected NO/NO_2-ratios at low NO_x generally refer to missing oxidants converting NO to NO_2 (Hosaynali Beygi et al., 2011; Reed et al., 2016) or to a measurement error due to an instrumental background or a positive interference from thermal labile NO_x reservoir species (Reed et al., 2016; Silvern et al., 2018).

Line 250 and following. Does Fig. S1 show the ratio of actinic flux in the 4 hour window centered around noon to the total measured actinic flux? Or is Fig. S1 a ratio obtained by fitting a Gaussian, between zeroes in the AM and PM?

You are right, Figure S1 shows the ratio of the actinic flux in the 4 hour window (centered to noon) to the total measured actinic flux of that particular day. The Gaussian Fit was only used to estimate noontime of each particular day. We have revised caption of Figure S1. Now the first sentence of the caption of supplementary Figure S1 says: Ratio of the noontime actinic flux (± 2h around noon) with regard to the total actinic flux $j(NO_2)$ of that particular day.

Comment 4: Lines 266-270, typos for O singlet D. Elsewhere, the "1" is in its proper place as a superscript.

Thank you for noticing. Now it says on Page 11, Line 276: $O(^1D) + H_2O \rightarrow 2OH$

Comment 5: Line 285. Am I correct that insofar as ozone production is concerned the only use of the HO2 and OH measurements is their contribution to the loss rate of ozone (and hence their effect on net ozone production)?

HO_x data have been used to calculate net ozone production rates, however HO_2 has also been used as a reality test: The peroxy radical estimate based on Eq. 3 was compared to measured HO_2 in Section 3.2 (Page 21, L 450).

Comment 6: Line 373. “We find that the median NOx(model)/NOx(measurement)-ratio throughout the whole campaign is 0.91, indicating that the model underestimates NOx by roughly 10 %.” The median of what? Could you please specify what items you are taking the median of; i.e., what are the data points. Ratios by Region? Days? Individual data points. I may have missed it; how long are data points? Equal to the 5 minute instrument averaging time?

The median NO_x(model)/NO_x(measurement) has been calculated as the median of five minute individual data points of the whole data set of the campaign. We have cleared out the misunderstanding in the text, now it says on Page 17, L395-396 following: We find that the median NO_x(model)/NO_x(measurement)-ratio of all five minute averaged data points of the whole campaign is 0.91, indicating that the model underestimates NO_x by roughly 10 %.

Comment 7: Line 391. “Noontime RO2 was estimated based on Eq. 3. As the steady state assumption will not hold for air masses originating from fresh emissions (times to acquire steady state estimated from the inverse sum of the loss and production terms for NO2 typically ranged from 1-2 minutes during AQABA) and for fast changes in the actinic flux,” What I think you want to say is mis-stated. As written, it says: We can’t use samples that had fresh emissions, so we used samples taken when actinic flux was slowly changing. Was the data screened to eliminate time periods in which NOx (or less likely O3) was rapidly varying? From the looks of the actinic flux plot you did not have many clouds giving rapid variations in jNO2. I would be surprised if the time window around noon could not have been wider. How much does jNO2 change between, say noon-3 hours and noon – 175 minutes and what change in HO2 does that produce?

Please note that before performing photochemistry calculation, the whole data set was filtered based on a stack filter which was established based on parameters such as wind direction, wind speed, variability in NO data, O_3, SO_2 (see Lines 209-211). However rapid changes in the actinic flux $j(NO_2)$ were observed e.g. after sunrise and before sunset. For ± 2h around noon the variation of the actinic flux (within the 4 hour period) was about 7 %, whereas the variation of the actinic flux within a 6-hour window (± 3h around noon) would be at least 20 % and assumptions that the actinic flux does not change within this time frame would not have been supportable. Differences in the actinic flux between noon-3 hours and noon-175 minutes would already be about 2 % of the maximum noontime value (and about the same change in HO_2). Differences in the actinic flux between noon-2 hours and noon–115 minutes would also be about 1-2 % of the maximum noontime value (slightly less than for 6 hours), but however expecting to decrease to zero towards noontime. Constant RO_2 and NOPR can be rather assumed for a 4-hour window around noon than for a 6-hour window around noon.

Comment 8: Figure 6. Obtaining peroxy radical concentrations from photostationary state calculations is not easy. Line 413 “the total uncertainty in the RO2 estimates is estimated at 14%. This is a way too optimistic estimate of the uncertainty of RO2. Instrument precision is too high and no account (except for NO2) is taken of biases. Even still, the PSS is a difference in two numbers, often of comparable magnitude. I’m not certain the error propagation was correctly performed. I would like to see the formula that represents “errors added in quadrature”. Compare those results with a simple Monte Carlo calculation that can be done on a spreadsheet. And keep in mind that the result will not take into account errors in rate constants.

We agree that obtaining RO_2 from PSS calculations is not trivial and very much depends on the errors of the used quantities. The TMU in RO_2 was estimated based on Gaussian error propagation by means of the estimate of the largest error possible. RO_2 is calculated by

$$[\mathrm{RO_2}] = \frac{j(\mathrm{NO_2})\cdot[\mathrm{NO_2}] - k_{\mathrm{NO+O_3}}\cdot[\mathrm{NO}][\mathrm{O_3}]}{k_{\mathrm{NO+HO_2}}\cdot[\mathrm{NO}]}.$$

The relative uncertainty in the RO_2 data has to be calculated from the relative uncertainty of NO, NO_2, O_3 and $j(NO_2)$ at roughly 6 %, 9 % (instead of 7 %), 2 % and 10 %, respectively, which yields a relative uncertainty of 15 % for RO_2.

$$\Delta RO_2 = \sqrt{\Delta NO^2 + \Delta NO_2^2 + \Delta O_3^2 + \Delta j(NO_2)^2} = \sqrt{6\%^{\,2} + 9\%^{\,2} + 2\%^{\,2} + 10\%^{\,2}} \approx 15\ \%$$

The relative uncertainty in RO_2 has been revised in the manuscript, now it says on Page 20 line 434-437: Based on the total measurement uncertainties of the measured quantities in Eq. 3, the uncertainty in RO_2 is estimated by means of the largest error possible at 15 %.

$$\Delta RO_2 = \sqrt{\Delta NO^2 + \Delta NO_2^2 + \Delta O_3^2 + \Delta j(NO_2)^2} = \sqrt{6\%^{\,2} + 9\%^{\,2} + 2\%^{\,2} + 10\%^{\,2}} \approx 15\ \% \qquad (9)$$

Note that our calculation assumes that errors in the used rate coefficients are negligible.

Comment 9: Line 416. "Negative values for all regions are regularly found in the vicinity of fresh emissions and air masses not in photochemical equilibrium" That might be the explanation. It would useful to quantify this point. HO2 and RO2 concentrations will be low in a high NOx environment. The negative values may reflect the measurement accuracy needed to distinguish, for example, – 5 ppt RO2 from zero.

Note that the uncertainty of the best estimates of RO_2 for each day/each region is estimated at 15 %. A reason why negative values were regularly found in the vicinity of fresh emissions is that the assumption of photostationary steady state (PSS) might not be fulfilled for fresh emissions. Time to acquire PSS was estimated as the inverse sum of the loss and production terms of NO_2 and was of the order of 1-2 minutes during AQABA, depending on the particular conditions (temperature, radiation, ozone concentration). The assumption that the regarded air masses were in PSS might not be true in the vicinity of fresh emissions (with transport time from source to instrument of less than 2 minutes). For these air masses production of NO_2 (oxidation of NO) prevailed over photolysis of NO_2 leading to $j(NO_2) \cdot [NO_2] - k_{NO+O_3} \cdot [NO][O_3] < 0$. Negative values might hence simply reflect that the regarded air mass has not reached PSS.

Comment 10: Figure 7. Here the RO2 data looks much better. There are differences mentioned in the text. but for this reader could you please provide a concise reason why Fig. 7. looks so much better than Fig. 6. Is it the data groupings? I assume that in both Fig. 6 and 7. the blue RO2 data is from Eq. 3. I am not totally positive because you were measuring HO2 and some fraction of RO2.

Figure 7 has been processed based on five minute data points in each region whereas Figure 6 has been processed for single days which might be more biased by single data outliers. Grouping into regions rather than for single days allows for a statistically more established estimate.

Comment 11: Line 421. As peroxy radicals are short-lived molecules generated from the oxidation of VOCs, enhanced RO2 concentrations observed over the Arabian Gulf are most likely due to high VOC observed over the Arabian Gulf are most likely due to high VOC emissions from intense oil and gas activities in the region. High HO2 can also occur in aged air masses in which NOx and VOCs have reacted away but still have significant O3 and (perhaps) HCHO. Photolysis could then yield peroxy radicals.

We have added the comment to the manuscript on Page 21, L. 447,448. However high HO_2 and RO_2 can also occur in aged air massed with low NO_x and VOCs but still significant O_3 (and perhaps HCHO whose photolysis would then yield peroxy radicals).

Comment 12: Line 440. Regarding the extrapolated actinic flux curve to get a daily ozone production. j(1OD) decreases early and late in the day faster than J(NO2). Not sure how much difference it makes. I would be very leery of this extrapolation over land; I'm assuming that you are far enough away that varying traffic and boundary layer heights are not a concern.
Except for $j(O^1D)*\alpha*[O_3]$ all other terms will scale with $j(NO_2)$. However errors due to a different diurnal profiles of $j(O^1D)$ will remain insignificant with respect to the relative uncertainty of NOPR, as NOPR are mainly determined by $k*[NO]*[RO_2]$ and loss reactions due to OH and HO_2.

Comment 13: Line 455 "the uncertainty of the regional NOPR is 40 % which has been estimated by error propagation" I don't disagree with this value. Merely surprised at its magnitude compared to a 15% uncertainty for RO2 from Eq. 3.
The uncertainty in NOPR was estimated by means of the largest error possible and is mainly driven by the high uncertainty in OH and HO_2 (each 20 %) and by the uncertainty in RO_2 (15 %). Diurnal net ozone production rates were estimated by scaling the median hourly noontime value to a diurnal value (by multiplying by the hourly value by 4 due to a 4-hour window around noon and by further dividing by 0.461 (noontime fraction (± 2h) of jNO_2). Strictly speaking, the relative uncertainty (6 %) in the division by 0.461, referred to as Δs (see Supplements Figure 1), also needs to be accounted for when estimating the uncertainty in NOPR. Also the error in α (Eq. 5) is rather determined by the error in H_2O (5 %) than from its relative variation over the campaign (relative variation ~ 21 %). This yields a measuremrent uncertainty for NOPR of

$$\Delta\mathrm{NOPR} = \sqrt{\Delta\mathrm{NO}^2 + \Delta\mathrm{NO}_2^2 + \Delta\mathrm{O}_3^2 + \Delta j(\mathrm{NO}_2)^2 + \Delta j(\mathrm{O}^1\mathrm{D})^2 + \Delta\alpha^2 + \Delta\mathrm{RO}_2^2 + \Delta\mathrm{OH}^2 + \Delta\mathrm{HO}_2^2 + \Delta s^2}$$
$$= \sqrt{6\%^2 + 9\%^2 + 2\%^2 + 10\%^2 + 10\%^2 + 5\%^2 + 15\%^2 + 20\%^2 + 20\%^2 + 6\%^2} \approx 38\,\%.$$

We have corrected the error in NOPR from 40 % to 38 % in the manuscript and specified error calculation in detail also for NOPR in the manuscript.

On Page 12, L281 now it says: The error in α is mainly determined by the error of H_2O at 5 %.
On Page 21, L463 now it says: These noontime values are scaled to diurnal production rates (Figure 8). As photochemical net ozone production is in good approximation linear with actinic flux $j(NO_2)$ and as on average (46.1 ± 2.8) % of the total $j(NO_2)$ occurred ± 2h around noon, the median noontime NOPR estimate was multiplied by 4/0.461 ≈ 8.68 to obtain a diurnal value. The error in the total actinic flux located ± 2h around noon is estimated from the standard deviation of the best estimate of 0.461 at $\Delta s \approx 6$ %.
On Page 23, L 455 now it says: Based on the total measurement uncertainties of the measured quantities in Eq. 3, the systematic error in NOPR is estimated from error propagation by means of the largest error possible at 38 %.

$$\Delta\mathrm{NOPR} = \sqrt{\Delta\mathrm{NO}^2 + \Delta\mathrm{NO}_2^2 + \Delta\mathrm{O}_3^2 + \Delta j(\mathrm{NO}_2)^2 + \Delta j(\mathrm{O}^1\mathrm{D})^2 + \Delta\alpha^2 + \Delta\mathrm{RO}_2^2 + \Delta\mathrm{OH}^2 + \Delta\mathrm{HO}_2^2 + \Delta s^2}$$
$$= \sqrt{6\%^2 + 9\%^2 + 2\%^2 + 10\%^2 + 10\%^2 + 5\%^2 + 15\%^2 + 20\%^2 + 21\%^2 + 6\%^2} \approx 38\,\%.$$

Comment 14: Line 473. "Although EMAC predicts high ozone levels over the Arabian Sea, it also reports the lowest NOPR in this region. Deviations between model-calculated estimate and the estimate based on measured tracer data over the Mediterranean and over the Southern Red Sea could be linked to NOx being overestimated in the model in these regions." I'm not following. There is a low net ozone production rate. which to me implies that the model has a too low NO concentration, but you say that the model overpredicts NOx.
As demonstrated in Figure 4, the model overpredicts the NO_x measurement over the Mediterranean and the Southern Red Sea. As these regions are classified as rather NO_x

sensitive regimes (see Figure 10), higher NO_x (in the model) will likewise imply higher NOPR (under stagnant chemistry, i.e. NO_x sensitivity). The text is not fully clear and will be rewritten on P. 23 L502-505 as: Although EMAC predicts high ozone levels over the Arabian Sea, it also reports the lowest NOPR in this region. On the other side, the large overestimation of the model-calculated estimate NOPR against the one based on measured tracer data over the Mediterranean and over the Southern Red Sea could be linked to NO_x being overestimated in these regions.

Comment 15: Section 3.4 VOC and NOx sensitivity. Makes sense.
We have changed the title of chapter 3.4 to VOC- and NO_x-sensitivity.