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Interactive comment on "Net ozone production and its relationship to NO$_x$ and VOCs in the marine boundary layer around the Arabian Peninsula" *by* Ivan Tadic et al.

Anonymous Referee #2

Received and published: 14 February 2020

Review of "Net ozone production and its relationship to NOy and VOCs in the marine boundary layer around the Arabian Peninsula" by Tadic et al

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.

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 ben 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?

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 ring-down may take care of the NO2 instrumental background but how does it take care of the random errors?

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.

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.

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?

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

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)?

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?

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?

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.

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.

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.

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.

12. Line 440. Regarding the extrapolated actinic flux curve to get a daily ozone pro-

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duction. 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.

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. . 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.

15. Section 3.4 VOC and NOx sensitivity. Makes sense.

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