Atmos. Chem. Phys. Discuss.,
https://doi.org/10.5194/acp-2019-1031-RC1, 2020

Atmospheric Chemistry and Physics Discussions

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 #1

Received and published: 30 January 2020

The authors present an analysis of net O3 production calculated from ship-borne trace gas measurements obtained during the AQABA campaign, mostly in July and August 2017. In the Oman Gulf, the Northern Red Sea, and the Arabian Gulf the authors found the highest values ranging from 14 ppb day-1 to 28 ppb day-1. Based on HCHO/NO2 ratios, in most areas O3 formation was NOx limited apart from the Northern Red Sea, which was located in the VOC-NOx limitation transition zone. The Arabian Sea and Arabian Gulf areas showed maximum HCHO/NO2 values, clearly indicating NOx limitation. This paper shows some interesting data from an area, which often lacks robust air quality data, but which is also an area with significant (and increasing) anthropogenic emissions, mostly related to oil and gas exploration. The paper is well-written and

deserves publication. However, I was hoping the authors could address some of my concerns.

Page 1 L22-24: According to Fig 10 net O3 formation actually mostly occurs in NOx limitation regimes, not in the transition regime, as the authors mention here. Also, it seems Fig 10 does not support the findings by Pfannerstill et al. (2019) as stated by the authors on page 25 (L509-511). All, but one median, is above the threshold of HCHO/NO2 > 2. I also doubt that a HCHO/NO2 median of 2.2 (for OG) would signify a tendency towards VOC limitation (L511-512).

Page 3, L58-59: The reference Zhou et al (2014) shows up a couple of times in this paper. While I agree that it makes sense to compare the authors' Middle East study area with the Houston area (e.g. some similar emissions; similar latitude) there are better publications for the Houston case which include direct measurements of OH, HO2, and also O3 production itself among many other measurements (e.g. Chen et al., 2010; Mao et al, 2010; Ren et al. 2013). Also, I doubt that the term marine environment shows up in Zhou et al.

Page 3, L80-86: This explanation is confusing. It seems there is a main sampling inlet (not sure what instruments were connected), but for HCHO and NOx sampling was done via a 1/2" PFA tubing (not sure how long the tube was), and for the other trace gas measurements (what were those?) it was done in a different way. May be a chart showing the experimental design would be helpful.

Page 6, L144: What was the flow of the calibration gas into the zero air?

Page 6, L157: What do the authors mean by "notably high"?

Page 11, L259: I guess the authors mean Lu et al. (2010) here.

Page 12, L276-277: The loss mechanism through H2O is important. Also, it seems to vary a lot. Some parts of the ship cruising legs might have already been exposed high humidity due to the Indian monsoon system. It would be good to see the absolute

humidity variation along the legs similar to Figs 3 and S4.

Page 12, L281-282: At least, the authors want to include an estimate for the potential contribution of halogens.

Page 12, Eq. 7 and Fig 9: It would be nice to see a break-down of the different terms in Eq. 7 for different legs as shown in Fig. 9 to evaluate what processes might be most relevant/different in those different legs.

Page 13, L310: Authors mention NOx values of several hundred ppbs. Where do they show up in Figs. 3, S2, and S3? What were the megacities along the cruising legs? I could think about Cairo, but according to Fig 3 NOx values do not show extremely high values.

Page 13, L311-312: During the first leg very high O3 values are found in the Arabian Gulf and potentially in the area of the Suez Canal. In the second leg those high O3 values are pretty much gone. I doubt emissions have changed. I also doubt that weather conditions have changed drastically. What were the reasons for those distinct changes?

Page 16, L334-355: This section should include some more explanations: it seems there is a huge variation in NOx and O3 in AG (also a huge variation in NOPR as shown in Fig 9). What is the major driver of this: point sources from ships? Why are the highest NOx values in OG and why are some of the lowest O3 values found in OG? Why would you consider air masses over the Mediterranean as photochemically aged air masses due to the small whisker-interval, while the whisker-plots for AS and OG show pretty much the same with, but at much lower absolute O3 ranges. There are no emission sources in that area of the Mediterranean?

Page 17, L367: As I understand it Velchev et al. (2011) show O3 data from the Western Mediterranean. A reference looking closer to the area the authors studied would be Kouvarakis et al (2002).

Page 17, L369: Edwards et al. (2014) is not a good reference here. Edwards et al report wintertime O3 in cold-pool conditions, i.e. extremely low boundary layer heights. The meteorological conditions reported in Edwards et al are pretty different from the ones observed in the Middle East during summertime. Also, there is no word on the impact of narrow shipping lanes in Kleinman et al (2005) and Zhou et al (2014). O3 in Houston is predominantly driven by emissions from all kinds of petrochemical industries (including refineries, but no oil exploration) located in the Ship Channel area.

Page 25, L516-517: Actually, Figure 10 shows that in almost all areas O3 formation is NOx limited. However, the authors say that this is typical for photochemically aged air masses over the Mediterranean. As already mentioned further above, why do the authors explicitly consider the Mediterranean area having aged air masses? It is even more surprising as the results for the Mediterranean area in Figure 10 indicate that the Box-Whisker plot stretches into the transition between NOx and VOC limitation.

Page 25. L517-519: Why would higher NOx lead to higher O3 pollution? For instance, according to Figure 4, OG has the highest NOx values, but also pretty low O3 values. With regard to NOPR, the Box-Whisker plot for OG shows positive, but also large negative values. In any case NOPR values are significantly lower than for AG, for instance.

Table 1: This table can go into the supplement.

Figure 7: The legend mentions "Measurements", the figure captions says "estimated". From Eq 3 I understand that RO2 was neither measured nor estimated, but calculated. Also, what would be the interpretation of the negative RO2 concentrations (blue Box-Whisker plots) when calculated from Eq 3?

Figures S2 and S3: It would be nice to see the time series of OH and HO2 here as well

References:

Chen et al (2010): A comparison of chemical mechanisms based on TRAMP-2006 field data, Atmos. Environ., 44, 4116-4125, doi:10.1016/j.atmosenv.2009.05.027

Kouvarakis et al (2002): Spatial and temporal variability of tropospheric ozone (O3) in the boundary layer above the Aegean Sea (Eastern Mediterranean), J. Geophys. Res., 107, 8173, 10.1029/2000JD000081

Mao et al (2010): Atmospheric Oxidation Capacity in the Summer of Houston 2006: Comparison with Summer Measurements in other Metropolitan Studies, Atmos. Environ., 44, 4107-4115, doi:10.1016/j.atmosenv.2009.01.013

Ren et al (2013): Atmospheric Oxidation Chemistry and Ozone Production: Results from SHARP 2009 in Houston, Texas, J. Geophys. Res., 118, 5770-5780, doi:10.1002/jgrd.50342

Interactive comment on Atmos. Chem. Phys. Discuss., https://doi.org/10.5194/acp-2019-1031, 2019.