Reply to Reviewer Report 1

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 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.

Dear reviewer, thank you very much for reviewing our manuscript and for the insightful comments. Below we provide detailed responses to your comments. Please find revised graphs at the end of the document, which were compiled based on your comments.

Comment 1: 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).

Indeed a median HCHO/NO_2-ratio of 2.2 does not fall within plain VOC limitation as deduced by Duncan et al. (2010), which needs to be re-written. Although Pfannerstill et al. (2019) highlight the scatter in the attribution of ozone production to NO_x- and VOC-limitation, their study shows that ozone production over the Arabian Sea over the Arabian Gulf is rather NO_x-limited, whereas the Gulf of Suez is characterized by a strong VOC-limitation (page 11516 and page 11517, Figure 9 [Pfannerstill et al., 2019]). We have revised Page 1 L21-25 to: Constrained by HCHO/NO_2-ratios, our photochemistry calculations show that net ozone production in the MBL around the Arabian Peninsula occurs mostly in NO_x-limitation regimes with a significant share of ozone production occurring in the tranisition regime between NO_x- and VOC-limitation over the Mediterranean and more significantly over the Northern Red Sea and Oman Gulf.

Comment 2: 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.

We have removed the term "marine environment" in the context of Zhou et al. (2014) (also on P23 L 473) and we have revised the manusript as suggested on Page 3, L58,59 to: Measurements performed in the Houston Ship Channel revealed NOPR of the order of several tens of ppb h^{-1} (Chen et al., 2010; Mao et al., 2010; Ren et al., 2013).

Comment 3: 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.
Please note that air was drawn from the stainless steel common inlet into each measurement container via bypass systems. NO_x (CLD measurements) and HCHO measurements were located in one lab container (both sampling air from the same bypass) and NO_2 (CRDS measurements) and O_3 in another lab container. We have revised Page 3, L82-86 to: A 6 m high, 20 cm diameter cylindrical stainless steel common inlet was installed on the front deck of the vessel to sample air at a total mass flow rate of 10,000 SLM. NO and NO_2 chemiluminescence measurements were obtained at a total bypass flow rate of 28.5 SLM sampling air from the common inlet with a residence time in the tubing of ~3 s. HCHO, NO_2 cavity ring-down spectroscopy and O_3 measurements were obtained with similar bypass systems sampling air from the common inlet. H_2O vapor was measured on the top of the ship mast in the front.

Comment 4: Page 6, L144: What was the flow of the calibration gas into the zero air?
The NO calibration flow into the zero air was 4.5 sccm. We have revised the manuscript. Now it says on Page 6, L 143-145: Zero air measurements and NO calibrations were performed with a total mass flow of 3.44 SLM achieving an overflow of 0.44 SLM to guarantee ambient air free standard measurements. The calibration gas was added at 4.5 sccm to the zero air flow.

Comment 5: Page 6, L157: What do the authors mean by "notably high"?
Alkenes can react with ozone to produce a chemiluminescent signal which will bias NO measurement obtained by chemiluminescence. To subtract such interferences, the CLD has been equipped with a prechamber to which the sampled air can be directed during prechamber measurements. As the reaction of ozone with alkenes will be much slower than the reaction of NO and with ozone, the CLD will be measuring only the signal from the reaction of alkenes during prechamber measurements. It should be noted that the signal from the reaction of alkenes with ozone observed during a prechamber measurement will also slightly decrease. Regions where alkenes are strongly varying in time and magnitude might be plagued by a measurement offset. We have revised Page 6, L152f: However, in regions where alkene concentrations are strongly varying in time and magnitude, the CLD is prone to enhanced backgrounds due to the interference of alkenes with ozone in the instrument.

Comment 6: Page 11, L259: I guess the authors mean Lu et al. (2010) here.
Thank you very much for noticing this typo. Now it says Lu et al. (2010) instead of Lu et al. (2016) on page 11, L259.

Comment 7: 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.
Figures showing the absolute variation along both legs have been added to the supplement. On P13 L336 now it says: Supplementary Figure S5 shows the variation of the absolute humidity around the Arabian Peninsula.

Comment 8: Page 12, L281-282: At least, the authors want to include an estimate for the potential contribution of halogens.
Based on oxidative pairs, Bourtsoukidis et al. found that the majority of the samples they collected during AQABA were characterized by a OH/Cl-ratio of ~ 200:1 (Bourtsoukidis et al., 2019, Non-methane hydrocarbon (C_2-C_8) sources and sinks around the Arabian Peninsula,

doi:10.5194/acp-19-7209-2019). Measured daytime OH concentrations were of the order of $5 \cdot 10^6$ molec cm^{-3}, hence the Cl radical concentration can be estimated at $2.5 \cdot 10^4$ molec cm^{-3}. Incorporating an ozone loss due to the reaction of O_3 with Cl (at Cl concentrations of $2.5 \cdot 10^4$ molec cm^{-3}) into the NOPR (Eq. 7) would decrease the diurnal net ozone production rates by roughly 0.2 ppb_v day^{-1} over the Arabian Sea and at most 0.6 ppb_v day^{-1} over the other regions. We have revised the manuscript as follows on page 12, L292-297: Based on oxidative pairs, Bourtsoukidis et al. (2019) have classified the majority of their samples collected during AQABA by an OH/Cl-ratio of 200:1. As measured daytime OH concentrations were of the order of $5 \cdot 10^6$ molecule cm^{-3}, the estimate would yield a Cl concentration of $2.5 \cdot 10^4$ molecule cm^{-3}, which would decrease the estimated diurnal net ozone production rates by roughly 0.2 ppb_v day^{-1} over the Arabian Sea and at most 0.6 ppb_v day^{-1} over the other regions, which does not substantially alter the here presented findings. The noontime chemical ozone loss rate can be summarized by

Comment 9: 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.
We have included regional box-whisker plots (according to Figure 9) of the four terms of Eq. 7 in the supplements. We have revised the manuscript on Page 21, L444: A break-down of the different terms of Eq. 7 in the six regions is included in the supplementary Figures S10 – S13.

Comment 10: 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.
Values of up to several hundred of ppb_v NO_x were observed when measuring own ship stack, stack of bypassing ships or when being at anchor in the direct vicinity of Jeddah or Kuwait City. Data measured during these time periods have been removed from the final data set as contamination by the ship exhaust itself could not be excluded for these period. Megacities along the cruising legs generally include Cairo, Kuwait City, megacities in the UAE and Jeddah (Saudi Arabia).

Comment 11: 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?
Based on back trajectories, previous studies (Pfannerstill et al., 2019) also already highlighted different air mass origins during the two legs for the air sampled e.g. over the Arabian Gulf. While during the first leg northwestern wind from Kuwait/Iraq was encountered, northeastern winds from Iran were encountered during the second leg over the Arabian Gulf. For the area of Suez, data coverage during the first leg (due to instrumental mal function and applied stack filter) is not as exhaustive as during the second leg. We would classify these changes of concentrations in the Suez region as insignificant (see also Figure S2 and the data coverage for the Suez region before July 06th 2017). We have revised the manuscript on Page 16, L360-363 as follows: However, a significantly larger whisker-interval of observed ozone of 31.4 ppb_v over the Gulf of Oman indicates increasing amounts of pollution and advection from the Arabian Gulf where extreme events of ozone were observed several times during the campaign with maximum mixing ratios of up to 170 ppb_v when wind was coming from Kuwait/Iraq. Please note that during the second leg wind was coming from Iran (Pfannerstill et al., 2019).

Comment 12: 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?

Reasons for large variations of NO_x and O_3 over the AG are point sources (ship, oil and gas processing) as well as a change in the general wind direction observed during both legs. NO_x are high over the OG due to the magnitude of emissions from vessels. O_3 is generally very low over the OG because it has been partly characterized as VOC-limited and high NO_x values may contribute to net ozone destruction. Air over the Mediterranean has previously been characterized as photochemically processed emissions from Eastern Europe (Turkey, Greece) (Destroff et al., 2017; Pfannerstill et al., 2019). We have included Destroff et al., "Volatile organic compounds (VOCs) in photochemically aged air from the eastern and western Mediterranean, 2017, doi:10.5194/acp-17-9547-2017 as a reference. Page 16, L356-372 following now say (please note that only the underlined sentences have been changed): **The low O_3 mixing ratios over the Arabian Sea was accompanied by the smallest variability (whisker-interval: 15.1 ppb_v). Although observing highest NO_x over the Oman Gulf, O_3 observed over the Oman Gulf was amongst the lowest detected throughout the whole campaign, which can be partly explained by the fact that high NO_x lead to low ozone production or even net ozone destruction. However, a significantly larger whisker-interval of observed ozone of 31.4 ppb_v over the Gulf of Oman indicates increasing amounts of pollution and advection from the Arabian Gulf where extreme events of ozone were observed several times during the campaign with maximum mixing ratios of up to 170 ppb_v when wind was coming from Kuwait/Iraq. Please note that during the second leg wind was coming from Iran (Pfannerstill et al., 2019).** The whisker-interval over the Arabian Gulf was 100.9 ppb_v, more than six times higher than that over the Arabian Sea. **Reasons for large variations of both NO_x and O_3 over the Arabian Gulf were a multitude of point sources as well as a change in the observed wind direction with air masses coming from Iraq/Kuwait area during the first leg and air masses coming from Iran during the second leg (Pfannerstill et al., 2019).** Over the Mediterranean, the Northern Red Sea and the Southern Red Sea, median ozone was 61.5 ppb_v, 64.2 ppb_v and 46.9 ppb_v, respectively. The whisker-interval over the Northern Red Sea and the Southern Red Sea were 44.2 ppb_v and 31.6 ppb_v, respectively. **Air masses over the Mediterranean were characterized as photochemically aged due to their impact by northerly winds (Etesians) which bring processed/oxidated air from eastern Europe (Turkey, Greece) to the Mediterranean area (Derstroff et al., 2017; Pfannerstill et al., 2019). This photochemical ageing/oxidation over the Mediterranean leads to a rather small whisker-interval of 18.7 ppb_v in ozone.**

Comment 13: 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).

We have now replaced (Velchev et al., 2011) by (Kouvarakis et al., 2002) on page 17, L391.

Comment 14: 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.

We agree that Edwards et al., 2014 is not the best reference in here, which has been removed in this context. Also Kleinman et al. (2005) and Zhou et al. (2014) have been removed in the

context of shipping lanes. Instead we have included Mazzuca et al., 2016 “Ozone production and its sensitivity to NO_x and VOCs: results from the DISCOVER-AQ field experiment, Houston 2013“, doi:10.5194/acp-16-14463-2016. On page 17, L392 now it says: The latter are consistent with O_3 mixing ratios reported from regions influenced by oil and gas processing (Pfannerstill et al., 2019) and shipping lanes such as the Houston Ship Channel (Mazzuca et al., 2016).

Comment 15: 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.
The Mediterranean area is considered having aged air masses as it is impacted by processed emissions from eastern Europe (Destroff et al., 2017; Pfannerstill et al., 2019). We have removed the statement that photochemical ageing of air masses over the Mediterranean leads to NO_x-limitation, however it should be noted that on August 29th 2017 we were lying at anchor in front of Malta with a magnitude of pollution sources nearby. This day is characterized by a low HCHO/NO2-ratio and explains why the Box-Whisker-Plot for the Mediterranean stretches into the transition between NOx- and VOC-limitation. Page 25, L544 now says: Ozone production over the Mediterranean was classified as rather NO_x-limited, however partly being in the transition regime between NO_x- and VOC-limitation, which can be explained by measurements obtained on 29 August 2017 when laying at anchor in front of Malta with a multitude of (NO_x)-emissions from nearby situated vessels. Average noontime NO_x on that particular day was about three times as large as the regional average noontime NO_x observed over the whole Mediterranean area.

Comment 16: 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.
Indeed, the passage needs more characterization. We have re-written the passage. Now it says on P25 L549: Note that a further increase in NO_x-emissions from increased shipping in the Arabian Gulf may initially lead to higher ozone production. However, a further increase in NO_x might eventually lead to a change from NO_x- to VOC-sensitivity and a decrease in ozone production for this region, as observed for the Oman Gulf (median $HCHO/NO_2$-ratio of 2.2 and average O_3 of 34 ppb_v). See supplementary Table ST9 for detailed statistics on regional $HCHO/NO_2$-ratios.

Comment 17: Table 1: This table can go into the supplement.
We have moved the table into the supplement and numbered the tables in the manuscript and supplement accordingly.

Comment 18: 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?
The legends (Figure 7) now says Estimated based on measured data and EMAC. Also the legend for Figure 9 now says Estimated based on measured data and Estimated based on simulated data.

Comment 19: Figures S2 and S3: It would be nice to see the time series of OH and HO2 here as well.

We have added the time series of OH and preliminary HO_2 to Figures S2 and S3.

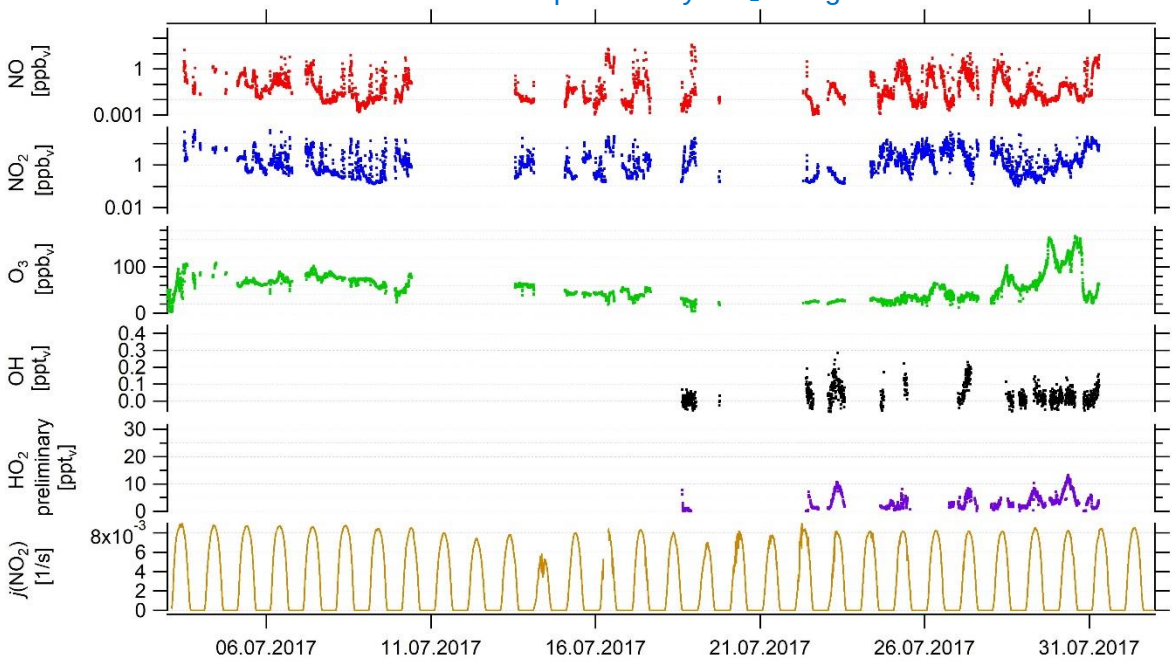

Figure S2: Timeline of NO, NO_2 (both CLD), O_3, OH, HO_2 preliminary and $j(NO_2)$ data during the first leg. See Table ST1 for additional information on the ship cruise. Note that HO_2 data are prelimary.

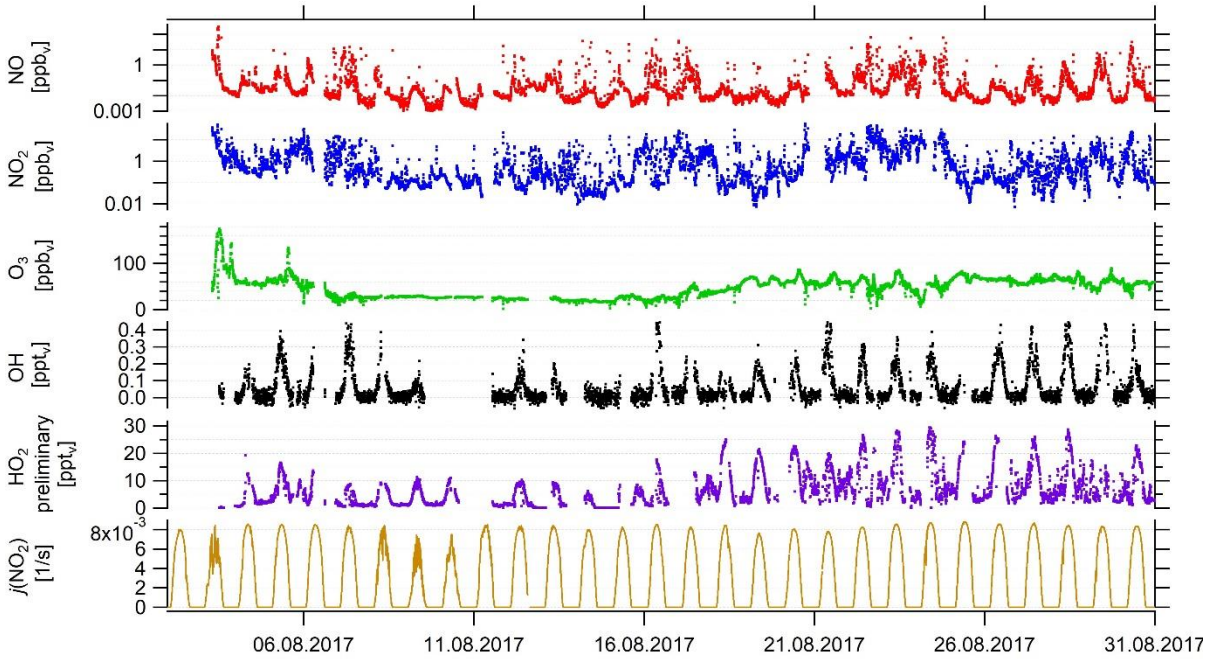

Figure S3: Timeline of NO, NO_2 (both CLD), O_3, OH, HO_2 preliminary and $j(NO_2)$ data during the second leg. See Table ST1 for additional information on the ship cruise. Note that HO_2 data are preliminary.

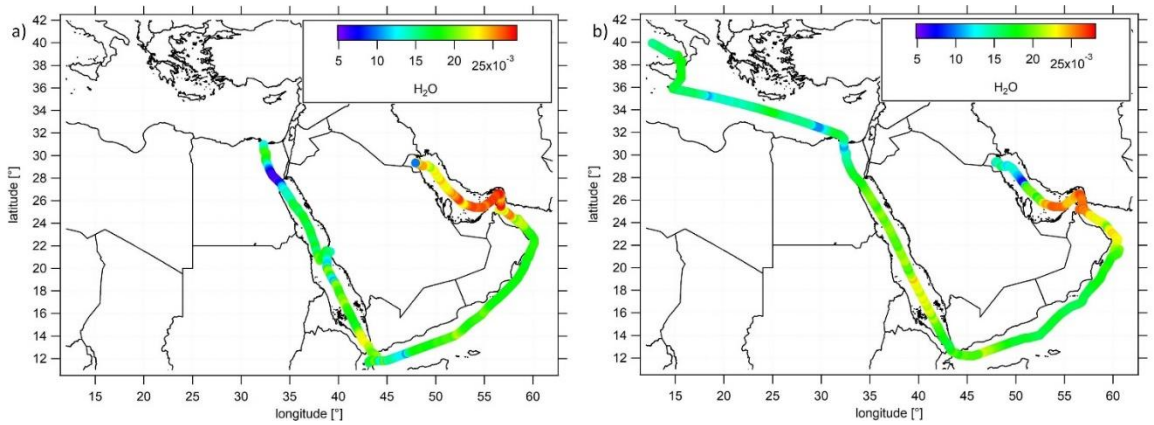

Figure S5: Ship cruises with color-scaled absolute humidity a) during the first and b) the second leg.

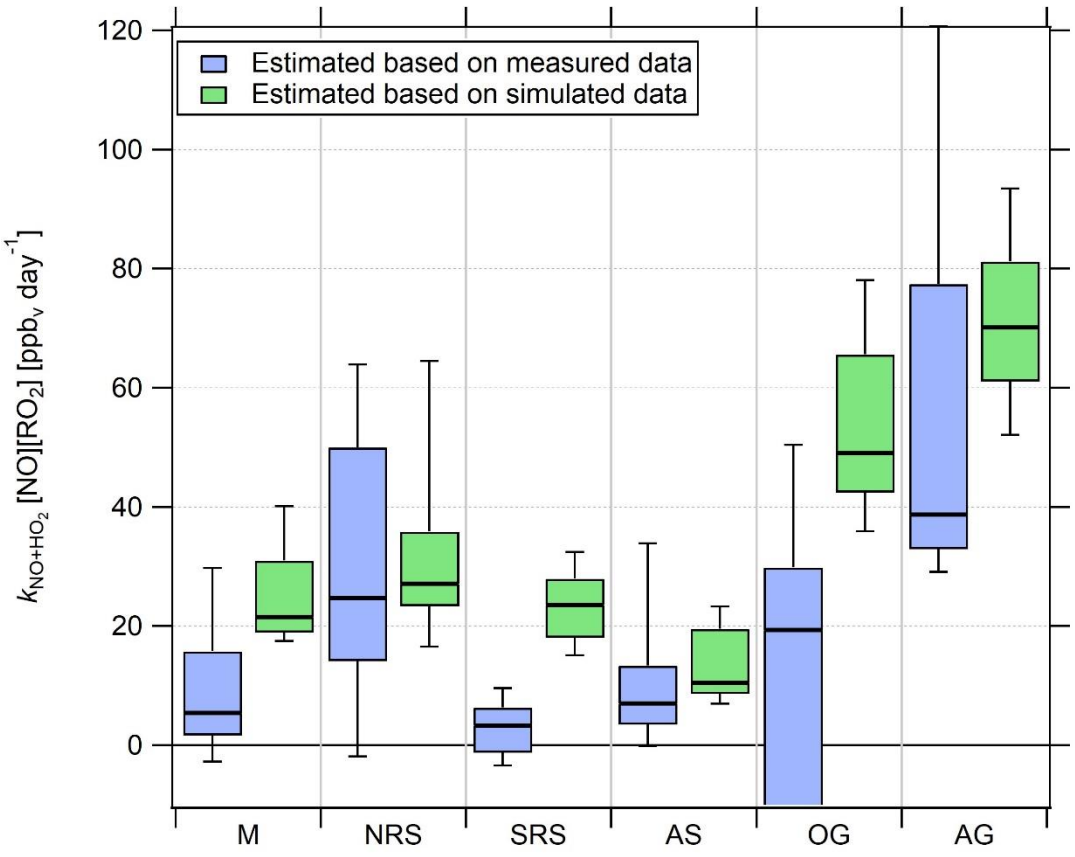

Figure S10: Comparison of the regional, absolute contribution of $k_{NO+HO_2}[NO][RO_2]$ to NOPR in the six different regions investigated during AQABA. The horizontal black bar indicates the median value, the box the 25- and 75-percentiles and the whiskers the 10- and 90-percentiles.

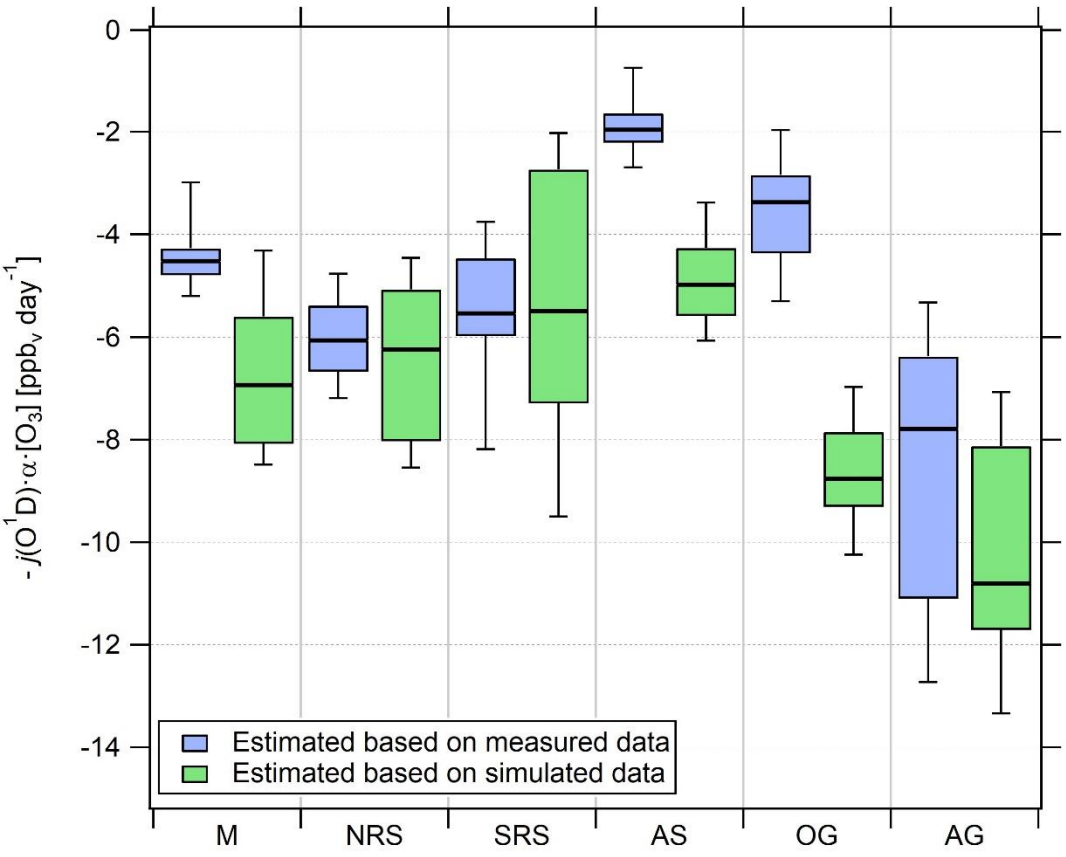

Figure S11: Comparison of the regional, absolute contribution of $-j(\mathrm{O^1D}) \cdot \alpha \cdot [\mathrm{O_3}]$ to NOPR in the six different regions investigated during AQABA. The horizontal black bar indicates the median value, the box the 25- and 75-percentiles and the whiskers the 10- and 90-percentiles.

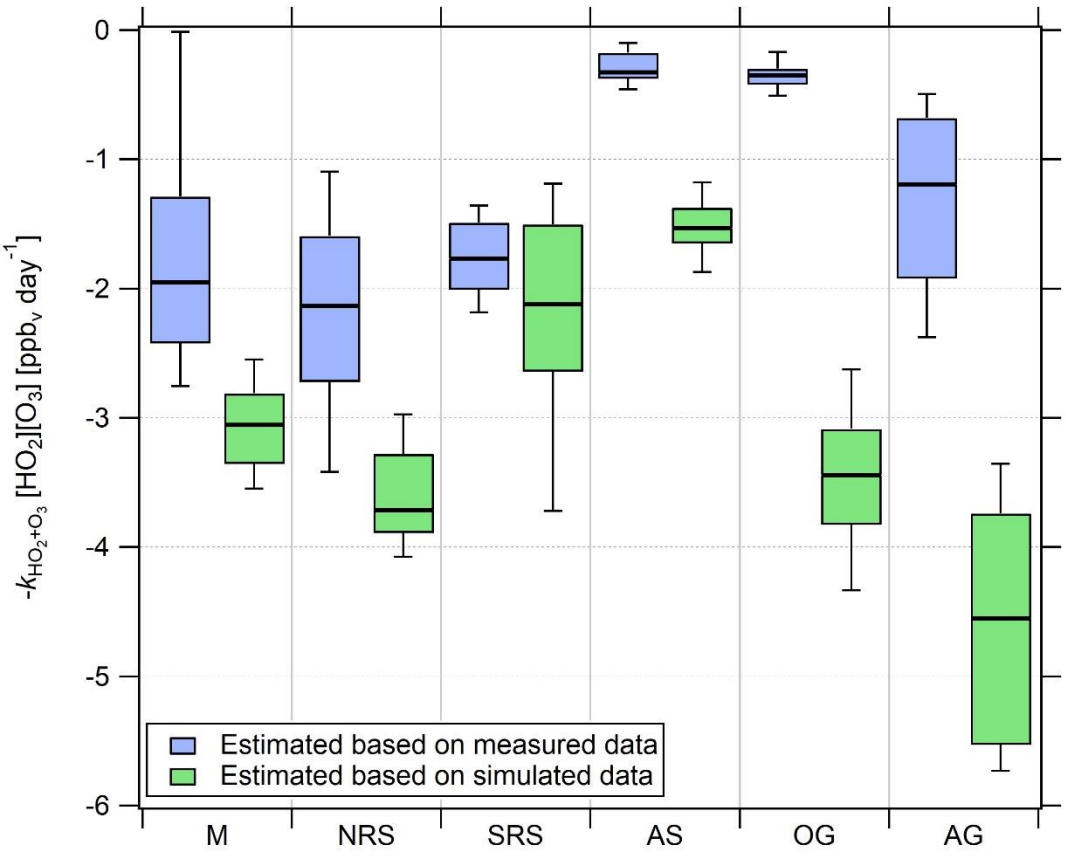

Figure S12: Comparison of the regional, absolute contribution of $-k_{HO_2+O_3}[HO_2][O_3]$ to NOPR in the six different regions investigated during AQABA. The horizontal black bar indicates the median value, the box the 25- and 75-percentiles and the whiskers the 10- and 90-percentiles.

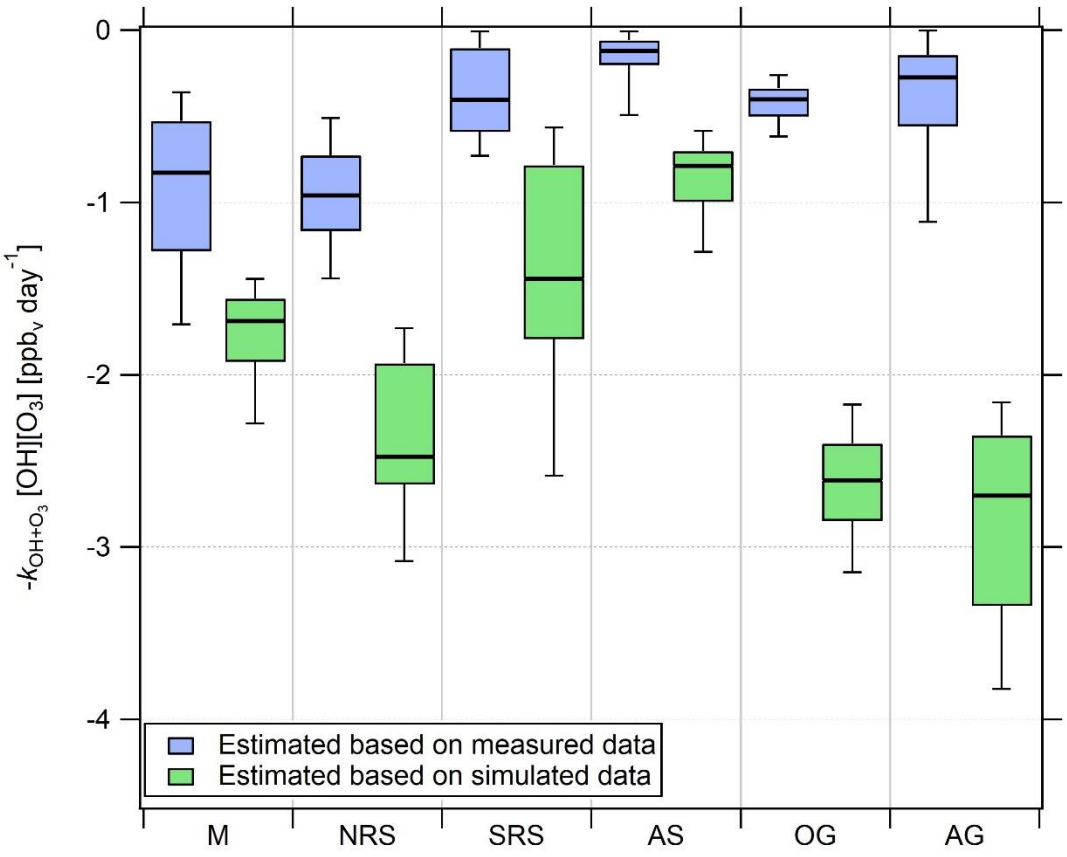

Figure S13: Comparison of the regional, absolute contribution of $-k_{OH+O_3}[OH][O_3]$ to NOPR in the six different regions investigated during AQABA. The horizontal black bar indicates the median value, the box the 25- and 75-percentiles and the whiskers the 10- and 90-percentiles.