# Net ozone production and its relationship to NO<sub>x</sub> and VOCs in the marine boundary layer around the Arabian Peninsula

Ivan Tadic<sup>1</sup>, John N. Crowley<sup>1</sup>, Dirk Dienhart<sup>1</sup>, Philipp Eger<sup>1</sup>, Hartwig Harder<sup>1</sup>, Bettina Hottmann<sup>1</sup>, Monica Martinez<sup>1</sup>, Uwe Parchatka<sup>1</sup>, Jean-Daniel Paris<sup>2</sup>, Andrea Pozzer<sup>1,4</sup>, Roland Rohloff<sup>1</sup>, Jan Schuladen<sup>1</sup>, Justin Shenolikar<sup>1</sup>, Sebastian Tauer<sup>1</sup>, Jos Lelieveld<sup>1,3</sup>, and Horst Fischer<sup>1</sup>

<sup>1</sup>Atmospheric Chemistry Department, Max Planck Institute for Chemistry, Mainz, Germany <sup>2</sup>Laboratoire des Sciences du Climat et de l'Environnement, LSCE/IPSL, CEA-CNRS-UVSQ, Université Paris-Saclay, Gifsur-Yvette, France

<sup>3</sup>Energy, Environment and Water Research Center, The Cyprus Institute, Nicosia, Cyprus

10 <sup>4</sup>International Centre for Theoretical Physics, Trieste, Italy

Correspondence to: Ivan Tadic (i.tadic@mpic.de)

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Abstract. Strongly enhanced tropospheric ozone mixing ratios have been reported in the Arabian Basin, a region with intense solar radiation and high concentrations of ozone precursors such as nitrogen oxides and volatile organic compounds. To analyze photochemical ozone production in the marine boundary layer (MBL) around the Arabian Peninsula, we use ship-

- 15 borne observations of NO, NO<sub>2</sub>, O<sub>3</sub>, OH, HO<sub>2</sub>, HCHO, actinic flux, water vapor, pressure and temperature obtained during the summer 2017 Air Quality and Climate in the Arabian Basin (AQABA) campaign, compare them to simulation results of the ECHAM-MESSy atmospheric chemistry (EMAC) general circulation model. Net ozone production rates (NOPR) were greatest with 16 ppb<sub>v</sub> day<sup>-1</sup> over both the Gulf of Oman and the Northern Red Sea and with 32 ppb<sub>v</sub> day<sup>-1</sup> over the Arabian Gulf. NOPR over the Mediterranean, the Southern Red Sea and the Arabian Sea did not significantly deviate from zero;
- 20 however, results for the Arabian Sea indicate weak net ozone production of 5 ppb<sub>v</sub> day<sup>-1</sup>, and net ozone destruction over the Mediterranean and the Southern Red Sea with -1 ppb<sub>v</sub> day<sup>-1</sup> and -4 ppb<sub>v</sub> day<sup>-1</sup>, respectively. Constrained by HCHO/NO<sub>2</sub>-ratios, our photochemistry calculations show that net ozone production in the MBL around the Arabian Peninsula occurs mostly in NO<sub>x</sub>-limitation regimes with a significant share of ozone production occurring in the transition regime between NO<sub>x</sub>- and VOC-limitation over the Mediterranean and more significantly over the Northern Red Sea and Oman Gulf.

#### 25 1 Introduction

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Revenues from exploitation of the great oil reserves in the states of and around the Arabian Peninsula have propelled remarkable economic development associated with industrialization and urbanization. Strong population growth and anthropogenic emissions of gases and particulates in the last few decades have resulted in the Middle East becoming a hotspot for air pollution and associated health effects, while it is also one of the regions worldwide where climate change is particularly

- 30 rapid (Lelieveld et al., 2016a). Unique meteorological conditions such as intense solar radiation, high temperatures and aridity, as well as strong anthropogenic emissions of volatile organic compounds (VOCs) and NO<sub>x</sub> (= NO + NO<sub>2</sub>) by on- and off-shore petrochemical industries, dense ship traffic, fossil energy production for air conditioning and desalination, and urban development are expected to further intensify in the future and contribute to photochemical ozone production (Lelieveld et al, 2009; Krotkov et al., 2016; Pfannerstill et al., 2019). Understanding the sources and sinks of NO<sub>x</sub> and other ozone precursors on and around the Arabian Peninsula is therefore of major importance for atmospheric chemistry studies, including the
- investigation of net ozone production rates (NOPR) (Monks et al., 2015; Reed et al., 2016; Bozem et al., 2017).

NO<sub>x</sub> plays a central role in atmospheric photochemistry (Nakamura et al., 2003; Tuzson et al., 2013; Reed et al., 2016). It is the primary precursor for tropospheric ozone (O<sub>3</sub>), secondary organic aerosols and photochemical smog in urban areas (Hollaway et al., 2012; Javed et al., 2019). Main ground-based sources of NO and NO<sub>2</sub> are fossil fuel combustion and to a lesser extent bacterial processes in soils, and both lightning and aircraft emissions in the upper troposphere (Nakamura et al., 2003; Miyazaki et al., 2017; Javed et al., 2019). Transport of NO<sub>x</sub> in the atmosphere is relatively limited due to its short lifetime of a few hours (Reed et al., 2016). It is removed from the troposphere mainly by conversion to HNO<sub>3</sub> (via reaction with OH) during the day, or the formation of N<sub>2</sub>O<sub>5</sub> (in the reaction of NO<sub>2</sub> with NO<sub>3</sub> at night-time), which also leads to formation of nitric acid by heterogeneous hydrolysis on aerosol surfaces (Crutzen, 1973; Liu et al., 2016; Reed et al., 2016). Ultimately, the

- 45 deposition of HNO<sub>3</sub> constitutes the major loss process of NO<sub>x</sub> from the atmosphere. Ozone is a secondary pollutant that is photochemically formed in the troposphere from its precursors NO<sub>x</sub> and VOCs (Bozem et al., 2017; Jaffe et al., 2018). It is an important greenhouse gas, an atmospheric oxidant and the most important primary precursor for OH (Lelieveld et al., 2004; Monks et al., 2015; Bozem et al., 2017). O<sub>3</sub> in the planetary boundary layer causes health damage, notably respiratory diseases, and reduces crop yields (Monks et al., 2015; Jaffe et al., 2018).
- 50 NO<sub>x</sub> and O<sub>3</sub> mixing ratios in the troposphere vary from less than 20 ppt<sub>v</sub> and 10 ppb<sub>v</sub>, respectively, for pristine conditions such as the remote marine boundary layer (MBL) up to mixing ratios of several hundreds of ppb<sub>v</sub> in regions with heavy automobile traffic and in international shipping lanes (for NO<sub>x</sub>) and downwind of urbanized areas (for O<sub>3</sub>) (Reed et al., 2016; Jaffe et al., 2018). Low NO<sub>x</sub> environments such as the clean MBL and the lower free troposphere are considered net ozone destruction regimes whereas the upper troposphere and areas with anthropogenic emissions of ozone precursors are regions of net ozone
- 55 production (Klonecki and Levy, 1997; Bozem et al., 2017). Measurements performed in the Houston Ship Channel revealed NOPR of the order of several tens of ppb h<sup>-1</sup> (Chen et al., 2010; Mao et al., 2010; Ren et al., 2013).

In the last decade much effort has been successfully devoted to the mitigation of  $NO_x$  emissions over Europe and America, and levels of reactive nitrogen trace gases have decreased (Miyazaki et al., 2017). But in Asia, India and the Middle East,  $NO_x$  emissions have substantially increased during the last decade so that the global  $NO_x$  burden has essentially remained constant

- 60 (Miyazaki et al., 2017). NO<sub>x</sub> emissions by ocean-going vessels have attracted considerable attention as they are reported to account for 15 % of the global NO<sub>x</sub> emission burden (Celik et al., 2019). Model calculations suggest that the Arabian Gulf, with an estimated annual NO<sub>x</sub> emission density of about one ton km<sup>-2</sup> from ship traffic, is among the regions with highest NO<sub>x</sub> emission densities worldwide (Johansson et al., 2017). Although NO<sub>x</sub> emissions in the Red Sea and Arabian Sea areas were reported to be three and five times smaller than for the Arabian Gulf, respectively, these values are still 50-100 times larger
- 65 than the emission density reported for the South Pacific Ocean, for example (Johansson et al., 2017).

In the present study, we characterize photochemical NOPR in the MBL around the Arabian Peninsula. In Sect. 2, the campaign, instrument description, data processing and a description of the methods used in this study is presented. In Sect. 3, mixing ratios of nitrogen oxides and ozone around the Arabian Peninsula are reported. Based on concurrent measurements of  $HO_x$ , actinic flux, temperature and pressure, noontime  $RO_2$  mixing ratios are estimated and used to calculate NOPR in the different

70 regions around the Arabian Peninsula. Observation-based analysis of HCHO/NO<sub>2</sub>-ratios will be used to distinguish between NO<sub>x</sub>- or VOC-limited chemistry in the particular regions. A comparison of the results with data retrieved from the 3D global circulation model EMAC is also included.

#### **2** Experimental

#### 2.1 AQABA campaign

- 75 The AQABA ship campaign (<u>A</u>ir <u>Q</u>uality and Climate in the <u>A</u>rabian <u>Ba</u>sin) investigated the chemical composition of the MBL around the Arabian Peninsula. From late June to early September 2017, the *Kommandor Iona* Research and Survey Vessel sailed from Toulon (France) to Kuwait and back in order to perform gas-phase and particle measurements in the region. The gas-phase and aerosol measurement instrumentation was housed in five laboratory containers on the front deck. 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<sub>2</sub> 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<sub>2</sub> cavity ring-down spectroscopy and O<sub>3</sub> measurements were obtained with similar bypass systems sampling air from the common inlet. H<sub>2</sub>O vapor was measured on the top of the ship mast in the front. The OH and HO<sub>2</sub> detection units were placed on the prow to allow for inlets with residence times less than 10 ms.
- 85 The Kommandor Iona left Malta in late June 2017 traversing the Mediterranean Basin, the Suez Canal and the Northern Red Sea. A 3 day stop over at KAUST University (Saudi Arabia) was made from 11 July 2017 to 13 July 2017 before passing the Southern Red Sea area. On 17 July 2017, we briefly stopped at Djibouti port before passing the Gulf of Aden, the Arabian Sea

and the Gulf of Oman. Kuwait at the northern end of the Arabian Gulf marked the turning point of the ship cruise where, during a second 3-day stop-over, scientific staff was exchanged. The *Kommandor Iona* started the second leg on 03 August

90 2017 arriving in Toulon (France) in early September 2017 without any further stops. Figure 1 shows the ship's route subdivided into six different regimes.



Figure 1: Ship cruises during both legs and color-coded subdivision into six different regimes. The following abbreviations will be used: AG for Arabian Gulf (purple), OG for Oman Gulf (dark blue), AS for Arabian Sea (blue), SRS for Southern Red Sea (green), NRS for Northern Red Sea (yellow), M for Mediterranean (red).

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To enhance the statistical significance of our results and due to comparable signatures of the NO<sub>x</sub> and O<sub>3</sub> measurements in the northern part of the Red Sea, the Suez Gulf and the Suez Canal, we have combined these regions which are represented by the 'Northern Red Sea' (NRS). For the same reasons we have merged the Gulf of Aden with the Arabian Sea (AS). See supplementary Table ST1 for the range of latitudinal and longitudinal coordinates of the different regions and supplementary Table ST2 for a detailed day to day description of the route.

#### 2.2 Measurements of nitrogen oxides during AQABA

Chemiluminescent detection of NO and NO<sub>2</sub> is a widely applied method to quantify mixing ratios from the ppm<sub>v</sub> down to the

- 105 low ppt<sub>v</sub> range (Nakamura et al., 2003; Pollack et al., 2011; Hosaynali Beygi et al., 2011; Reed et al., 2016). During AQABA we deployed a compact, robust and commercially available two-channel chemiluminescence instrument CLD 790 SR (ECO Physics AG, Dürnten, Switzerland) that has been optimized for in situ field measurements during the last decade (Hosaynali Beygi et al., 2011). The measurement principle of the CLD is based on the addition of O<sub>3</sub> to NO to produce stoichiometric quantities of excited state NO<sub>2</sub><sup>\*</sup> that will emit an infrared photon ( $\lambda > 600$  nm) forming the chemiluminescent detection
- 110 principle for NO (Drummond et al., 1985; Reed et al., 2016). Both channels feature an identical layout and were operated at a mass flow of 1.5 SLM during AQABA. One channel of the CLD (NO<sub>c</sub>-channel) has additionally been equipped with a LED solid state photolytic converter (Droplet Measurement Techniques, Boulder, Colorado) installed upstream of the O<sub>3</sub> addition to selectively photolyze NO<sub>2</sub> to NO, which is subsequently measured. In this section, we will concentrate on modifications made prior to the campaign and especially on operational conditions of the photolytic converter during the campaign. Further
- 115 details on the measurement principle are described elsewhere (Pollack et al., 2011; Hosaynali Beygi et al., 2011; Reed et al., 2016).

During AQABA, the cylindrical photolytic converter (length 14 cm, volume ~ 0.079 l) was operated at a constant pressure of 95 hPa yielding a residence time of ~ 0.3 s. The photolytic NO<sub>2</sub> converter features a set of 200 UV LED units attached to each end of the converter. The emission profile of the UV LED units was characterized in laboratory measurements to peak at 398

- 120 nm with a Full Width at Half Maximum (FWHM) of 16 nm. The UV-induced positive bias in the NO<sub>2</sub>-measurement due to photolysis of BrONO<sub>2</sub>, HONO, NO<sub>3</sub> and ClNO<sub>2</sub> to produce NO was estimated at 6.1 %, 2.8 %, 2.7 % and 1.2 %, 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<sub>y</sub> compound as the respective molecular quantum yield was estimated conservatively at 1. Note that the values represent percent interferences if the interferent had the
- 125 same concentration as NO<sub>2</sub>. Due to small daytime concentrations of these molecules in the MBL, a UV-induced bias was neglected for the observations in this study. To limit wall loss of NO<sub>2</sub>, the inner cavity surface is made of PTFE (polytetrafluoroethylene), which may potentially provide a reservoir (via surface adsorption) for NO<sub>y</sub> that can thermally dissociate to increase the background signal of the NO<sub>2</sub> measurement (Reed et al., 2016). The conversion efficiency  $K_e$  of the photolytic NO<sub>2</sub> conversion was estimated by gas phase titration (SYCOS K-GPT-DLR, ansyco, Karlsruhe, Germany) several
- 130 times before, during and after the campaign at (29.4 ± 0.9) % allowing the calculation of NO<sub>2</sub> concentrations by  $[NO_2] = \frac{[NO_c] [NO]}{\kappa_e}$ . To avoid chemical interferences due to adding ozone in excess during a gas phase titration, a small but not vanishing amount of NO has always been left unoxidized during gas phase titrations.

During AQABA, regular dry zero-air measurements as well as NO and NO<sub>2</sub> calibrations were performed autonomously over a 10 minute period every 6 hours to accurately quantify the instrumental background and to correct for sensitivity drifts. An

- 135 autonomous cycle of '2 min zero air measurements 2 min NO calibration 2 min zero air measurement 2 min NO<sub>2</sub> calibration 2 min zero air measurement' was implemented. Continuous flows NO and NO<sub>2</sub> calibration gases were added to the synthetic airflow or directed to a pump by switching solenoid valves. The NO calibration standard (1.954  $\pm$  0.039 ppm<sub>v</sub> NO in N<sub>2</sub>, Air Liquide, Germany) used during the campaign was compared to a primary standard (5.004  $\pm$  0.025) ppm<sub>v</sub> (NPL, Teddington, UK) after the campaign yielding an effective NO mixing ratio of (2.060  $\pm$  0.057) ppm<sub>v</sub> in the NO
- 140 calibration gas. Zero air measurements and NO calibrations were performed with a total 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. During AQABA, NO calibrations at 2.5 ppb<sub>v</sub> were achieved. During the first leg of the campaign, zero air was sampled from a bottle (Westfalen AG, Germany), whereas during the second leg zero air was generated from a zero air generator (Air Purifier CAP 180, acuraLine). Zero air measurements generated with the zero air generator were statistically
- 145 not significantly different from those achieved by a bottle. To correctly account for the photomultiplier background and chemical interferences due to reactions of ozone with ambient alkenes additional pre-chamber measurements were performed every 5 minutes as well as at the beginning of zero air measurements and calibrations for 25 s each. This correction is removing a large fraction of the interference signal from alkenes. 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
- 150 instrument. A schematic setup of the two-channel CLD instrument is given in Figure 2.



Figure 2: Schematic setup of the two channel CLD instrument in the configuration used during AQABA. NO and NO<sub>2</sub> calibration gases were running continuously and were added to the zero airflow by switching the respective solenoid valves.

155 The total measurement uncertainty (TMU) in NO has been calculated at 6 % at an integration time of 5 minutes and a confidence level of  $1\sigma$  by adding the precision (5 %) and the error of the calibration gas mixture (3 %) in quadrature: TMU([NO]) =  $\sqrt{(5\%)^2 + (3\%)^2} \approx 6\%$ . The limit of detection in the NO channel was estimated as the full width at half maximum of the frequency distribution of all zero air measurements obtained during the campaign to be 9 ppt<sub>v</sub> at a 5 min integration time and a confidence level of  $1\sigma$ . The TMU in NO<sub>2</sub> has been estimated by error propagation.

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$$\operatorname{TMU}([\operatorname{NO}_2]) = \frac{1}{[\operatorname{NO}_2]} \cdot \sqrt{\left(\frac{\Delta[\operatorname{NO}_c]}{K_e}\right)^2 + \left(\frac{\Delta[\operatorname{NO}]}{K_e}\right)^2 + \left(\frac{\Delta K_e \cdot ([\operatorname{NO}_c] - [\operatorname{NO}])}{K_e^2}\right)^2}$$

Note that the total measurement uncertainty of the NO<sub>c</sub>-channel data has also been calculated at 6 % at an integration time of 5 minutes and a confidence level of  $1\sigma$  by adding the precision and the error of the calibration gas mixture in quadrature. Over the course of the campaign the median and the average relative uncertainty of NO<sub>2</sub> are 8 % and 16 %, respectively. The median is lower than the average as NO is practically zero during nighttime. During nighttime the relative error of the NO<sub>2</sub> data points

- 165 is about 6.7 %. Note for convenience that is exactly the value calculated from errors in quadrature (if NO is practically zero during nighttime):  $\sqrt{6\%^2 + 0\%^2 + 3\%^2} \approx 6.7$  %. The relative uncertainty in NO<sub>2</sub> has been estimated as a conservative upper limit at 16 % as the average of the relative uncertainty of all data points obtained during AQABA. As the zero air measurements in the NO<sub>2</sub> channel produced an increased background affected by memory effects after exposure to high NO<sub>x</sub> levels e.g. during measurements of stack emissions, the NO<sub>2</sub> raw data were initially processed without converter background subtraction. As we
- 170 therefore expect the CLD NO<sub>2</sub> data to be offset due to not being initially background corrected, the converter background was estimated at 112 ppt<sub>v</sub> from the centre of a Gaussian fit representing the difference of 1-minute averaged CLD NO<sub>2</sub> and concurrent cavity ring-down spectroscopy (CRDS) NO<sub>2</sub> measurements for data points below 10 ppb<sub>v</sub>. Setting the threshold for calculating the difference of the two concurrent data sets to 10 ppb<sub>v</sub> is somewhat arbitrary, however, changing this limit to 5 ppb<sub>v</sub> or 20 ppb<sub>v</sub> does not significantly vary the estimated offset of the CLD NO<sub>2</sub> data. The offset correction of 112 ppt<sub>v</sub> was
- 175 taken as the ultimate absolute measurement uncertainty of the CLD NO<sub>2</sub> measurement. Further corrections of to the final CLD data include residence time corrections as well as corrections for NO and O<sub>3</sub> losses and the subsequent formation of NO<sub>2</sub> in the sampling line (Ryerson et al., 2000). Both NO and NO<sub>2</sub> CLD data have also been corrected for nonlinearities for concentrations higher than 55 ppb<sub>y</sub>, as experienced during probing of stack emissions.

#### 2.3 Further measurements used in this study

- 180 An extensive set of concurrent measurements providing mixing ratios of O<sub>3</sub>, NO<sub>2</sub>, HCHO, OH, HO<sub>2</sub>, absolute humidity and actinic flux, temperature and pressure data obtained during AQABA was used in this study. Ozone was measured with an absorption photometer (Model 202 Ozone Monitor, 2B Technologies, Boulder, Colorado) based on the well-established absorption of the mercury line in the Hartley band at 254 nm (Viallon et al., 2015). Eliminating water and particle interferences during sampling was achieved via sampling through a nafion tube and a Teflon filter. The ozone monitor was zeroed ten times
- 185 during the campaign. NO<sub>2</sub> was further measured by cavity ring-down spectroscopy (Sobanski et al., 2016) and used for correcting the instrumental background of the CLD NO<sub>2</sub> data, as described above (the correction was taken as the ultimate absolute measurement uncertainty in the CLD NO<sub>2</sub> data). Note that in this study we will use the NO<sub>2</sub> CLD data rather than the NO<sub>2</sub> CRDS data as the temporal coverage of the CLD NO<sub>2</sub> data over the course of the campaign is about 60 % compared to about 35 % for the cavity ring-down measurement. Formaldehyde (HCHO) was measured with an Aerolaser 4021 (AERO-
- 190 LASER GmbH, Garmisch-Partenkirchen, Germany), which is a fully automatized monitor based on the Hantzsch technique (Kormann et al., 2003). H<sub>2</sub>O measurements were obtained using a cavity ring-down spectroscopy monitor (PICARRO G2401, Santa Clara, California) supervised by Laboratoire des Sciences du Climat et de l'Environnement (LSCE) (Kwok et al., 2015).

Measurements of OH and HO<sub>2</sub> were performed with the custom-built  $\underline{\mathbf{H}}$ ydr $\underline{\mathbf{O}}$ xyl  $\underline{\mathbf{R}}$ adical measurement  $\underline{\mathbf{U}}$ nit based on fluorescence  $\underline{\mathbf{S}}$ pectroscopy (HORUS) instrument based on laser-induced fluorescence (LIF) spectroscopy of the OH molecule

- and NO titration of HO<sub>2</sub> to OH followed by LIF spectroscopy detection of the OH molecule (Martinez et al., 2010; Regelin et al., 2013). HO<sub>2</sub> data used in this study is still preliminary due to not yet corrected interference of organic peroxy radicals RO<sub>2</sub>. The largest uncertainty due to interference by contribution of RO<sub>2</sub> is 7 % or 3 ppt<sub>v</sub> whichever is higher. The 1 sigma accuracy of both OH and HO<sub>2</sub> 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<sub>2</sub> is estimated at  $\sqrt{20 \%^2 + 7 \%^2} \approx 21 \%$ . Wavelength resolved down-welling actinic flux was
- 200 measured with a spectral radiometer (model CCD Spectroradiometer 85237). The *j*-values for NO<sub>2</sub> and O<sub>3</sub> were not corrected for upwelling UV radiation and were estimated to have a ~ 10 % measurement uncertainty (Meusel et al., 2016). The radiometer was installed 10 m above sea level, respectively 5 m above the front deck surface. Decreases in sensitivity due to sensor contamination with e.g. sea-spray were corrected with a linear interpolation between two (daily) cleaning events. Temperature and pressure measurements were performed with the Shipborne **Eu**ropean **C**ommon **A**utomatic **W**eather **S**tation (EUCAWS),
- 205 a weather station specifically designed for ships. The weather station incorporates sensors, processing units, satellite positioning and communication systems in one device and is implemented and coordinated by the European National Meteorological Service EUMETNET. Table 1 lists the measurement methods and the TMU for each observation.

Molecule	Method	TMU	References
NO	chemiluminescence	6 %	Hosaynali Beygi et al., 2011
$NO_2$	photolysis-chemiluminescence	16 %	Hosaynali Beygi et al., 2011
$NO_2$	cavity ring-down spectroscopy	7 %	Sobanski et al., 2016
O <sub>3</sub>	UV absorbance	2 %	Viallon et al., 2015
ОН	LIF	20 %	Martinez et al., 2010
HO <sub>2</sub>	NO titration / LIF	21 %	Martinez et al., 2010
НСНО	Hantzsch technique	13 %	Kormann et al., 2003
H <sub>2</sub> O	cavity ring-down spectroscopy	5 %	Kwok et al., 2015
actinic flux	spectral radiometer	10 %	Meusel et al., 2016

Table 1: List of observations and gas phase measurements during AQABA. The TMU at a confidence level of  $1\sigma$  and at the particular temporal resolution as well as a reference of the measurement operability are given.

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The *Kommandor Iona* Research and Survey Vessel sailed whenever possible with the wind coming from the bow to avoid contamination by stack emissions. However, based on the relative wind direction, the variability in NO as well as the temporal evolution of  $NO_x$ ,  $SO_2$ , and  $O_3$  sections of data in which the air mass was contaminated by the ship's stack were identified. All

data used here to calculate RO<sub>2</sub> and NOPR have been filtered to remove contaminated air masses. Altogether, 21 % of the

- 215 sampling time was potentially contaminated by the ship exhaust of the KI of which 87 % occurred on the first leg. During the second leg the ship sailed against the wind and most of the data was free of stack contamination. Our analysis is based on a 5-minute running mean for each data set, whereby only averages that have been calculated at a temporal coverage greater than 30 % have been used. A time series of the NO, NO<sub>2</sub> (both CLD), O<sub>3</sub>, OH, HO<sub>2</sub> preliminary and *j*(NO<sub>2</sub>) measurements is given in the supplementary Figures S2 and S3.
- NO and NO<sub>2</sub> were measured from 03 July 2017 to 31 August 2017, O<sub>3</sub> was measured from 22 June 2017 to 01 September 2017, HCHO from 01 July 2017 to 31 August 2017 and OH and HO<sub>2</sub> from 18 July 2017 to 31 August 2017. For the analysis of peroxy radicals RO<sub>2</sub> and NOPR around the Arabian Peninsula we have removed data measured during the stop-overs in Jeddah (11 July to 13 July), Kuwait (31 July to 03 August) and during bunkering at Fujairah City (06 August, 07:00 – 15:00 UTC). Due to HO<sub>x</sub> data being available from 18 July 2017 onward, we have limited the net ozone production analysis to the 225 period after this date.

#### 2.4 Methods

The so-called NO<sub>x</sub>-O<sub>3</sub>-null cycle represents a rapid daytime cycling between NO, NO<sub>2</sub> and O<sub>3</sub>. Solar UV radiation photolyzes NO<sub>2</sub> to NO and O( $^{3}$ P) (R1) which will reform O<sub>3</sub> in the subsequent reaction with molecular oxygen O<sub>2</sub> (R2) (Leighton, 1961).

NO and  $O_3$  react to form NO<sub>2</sub> and  $O_2$  (R3). R1, R2 and R3 constitute a so called null cycle which establishes photostationary steady state (PSS) for both NO<sub>x</sub> and O<sub>3</sub> in mid latitudes during noon time on a time scale of ~100 s (Thornton et al., 2002; Mannschreck et al., 2004).

$$NO_2 + h\nu (\lambda < 424 \text{ nm}) \rightarrow NO + O(^{3}P)$$
(R1)

$$O_2 + O({}^3P) + M \to O_3 + M$$
 (R2)

(R3)

$$235 \quad \mathrm{NO} + \mathrm{O}_3 \to \mathrm{NO}_2 + \mathrm{O}_2$$

Under the assumption of PSS, the Leighton Ratio  $\varphi$  is unity (Leighton, 1961)

$$\varphi = \frac{j(NO_2) \cdot [NO_2]}{k_{NO+O_3} \cdot [NO][O_3]} = 1$$
(1)

with *j*(NO<sub>2</sub>) being the NO<sub>2</sub> photolysis rate [s<sup>-1</sup>]. In low NO<sub>x</sub> environments (< 100 ppt<sub>v</sub>) previous studies have indicated that further NO oxidizing trace gases such as peroxy radicals (HO<sub>2</sub>, RO<sub>2</sub>) and halogen monoxides (XO) may result in a deviation
from unity (Nakamura et al., 2003; Hosaynali Beygi et al., 2011; Reed et al., 2016).

$$NO + HO_2 \rightarrow NO_2 + OH$$

$$NO + RO_2 \rightarrow NO_2 + RO$$

$$NO + XO \rightarrow NO_2 + X$$
(R4)
(R5)
(R5)

Deviations from expected NO/NO<sub>2</sub>-ratios at low NO<sub>x</sub> generally refer to missing oxidants converting NO to NO<sub>2</sub> (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<sub>x</sub> reservoir species (Reed et al., 2016; Silvern et al., 2018). In the present study we include HO<sub>2</sub> and

 $R_iO_2$  into the production term for NO<sub>2</sub>.

$$j(NO_2) \cdot [NO_2] = k_{NO+O_3} \cdot [NO][O_3] + k_{NO+HO_2} \cdot [NO][HO_2] + [NO] \cdot \sum_i k_{NO+R_iO_2} \cdot [R_iO_2]$$
(2)

Assuming that the temperature-dependent rate coefficient for the reaction of each particular peroxy radical  $R_iO_2$  with NO 250 equals the rate  $k_{NO+HO_2}$  for Reaction R4 (Hauglustaine et al., 1996; Cantrell et al., 1997; Thornton et al., 2002), we can combine HO<sub>2</sub> and the sum of all organic peroxy radicals  $R_iO_2$  to the entity RO<sub>2</sub> that can be estimated using the steady state equation

$$[\mathrm{RO}_2] = \frac{j(\mathrm{NO}_2) \cdot [\mathrm{NO}_2] - k_{\mathrm{NO}+\mathrm{O}_3} \cdot [\mathrm{NO}][\mathrm{O}_3]}{k_{\mathrm{NO}+\mathrm{HO}_2} \cdot [\mathrm{NO}]}.$$
(3)

However, the steady state assumption is not valid if the sampled air parcel is affected by fresh emissions or fast changes in the actinic flux (Thornton et al., 2002). After sampling a fresh emission e.g. a ship plume, for which NO<sub>x</sub> went up typically to values of several tens of ppb<sub>v</sub> with simultaneous titration in O<sub>3</sub>, we assume that PSS is re-established on a time scale of 2 minutes (Thornton et al., 2002; Mannschreck et al., 2004). To best approximate PSS in our analysis we have restricted the estimation of RO<sub>2</sub> on time frames  $\pm$  2 h around noontime for which we expect the smallest relative changes in the actinic flux. Noontime for each day was determined as the centre of a Gaussian fit that was applied to the actinic flux data. We applied a Gaussian Fit to the actinic flux data as this fitting method is sufficient to estimate the centre of the diurnal actinic flux. To further limit the affect of periods for which PSS is not fulfilled, we use the median instead of the average that is often

- further limit the effect of periods for which PSS is not fulfilled, we use the median instead of the average that is often disproportionately biased by strong  $NO_x$  sources nearby. See supplementary Tables ST3, ST5 and ST7 for detailed statistics and a further motivation on regional averages and median values. See supplementary Figure S1 for a detailed illustration of the calculation of the fraction of the noontime integral.
- A further part of the analysis will be the investigation of NOPR. Ozone production is initiated by reactions that produce HO<sub>x</sub>, for which primary production is from the photolysis of ozone, formaldehyde, nitrous acid (HONO) and hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) (Thornton et al., 2002; Lu et al., 2010; Hens et al., 2014; Mallik et al., 2018). The production of ozone can be approximated by the rate of oxidation of NO with RO<sub>2</sub> (HO<sub>2</sub> +  $\Sigma_i R_i O_2$ ) to form NO<sub>2</sub> that will rapidly form O<sub>3</sub> (R1-R2) (Bozem

et al., 2017). For RO<sub>2</sub> we use the result from Eq. 3 that incorporates HO<sub>2</sub> and the sum of all further peroxy radicals  $\sum_i R_i O_2$ (Parrish et al., 1986; Thornton et al., 2002).

$$P(0_3) = k_{\rm N0+H0_2} \cdot [\rm N0][\rm R0_2]$$
(4)

Photochemical O<sub>3</sub> loss is mainly due to photolysis ( $\lambda < 340$  nm) in the presence of water vapor and the reactions of ozone with OH and HO<sub>2</sub> (Bozem et al., 2017).

$$0_3 + h\nu \ (\lambda < 340 \text{ nm}) \rightarrow 0_2 + 0(1\text{D})$$
 (R7.1)

$$275 \quad 0(^{1}D) + H_{2}O \rightarrow 2OH \tag{R7.2}$$

$$0 + OH \rightarrow HO + O$$
(R7.2)

$$0_3 + 0H \rightarrow HO_2 + O_2$$

$$0_3 + HO_2 \rightarrow 0H + 2O_2$$
(R8)
(R9)

 $\alpha$ , the fraction of O(<sup>1</sup>D) that reacts with H<sub>2</sub>O

$$\alpha = \frac{k_{0(1D)+H_20}[H_20]}{k_{0(1D)+H_20}[H_20]+k_{0(1D)+M}[M]}$$
(5)

280 was (10.6  $\pm$  2.2) % during AQABA with a quasi linear dependence on water concentrations. The error in  $\alpha$  is mainly determined by the error of H<sub>2</sub>O at 5 %. Furthermore, ozone is lost due to reactions with alkenes (R12) and halogen radicals (R13).

$$O_3 + \text{alkenes} \rightarrow \text{radicals}$$
 (R12)

$$0_3 + X \to 0_2 + X0 \tag{R13}$$

- We find that the loss rate is dominated by the photolysis of ozone with subsequent reaction of O(<sup>1</sup>D) with H<sub>2</sub>O, was 60 80 % of the total loss rate, followed by the reaction of O<sub>3</sub> with HO<sub>2</sub>, which makes up 10 30 % (note that the uncertainty in HO<sub>2</sub> radical concentrations mentioned above has no significant influence on the total O<sub>3</sub> loss rate, due to its small contribution). The remaining fraction (10-30 %) is due to the reaction of O<sub>3</sub> with OH. The reaction of ozone with ethene is on average 0.005 0.01 ppb<sub>v</sub> h<sup>-1</sup> and therefore generally less than 2 % of the total ozone loss rate (Bourtsoukidis et al., 2019). The reaction of O<sub>3</sub> with all alkenes will hence be neglected. Halogen radicals were not measured during AQABA and will not be incorporated into our study. 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 · 10<sup>6</sup> molecule cm<sup>-3</sup>, the estimate would yield a Cl concentration of 2.5 · 10<sup>4</sup> molecule cm<sup>-3</sup>, which would decrease the estimated diurnal net ozone production rates by roughly 0.2 ppb<sub>v</sub> day<sup>-1</sup> over the Arabian Sea and at most 0.6 ppb<sub>v</sub> day<sup>-1</sup> over the other regions, which
- 295 does not substantially alter the here presented results. The noontime chemical ozone loss rate can be summarized by

$$L(O_3) = [O_3] \cdot \left( \alpha \cdot j(O^1 D) + k_{OH+O_3} \cdot [OH] + k_{HO_2+O_3} \cdot [HO_2] \right).$$
(6)

NOPR presented in this study is finally calculated as the difference of Eq. 4 and Eq. 6.

$$NOPR = k_{NO+RO_2}[NO][RO_2] - [O_3] \cdot (\alpha \cdot j(O^1D) + k_{OH+O_3}[OH] + k_{HO_2+O_3}[HO_2]).$$
(7)

- Under the assumption of constant chemical composition for a given day, the NOPR is expected to have a diel cycle following 300 the measured actinic flux. Hence integrating the estimated NOPR over the course of a day based on the particular fractional noontime integral of  $j(NO_2)$  will yield a diurnal value for NOPR. A detailed calculation of the diurnal fractional integrals is given in the supplementary Figure S1. Note that all reaction rate constants used are from the IUPAC Task Force on Atmospheric Chemistry Chemical Kinetic Data Evaluation (Atkinson et al., 2004). Indications whether a chemical regime is  $NO_x$ -limited or VOC-limited can be derived from the ratio of HCHO to  $NO_2$ . Former studies have derived HCHO/ $NO_2$ -ratios from satellite measurements to establish whether ozone production is  $NO_x$ -limited or VOCs-limited. The results indicate  $NO_x$ -
- limitation for HCHO/NO<sub>2</sub> > 2 and prevailing VOC-limitation for HCHO/NO<sub>2</sub> < 1(Duncan et al., 2010).

#### 2.5 ECHAM/MESSy Atmospheric Chemistry (EMAC) model

EMAC is a 3D general circulation model that includes a variety of sub-models to describe numerous processes in the troposphere, their interaction with oceans and land surfaces and incorporates anthropogenic influences. Here we use the second development cycle of the Modular Earth Submodel System (MESSy2) (Jöckel et al., 2010) and ECHAM5 (Röckner et al., 2006) which is the fifth generation European Centre Hamburg general circulation model in the T106L31 resolution (corresponding to a quadratic grid of roughly 1.1° and 1.1°). The model has 31 vertical pressure levels and involves the complex organic chemistry mechanism MOM (Mainz Organic Mechanism) as presented by Sander et al. (2019) that includes further

developments of the version used by Lelieveld et al. (2016b). Here we use the lowest pressure level in a terrain following

315 coordinates (equivalent to the surface level) and simulations of NO, NO<sub>2</sub>, O<sub>3</sub>, OH, HO<sub>2</sub>,  $j(NO_2)$  and  $j(O^1D)$ . The sum of peroxy radicals was estimated as the sum of all radicals R<sub>i</sub>O<sub>2</sub> with less than four carbon atoms. Net ozone production based on data retrieved from EMAC was estimated as

 $NOPR = [NO] \cdot (k_{NO+HO_2}[HO_2] + \sum_i k_{NO+R_iO_2}[R_iO_2]) - [O_3] \cdot (\alpha \cdot j(O^1D) + k_{OH+O_3}[OH] + k_{HO_2+O_3}[HO_2]).$ (8) A list of all included peroxy radicals  $R_iO_2$  for the reaction with NO is given in the supplementary Table ST10.

#### 320 3 Results and discussions

#### 3.1 NO<sub>x</sub> and O<sub>3</sub> in the MBL around the Arabian Peninsula

During AQABA NO<sub>x</sub> mixing ratios varied over three orders of magnitude with lowest values of less than 50 ppt<sub>v</sub> observed in relatively pristine regions and highest values of more than 10 ppb<sub>v</sub> found in the vicinity of areas with strong anthropogenic influence or nearby passing ships. Ozone mixing ratios ranged from values of less than 20 ppb<sub>v</sub>, detected over the Arabian Sea,

- to more than 150 ppbv during episodes of severe pollution. Figures 3a) and 3b) show distributions of NOx measured during the first and second leg of the campaign (range from 0.1 ppbv to 20 ppbv) while Figure 3c) and 3d) show corresponding ozone mixing ratios covering a range from 20 ppbv to 100 ppbv, respectively. A classification of the different regions based on Box-Whisker-Plots, including the 25-75-percentile interval (box) and whiskers for the 10-90-percentile interval, is shown in Figure 4 and Figure 5 for NOx and O3, respectively. As average NOx is often influenced by fresh, localized emissions, we have
- 330 included the median (black bar) instead of the average in the Box-Whisker-Plot for NO<sub>x</sub>, which is less sensitive to extreme values. For O<sub>3</sub>, although the difference between median and mean is mostly negligible, we also use the median in Figure 5. NO<sub>x</sub> and O<sub>3</sub> averages, medians, standard deviations, 1<sup>st</sup> and 3<sup>rd</sup> quantiles and the number of data points quantified per region are given in the supplementary Table ST3. See supplementary Figure S4 for OH and preliminary HO<sub>2</sub> mixing ratios around the Arabian Peninsula. Supplementary Figure S5 shows that absolute humidity observed during AQABA ranges from lowest
- 335 values of less than 1 % observed in the Suez Golf during the first leg to about 3 % observed during both legs in the southeastern part of the Arabian Gulf and in the Strait of Hormuz. Although observing highest absolute humidity on both legs in the southeastern part of the Arabian Gulf, absolute humidity was very low on the first leg near Kuwait, where absolute humidity was about 1 %. These air masses were brought from the Kuwait/Iraq area into the MBL of the Arabian Gulf on the first leg, whereas a change of wind direction for the second leg resulted in winds coming from Iran area with moister air. For the rest

340 of the cruise, absolute humidity mixing ratio was about 1.5 % with variations being generally less than 0.5 %.



Figure 3: Ship cruises with color-scaled NO<sub>x</sub> mixing ratios (logarithmic scale) a) during the first and b) the second leg and colorscaled O<sub>3</sub> mixing ratios (linear scale) c) during the first and d) during the second leg. Note that both NO<sub>x</sub> and O<sub>3</sub> has been filtered for own stack contamination.



Figure 4: Comparison of measured (blue) and simulated (green) NO<sub>x</sub> mixing ratios 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.



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Figure 5: Comparison of measured (blue) and simulated (green) O<sub>3</sub> mixing ratios 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.

Overall, we find that NO<sub>x</sub> mixing ratios over the Northern Red Sea, the Gulf of Oman and the Arabian Gulf are approximately one order of magnitude higher than in the other three regions (Southern Red Sea, Arabian Sea, Mediterranean). NO<sub>x</sub> medians over the Arabian Gulf, the Northern Red Sea and the Gulf of Oman are 1.26 ppb<sub>v</sub>, 1.76 ppb<sub>v</sub> and 2.74 ppb<sub>v</sub>, respectively. Lower median NO<sub>x</sub> mixing ratios were measured over the Southern Red Sea (0.46 ppb<sub>v</sub>), the Mediterranean (0.25 ppb<sub>v</sub>) and the Arabian Sea (0.19 ppb<sub>v</sub>). With respect to observed O<sub>3</sub> mixing ratios, the Arabian Sea is the only region representing remote MBL conditions with lowest median and average O<sub>3</sub> of 21.5 ppb<sub>v</sub> and 22.5 ppb<sub>v</sub> respectively, followed by the Gulf of Oman where median and mean O<sub>3</sub> were 31.5 ppb<sub>v</sub> and 34 ppb<sub>v</sub>, respectively. The low O<sub>3</sub> mixing ratios over the Arabian Sea were

accompanied by the smallest variability (whisker-interval: 15.1 ppb<sub>v</sub>). Although observing highest NO<sub>x</sub> over the Oman Gulf,  $O_3$  observed over the Oman Gulf was amongst the lowest detected throughout the whole campaign, which can partly be explained the fact that high NO<sub>x</sub> eventually leads to ozone destruction. The immediate vicinity of point sources in this region,

365 which leads to higher NO<sub>x</sub> (before it is lost by reaction with OH and deposition to the surface) and titration of O<sub>3</sub> (note the relatively low regional O<sub>3</sub> median of 31.5 ppb<sub>v</sub>), may partly explain why NO<sub>x</sub> was highest over the Gulf of Oman. However, a significantly larger whisker-interval of observed ozone of 31.4 ppb<sub>v</sub> 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 ppbv when wind was coming from Kuwait/Iraq. Please note that during

- 370 the second leg wind was coming from Iran (Pfannerstill et al., 2019). The whisker-interval over the Arabian Gulf was 100.9 ppb<sub>v</sub>, more than six times higher than that over the Arabian Sea. Reasons for large variations of both NO<sub>x</sub> and O<sub>3</sub> 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<sub>v</sub>, 64.2 ppb<sub>v</sub> and 46.9
- 375 ppb<sub>v</sub>, respectively. The whisker-intervals over the Northern Red Sea and the Southern Red Sea were 44.2 ppb<sub>v</sub> and 31.6 ppb<sub>v</sub>, respectively. Air masses over the Mediterranean were characterized as photochemically aged due to their impact by northerly winds (Etesians) which bring processed/oxidized 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<sub>v</sub> in ozone. In summary, median NO<sub>x</sub> over the Oman Gulf was 56 % and 117 % higher than
- 380 over the Northern Red Sea and the Arabian Gulf, respectively. However, the highest  $NO_x$  average was measured over the Northern Red Sea at 4.69 ppb<sub>v</sub>, similar to the values observed over the Oman Gulf (4.16 ppb<sub>v</sub>) and the Arabian Gulf (3.65 ppb<sub>v</sub>). Note that highest  $NO_x$  mixing ratios over the Oman Gulf and over the Northern Red Sea are not always associated with high  $O_3$  mixing ratios. We find that average ozone was highest over the Arabian Gulf with 74 ppb<sub>v</sub> followed by the Northern Red Sea region (63.4 ppb<sub>v</sub>). The average ozone mixing ratio over the Oman Gulf was 34 ppb<sub>v</sub>, which corresponds to 46 % of
- 385 the value observed over the Arabian Gulf. Photochemically aged air masses over the Mediterranean Basin show an ozone average of 61.6 ppb<sub>v</sub> and air masses encountered over the Northern Red Sea (O<sub>3</sub> median of 64.2 ppb<sub>v</sub>, O<sub>3</sub> average of 63.4 ppb<sub>v</sub>) are comparable to the Arabian Gulf.

Due to a number of large pollution sources in the region around the Arabian Peninsula such as passing ships, highly urbanized areas as well as on- and off-shore petrochemical processing, NO<sub>x</sub> levels were rarely as low as those found in remote locations 390 such as over the South Atlantic (Fischer et al., 2015) where NO<sub>x</sub> levels may be under 20 ppt<sub>v</sub>. Apart for a few occasions where  $NO_x$  was below 50 ppt<sub>v</sub> for short periods (Arabian Sea, the Southern Red Sea and the Mediterranean),  $NO_x$  levels during AQABA generally ranged from 100 ppt<sub>v</sub> up to several ppb<sub>v</sub>. The campaign NO<sub>x</sub> median of 0.65 ppb<sub>v</sub> and mean value of (2.51  $\pm$  5.84) ppb<sub>v</sub> is comparable to urban sites (Kleinman et al., 2005). A detailed emission density analysis performed by Johansson et al. (2017) shows that NO<sub>x</sub> emissions on and around the Arabian Peninsula are amongst the highest worldwide, which could 395 explain the rather high NO<sub>x</sub> level in the MBL around the peninsula (Johansson et al., 2017; Pfannerstill et al., 2019).  $O_3$  mixing ratios measured during AQABA were also very variable with  $O_3$  mixing ratios ranging between less than 20 ppb<sub>v</sub> in the remote MBL (Fischer et al., 2015) to 60-70 ppby in the Mediterranean (consistent with previous ship-based measurements in the region (Kouvarakis et al., 2002) and as high as 150 ppb<sub>v</sub> measured over the Arabian Gulf region. 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 400 the Houston Ship Channel (Mazzuca et al., 2016).

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Figure 4 also shows that the general trend for NO<sub>x</sub> mixing ratios in the different regions is widely reproduced by the EMAC model. We find that the median NO<sub>x</sub>(model)/NO<sub>x</sub>(measurement)-ratio of all five minute averaged data points of the whole campaign is 0.91, indicating that the model underestimates NO<sub>x</sub> by roughly 10 %. The average ratio and its standard deviation are significantly larger at 2.57 and 5.71, respectively, indicating that single modeled data points strongly exceed the

- 405 measurements, especially during periods of low in situ  $NO_x$  (see supplementary Figure S6). Particularly over the Arabian Sea and the Southern Red Sea, the model generally simulates  $NO_x$  mixing ratios higher than 100 and 200 ppt<sub>y</sub>, respectively while the measurements indicate mixing ratios of less than 50 ppt<sub>v</sub> for certain periods. Furthermore, as expected, the model is not able to reproduce point sources such as passing ships for which we observe a significant underestimation of the measured  $NO_x$ . For ozone we find that the median  $O_3$ (model)/ $O_3$ (measurement)-ratio throughout the campaign is 1.23, indicating that over the
- 410 course of the campaign the model overestimates  $O_3$  by about 23 %. This could partly be related to the same limitation, i.e. the inability of the model to resolve point sources in which  $O_3$  is locally reduced due to titration by NO. While the model is in rather good agreement with the measurements over the Mediterranean, the Northern Red Sea and Southern Red Sea, large deviations are found over the Arabian Sea and the Oman Gulf, where the model overestimation with respect to the regional median is 63 % and 75 %, respectively. A possible explanation for the overestimation of both ozone and  $NO_x$  in pristine regions
- 415 such as over the Arabian Sea and the Oman Gulf could be related to the model resolution of  $1.1^{\circ} \times 1.1^{\circ}$ . Interpolation of model simulations along the Kommandor Iona ship track close to the coast at this resolution will most likely incorporate contributions from nearby land areas, affected by anthropogenic emissions. See supplementary Table ST3 and Table ST4 for further information and Figure S6 and S7 for additional scatterplots of measured and simulated regional median  $NO_x$  and  $O_3$ , respectively.

#### 420 3.2 Estimation of RO<sub>2</sub> around the Arabian Peninsula

Noontime  $RO_2$  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 NO<sub>2</sub> typically ranged from 1-2 minutes during AQABA) and for fast changes in the actinic flux, we have calculated Box-Whisker-Plots for  $\pm$  2 h around noontime for which we expect relatively minor changes in the actinic flux (Figure 6). The noontime of each day 425 was approximated by applying a Gaussian fit routine to the measured  $i(NO_2)$  values whereas  $i(NO_2)$  values being less than 10<sup>-</sup> <sup>3</sup> s<sup>-1</sup> were neglected. Due to the availability of OH and HO<sub>2</sub> data from 18 July 2017 onwards, we have limited the analysis to this period. Note that there are no noontime RO<sub>2</sub> estimates from 18 July to 21 July due to contamination by the ship exhaust and on 24 August 2017 due to missing data. The black bar in Figure 6 indicates the median value, with the Box-interval marking the 25- and 75-percentile and the whisker showing the 10- and 90-percentile. Figure 7 shows summarized regional trends of the RO<sub>2</sub> estimates for measured and simulated data.

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Figure 6: Timeline of median RO<sub>2</sub> noontime estimates from 22 July to 31 August 2017. Due to contamination by the ship exhaust itself, there is no data from 18 July to 21 July 2017. See annotations for the classification of the different regions.



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Figure 7: Comparison of Box-Whisker-Plots of the regional estimated noontime RO<sub>2</sub> median based on measured data and simulated RO<sub>2</sub> data for the period from 18 July 2017 onwards.

The relative uncertainty  $R([RO_2])$  associated with the RO<sub>2</sub> estimate has been calculated by error propagation of Eq. 3.

$$440 \quad R([RO_{2}]) = \frac{1}{[RO_{2}]} \cdot \sqrt{\left(\frac{\Delta j(NO_{2}) \cdot [NO_{2}]}{k_{NO+HO_{2}} \cdot [NO]}\right)^{2} + \left(\frac{\Delta [NO_{2}] \cdot j(NO_{2})]}{k_{NO+HO_{2}} \cdot [NO]}\right)^{2} + \left(\frac{\Delta [O_{3}] \cdot k_{NO+O_{3}} \cdot [NO]}{k_{NO+HO_{2}} \cdot [NO]}\right)^{2} + \left(\frac{\Delta [O_{3}] \cdot k_{NO+O_{3}} \cdot [NO]}{k_{NO+HO_{2}} \cdot [NO]}\right)^{2} + \left(\frac{\Delta [O_{3}] \cdot k_{NO+O_{3}} \cdot [NO]}{k_{NO+HO_{2}} \cdot [NO]}\right)^{2} + \left(\frac{\Delta [O_{3}] \cdot k_{NO+O_{3}} \cdot [NO]}{k_{NO+HO_{2}} \cdot [NO]}\right)^{2} + \left(\frac{\Delta [O_{3}] \cdot k_{NO+O_{3}} \cdot [NO]}{k_{NO+HO_{2}} \cdot [NO]}\right)^{2} + \left(\frac{\Delta [O_{3}] \cdot k_{NO+O_{3}} \cdot [NO]}{k_{NO+HO_{2}} \cdot [NO]}\right)^{2} + \left(\frac{\Delta [O_{3}] \cdot k_{NO+O_{3}} \cdot [NO]}{k_{NO+HO_{2}} \cdot [NO]}\right)^{2} + \left(\frac{\Delta [O_{3}] \cdot k_{NO+O_{3}} \cdot [NO]}{k_{NO+HO_{2}} \cdot [NO]}\right)^{2} + \left(\frac{\Delta [O_{3}] \cdot k_{NO+O_{3}} \cdot [NO]}{k_{NO+HO_{2}} \cdot [NO]}\right)^{2} + \left(\frac{\Delta [O_{3}] \cdot k_{NO+O_{3}} \cdot [O_{3}]}{k_{NO+O_{3}} \cdot [O_{3}] \cdot k_{NO+O_{3}} \cdot [O_{3}]}\right)^{2} + \left(\frac{\Delta [O_{3}] \cdot k_{NO+O_{3}} \cdot [O_{3}]}{k_{NO+O_{3}} \cdot [O_{3}] \cdot k_{NO+O_{3}} \cdot [O_{3}]}\right)^{2} + \left(\frac{\Delta [O_{3}] \cdot k_{NO+O_{3}} \cdot [O_{3}]}{k_{NO+O_{3}} \cdot [O_{3}] \cdot k_{NO+O_{3}} \cdot [O_{3}]}\right)^{2} + \left(\frac{\Delta [O_{3}] \cdot k_{NO+O_{3}} \cdot [O_{3}]}{k_{NO+O_{3}} \cdot [O_{3}] \cdot k_{NO+O_{3}} \cdot [O_{3}]}\right)^{2} + \left(\frac{\Delta [O_{3}] \cdot k_{NO+O_{3}} \cdot [O_{3}]}{k_{NO+O_{3}} \cdot [O_{3}] \cdot k_{NO+O_{3}} \cdot [O_{3}]}\right)^{2} + \left(\frac{\Delta [O_{3}] \cdot k_{NO+O_{3}} \cdot [O_{3}]}{k_{NO+O_{3}} \cdot [O_{3}] \cdot k_{NO+O_{3}} \cdot [O_{3}]}\right)^{2} + \left(\frac{\Delta [O_{3}] \cdot k_{NO+O_{3}} \cdot [O_{3}]}{k_{NO+O_{3}} \cdot [O_{3}] \cdot k_{NO+O_{3}} \cdot [O_{3}]}\right)^{2} + \left(\frac{\Delta [O_{3}] \cdot k_{NO+O_{3}} \cdot [O_{3}]}{k_{NO+O_{3}} \cdot [O_{3}] \cdot k_{NO+O_{3}} \cdot [O_{3}]}\right)^{2} + \left(\frac{\Delta [O_{3}] \cdot k_{NO+O_{3}} \cdot [O_{3}]}{k_{NO+O_{3}} \cdot [O_{3}] \cdot k_{NO+O_{3}} \cdot [O_{3}]}\right)^{2} + \left(\frac{\Delta [O_{3}] \cdot k_{NO+O_{3}} \cdot [O_{3}]}{k_{NO+O_{3}} \cdot [O_{3}] \cdot k_{NO+O_{3}} \cdot [O_{3}]}\right)^{2} + \left(\frac{\Delta [O_{3}] \cdot k_{NO+O_{3}} \cdot [O_{3}]}{k_{NO+O_{3}} \cdot [O_{3}] \cdot k_{NO+O_{3}} \cdot [O_{3}]}\right)^{2} + \left(\frac{\Delta [O_{3}] \cdot k_{NO+O_{3}} \cdot [O_{3}]}{k_{NO+O_{3}} \cdot [O_{3}] \cdot [O_{3}]}\right)^{2} + \left(\frac{\Delta [O_{3}] \cdot k_{NO+O_{3}} \cdot [O_{3}]}{k_{NO+O_{3}} \cdot [O_{3}] \cdot [O_{3}]}\right)^{2} + \left(\frac{\Delta [O_{3}] \cdot [O_{3}]}{k_{NO+O_{3}} \cdot [O_{3}]}\right)^{2}$$

Over the course of the campaign, the median relative  $RO_2$  uncertainty is 56 %. The average is 132 % and heavily biased by single data outliers and therefore not representative. The relative error associated with the  $RO_2$  calculation is hence estimated at 56 %. Note that our calculation assumes that errors in the used rate coefficients are negligible.

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We find median noontime RO<sub>2</sub> mixing ratios over the Mediterranean, the Northern Red Sea, the Southern Red Sea, the Arabian Sea and Oman Gulf of 16 ppt<sub>v</sub>, 28 ppt<sub>v</sub>, 15 ppt<sub>v</sub>, 33 ppt<sub>v</sub> and 22 ppt<sub>v</sub>, respectively, with each respective 75-percentile RO<sub>2</sub> being equal or less than 54 ppt<sub>v</sub>. Only over the Arabian Gulf, the RO<sub>2</sub> estimate yields a median noontime mixing ratio of 73 ppt<sub>v</sub> accompanied by the largest variations in the box-interval of the whole campaign. While the box-interval of the RO<sub>2</sub> estimate in the other regions is 25-57 ppt<sub>v</sub>, the box-interval over the Arabian Gulf is significantly higher at 165 ppt<sub>v</sub>. Negative values for all regions are regularly found in the vicinity of fresh emissions and air masses not in photochemical equilibrium. The elevated 90-percentile over the Arabian Sea is due to high RO<sub>2</sub> estimates during the first leg on 22 and 23 July.

Estimated  $RO_2$  mixing ratios based on measured tracer data are in general agreement with previous studies performed in marine boundary layer environments which report maximum mixing ratios between 30 and 55 ppt<sub>v</sub> around noontime (Hernandez et al., 2001). As peroxy radicals are short-lived molecules generated from the oxidation of VOCs, enhanced  $RO_2$  concentrations observed over the Arabian Gulf are most likely due to high VOC emissions from intense oil and gas activities in the region

- 455 (Bourtsoukidis et al., 2019; Pfannerstill et al., 2019). However high HO<sub>2</sub> and RO<sub>2</sub> can also occur in aged air masses with low NO<sub>x</sub> and VOCs but still significant O<sub>3</sub> (and perhaps HCHO whose photolysis would then yield peroxy radicals). Bourtsoukidis et al. report that spatial volume mixing ratios of ethane and propane over the Arabian Gulf were about a factor of 10-15 times higher than over the Arabian Sea and the Southern Red Sea (Bourtsoukidis et al., 2019). We find that the median noontime RO<sub>2</sub>(measurement estimate)/HO<sub>2</sub>(measurement)-ratio throughout the whole campaign is 1.88. Note that during single days,
- 460  $HO_2$  may be higher than the  $RO_2$  estimate, which is within the uncertainty of the  $RO_2$  estimate.

EMAC modelled, median noontime RO<sub>2</sub> mixing ratios estimated as the sum of simulated HO<sub>2</sub> and all simulated peroxy radicals with less than four carbon molecules are 41 ppt<sub>v</sub>, 46 ppt<sub>v</sub>, 38 ppt<sub>v</sub>, 41 ppt<sub>v</sub>, 50 ppt<sub>v</sub> and 49 ppt<sub>v</sub> over the Mediterranean, the Northern Red Sea, the Southern Red Sea, the Arabian Sea, the Oman Gulf and the Arabian Gulf, respectively. The observation based RO<sub>2</sub> estimate yields 16 ppt<sub>v</sub>, 28 ppt<sub>v</sub>, 15 ppt<sub>v</sub>, 33 ppt<sub>v</sub>, 22 ppt<sub>v</sub> and 73 ppt<sub>v</sub> respectively. We find that the median point by point RO<sub>2</sub>(model)/RO<sub>2</sub>(measurement estimate)-ratio from 18 July onward is 1.05 so that, on average, the model overestimates the measurement by 5 %. Please note that the observational variability is much higher than the modeled one and that the median of 1.05 is accompanied by a larger average (1.84) and a large variability (42.51). See supplementary Table ST5 and ST6 for further information and Figure S8 for an additional scatterplot of measured and simulated regional median RO<sub>2</sub>.

#### 3.3 Net ozone production rates around the Arabian Peninsula

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- 470 In the following, net ozone production rates (at noon) are calculated based on Eq. 7 for the different regions. These noontime values are scaled to diurnal production rates (Figure 8). As photochemical net ozone destruction 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  $4/0.461 \approx 8.68$  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  $\Delta s \approx 6$  %. Due to contamination
- 475 by the own ship exhaust and due to the availability of OH and  $HO_2$  data only from 18 July 2017 onwards, we have limited the analysis to the period from 22 July 2017 to 31 August 2017. A comparison of NOPR estimated based on measured and simulated data for the different regions is shown in Figure 9. A break-down of the different terms of Eq. 7 in the six regions is included in the supplementary Figures S10-S13.



480 Figure 8: Timeline of the diurnal NOPR from 22 July to 31 August 2017. NOPR calculations are limited to the time period from 22 July onwards due to missing HO<sub>x</sub> data and contamination by the ship exhaust itself before this period. See annotations for the classification of the different regions.



485 Figure 9: Diurnal net ozone production rates in the different regions. Related to the magnitude of pollution sources, the lower whisker of the NOPR estimate over the Oman Gulf is -324 ppb day<sup>-1</sup>.

The relative uncertainty associated with the NOPR estimate has been calculated by error propagation of Eq. 7.

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$$R(\text{NOPR}) = \frac{1}{\text{NOPR}} \cdot \left( \begin{pmatrix} k_{\text{NO}+\text{HO}_2} \cdot [\text{NO}] \cdot \Delta[\text{RO}_2] \end{pmatrix}^2 + (k_{\text{NO}+\text{HO}_2} \cdot \Delta[\text{NO}] \cdot [\text{RO}_2] \end{pmatrix}^2 + (\Delta[\text{O}_3] \cdot (\alpha \cdot j(\text{O}^1\text{D}) + k_{\text{OH}+\text{O}_3} \cdot [\text{OH}] + k_{\text{HO}_2+\text{O}_3} \cdot [\text{HO}_2] ) \end{pmatrix}^2 + (\Delta j(\text{O}^1\text{D}) \cdot [\text{O}_3] \cdot \alpha)^2 + (j(\text{O}^1\text{D}) \cdot [\text{O}_3] \cdot \Delta \alpha)^2 + (\Delta j(\text{O}^1\text{D}) \cdot [\text{O}_3] \cdot \alpha)^2 + (\Delta [\text{HO}_2] \cdot k_{\text{HO}_2+\text{O}_3} \cdot [\text{O}_3] )^2 + (\Delta [\text{OH}] \cdot k_{\text{OH}+\text{O}_3} \cdot [\text{O}_3])^2 + (\Delta [\text{HO}_2] \cdot k_{\text{HO}_2+\text{O}_3} \cdot [\text{O}_3])^2 \right)^2$$

Incorporating a relative error of 56 % associated with RO<sub>2</sub>, the median of the relative NOPR error of all data points obtained during AQABA is 69 %. The average relative uncertainty of NOPR is 15 % and strongly biased by single data outliers, which are in the case of NOPR significantly negative (due to fresh emissions and titration of O<sub>3</sub> by NO). Again the median is a more representative measure for the general uncertainty associated with the NOPR calculations. The relative error associated with

the NOPR estimates based on measured data is hence estimated at 69 %.

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Over the Mediterranean and the Southern Red Sea, NOPR values do not significantly deviate from zero (production equals loss) within the atmospheric variability. The best estimate indicates slight net ozone destruction for the Mediterranean and Southern Red Sea (- 1 ppb day<sup>-1</sup>) and (- 4 ppb day<sup>-1</sup>) respectively, and slight net production for the Arabian Sea (5 ppb day<sup>-1</sup>), which is significantly positive within the variability of the box-interval. Variations in NOPR calculated as the width of the 25-75-percentile-box yield comparable values of 9-11 ppb day<sup>-1</sup> for these three regions. Substantial net ozone production was inferred over the Oman Gulf, the Northern Red Sea, and the Arabian Gulf with the median values being 16 ppb day<sup>-1</sup>, 16 ppb day<sup>-1</sup> and 32 ppb day<sup>-1</sup>, respectively. Especially over the Red Sea we find a strong latitudinal gradient in net ozone production rates with higher values towards the northern end, while slight net ozone destruction of -4 ppb day<sup>-1</sup> is reported over the 505 southern part.

NOPR estimates for the Oman Gulf, the Northern Red Sea and the Arabian Gulf are comparable to results reported for dense traffic shipping routes such as the Houston Ship Channel with NOPR of a few tens of ppb h<sup>-1</sup> for periods of severe pollution (Zhou et al., 2014). Similar net ozone production rates have been reported for regions of Beijing in summer 2006 (Lu et al., 2010). For regions with low anthropogenic influence such as the Southern Red Sea and the Arabian Sea we estimate net ozone production that does not differ significantly from zero. This is due to the rather low NO<sub>x</sub> mixing ratios in the clean marine boundary layer (Bozem et al., 2017). Note that we calculated net ozone destruction only for a few days over the Southern Red Sea and the Arabian Sea, indicating that the marine boundary layer around the Arabian Peninsula is rarely free from anthropogenic influence owing to the multitude of on- and off-shore anthropogenic activities.

We find that model-calculated estimates of NOPR reproduce the trends observed for NOPR calculated from in situ 515 measurements except over the Mediterranean and the Southern Red Sea. 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 the model in these regions. In the model, pollution emissions, especially over the Oman Gulf and the Arabian Gulf, seem to be averaged over a large (1.1° grid size) region. High background concentrations of

- 520 ozone precursors hence contribute to net ozone production rates that compare to conditions observed in the Houston case (Zhou et al., 2014). Even in the more pristine regions such as over the Southern Red Sea and the Arabian Sea, the model is not able to reproduce net ozone destruction, which is consistent with the fact the ozone is generally too high and that  $NO_x$  levels below 0.1 ppb<sub>v</sub> are not found in the model. See supplementary Table ST7 and ST8 for further information and supplementary Figure S9 for an additional scatterplot of measured and simulated regional NOPR.
- 525 Measured OH and HO<sub>2</sub> as well as RO<sub>2</sub> estimated based on measured data are generally underestimating the concurrent simulated data. Speaking in terms of absolute amounts, we find that the break-down loss and productions terms of Eq. 7 (NOPR) based on measured data are generally underestimating the results based on simulated data. The deviations between measurement and model pretty much represent the differences observed in the noontime concentrations of the mentioned tracers. Largest deviations of the break-down loss terms, associated with reactions of O<sub>3</sub> with OH and HO<sub>2</sub>, are found over the
- 530 OG and AG, where also OH and HO<sub>2</sub> is significantly overestimated in the model. In the case of  $j(0^{1}D) \cdot \alpha \cdot [0_{3}]$  a slight overestimation by the estimate based on simulated data compared to the estimate based on measured data is observed. This is due to simulated absolute humidity being slightly larger than the concurrent measured data. Also we find that the break-down production term  $k_{NO+HO_{2}} \cdot [NO] \cdot [RO_{2}]$  estimated based on simulated data is generally larger than the estimate based on measured data. This pretty much reflects that noontime RO<sub>2</sub> is overestimated in the model by a factor of 2, except for the 535 Arabian Gulf where fair agreement is found.

## 3.4 VOC- and NO<sub>x</sub>-sensitivity

Ozone is photochemically formed when the precursors NO<sub>x</sub> and VOCs are abundant in the presence of sunlight (Bozem et al., 2017; Jaffe et al., 2018). In order to determine whether a chemical system is NO<sub>x</sub>- or VOC-limited or in a transition between those two regimes, one has to estimate the total amount of OH reactivity towards VOCs and towards NO<sub>x</sub>. Therefore the VOC/NO<sub>x</sub>-ratio is an important indicator of the behavior of NO<sub>x</sub>, VOCs and O<sub>3</sub> in a system. Since it is not feasible to precisely define all ambient VOCs (could be thousands), formaldehyde mixing ratios have been used as a proxy for the OH reactivity towards VOCs since it is a short-lived oxidation product of many VOCs that is often positively correlated with peroxy radicals

- (Sillman et al., 1995; Duncan et al., 2010). Sillman et al. first used afternoon concentrations of indicator species such as HCHO and total reactive nitrogen (NO<sub>y</sub>) to determine the sensitivity of ozone production to VOCs or NO<sub>x</sub> (Sillman et al., 1995). Their
   approach was later successfully transferred to space-based satellite observations by using the ratio of tropospheric columns of
- HCHO and NO<sub>2</sub> to determine the sensitivity of ozone production (Martin et al., 2004). Here we use HCHO/NO<sub>2</sub>-ratios (referred to as "Ratio") deduced by Duncan et al. as indicators for the sensitivity of ozone production to NO<sub>x</sub>- and VOC-limitations in

megacities in the United States with large amounts of anthropogenic  $NO_x$  and VOC emissions (Duncan et al., 2010). The Ratio is an indicator of surface photochemistry as most of the atmospheric column of HCHO and  $NO_2$  is located in the planetary

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boundary layer (Duncan et al., 2010). Duncan et al. have derived  $NO_x$ -limited ozone production regimes for HCHO/NO<sub>2</sub> > 2 and VOC-limited ozone production for HCHO/NO<sub>2</sub> < 1 (Duncan et al., 2010). For 1 < HCHO/NO<sub>2</sub> < 2 both NO<sub>x</sub> and VOC emission reductions may lead to a reduction in ozone. Figure 10 shows the Box-Whisker-Plot classification of the HCHO/NO<sub>2</sub>-ratio of the different regions during noontime.



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Figure 10: Box-Whisker-Plots of the HCHO/NO<sub>2</sub>-ratio for the different regions with the black bar indicating the median value. Red (ratio = 2) and green (ratio = 1) lines indicate the limits for HCHO/NO<sub>2</sub> deduced by Duncan et al. (2010) for NO<sub>x</sub>-limitation and VOC-limitation, respectively.

- 560 Median HCHO/NO<sub>2</sub>-ratios of 5, 7.7, 9.4 and 9.3 over the Mediterranean, the Southern Red Sea, the Arabian Sea and the Arabian Gulf respectively indicate tendencies towards  $NO_x$ -limited regimes. In a previous study based on measured OH reactivity, Pfannerstill et al. classified these regions as being mostly in a transition between  $NO_x$ - and VOC-limitation, with a tendency towards  $NO_x$ -limitation (2019). Median HCHO/NO<sub>2</sub>-ratios of 1.4 and 2.2 estimated over the Northern Red Sea and the Oman Gulf signify tendencies towards VOC-limitation. However, none of the medians of the six regions falls below the
- 565 VOC-limit deduced by Duncan et al. (2010).

Over the Red Sea we find a latitudinal gradient in the HCHO/NO<sub>2</sub>-ratio, similar to the gradients for NO<sub>x</sub> and NOPR. Due to very low NO<sub>x</sub> over the Southern Red Sea,  $O_3$  production is NO<sub>x</sub>-limited, changing into a more VOC-limited regime over the Northern Red Sea. Ozone production over the Mediterranean was classified as rather NO<sub>x</sub>-limited, however partly being in the transition regime between NO<sub>x</sub>- and VOC-limitation, which can be explained by measurements obtained on 29 August 2017

- 570 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.  $NO_x$  limitation is also inferred for the relatively clean Arabian Sea and the polluted Arabian Gulf atmosphere. Note that a further increase in  $NO_x$ -emissions from 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 575 in ozone production for this region, as observed for the Oman Gulf (median HCHO/NO<sub>2</sub>-ratio of 2.2 and average  $O_3$  of 34
- ppb<sub>v</sub>). See supplementary Table ST9 for detailed statistics on regional HCHO/NO<sub>2</sub>-ratios.

#### **4** Conclusion

- In situ observations of NO, NO<sub>2</sub>, O<sub>3</sub>, HCHO, OH, HO<sub>2</sub>, absolute humidity, actinic flux, temperature and pressure were carried out in the marine boundary layer around the Arabian Peninsula during the AQABA ship campaign from late June to early September 2017. Concentration ranges of both NO<sub>x</sub> and O<sub>3</sub> clearly showed anthropogenic influence in the MBL. NO<sub>x</sub> was highest over the Arabian Gulf, the Northern Red Sea and the Oman Gulf. Lowest NO<sub>x</sub> was observed over the Arabian Sea and over the Southern Red Sea during the second leg. O<sub>3</sub> mixing ratios were highest over the Arabian Gulf. We observed a latitudinal gradient in O<sub>3</sub> concentrations with higher values towards the northern part of the Red Sea. Although comparable O<sub>3</sub>
- 585 averages were measured over the Northern Red Sea and over the Mediterranean, lower variability over the Mediterranean towards the end of August 2017 indicates photochemically more extensively aged air masses. The lowest regional O<sub>3</sub> mixing ratio average was detected over the Arabian Sea, which is broadly comparable to remote marine boundary layer conditions in the Northern Hemisphere.
- Noontime RO<sub>2</sub> estimates based on deviations from the Leighton Ratio yield median values around the Arabian Peninsula amount to 15 – 33 ppt<sub>v</sub> for all regions except over the Arabian Gulf where the median is 73 ppt<sub>v</sub>. The uncertainty due to the missing up-welling actinic flux portion is expected to be insignificant. Furthermore, we estimated noontime and diurnal NOPR based on Eq. 6 and the integral over the actinic flux. Highest diurnal NOPR were observed over the Oman Gulf, the Northern Red Sea and the Arabian Gulf with median values of 16 ppb<sub>v</sub> day<sup>-1</sup>, 16 ppb<sub>v</sub> day<sup>-1</sup> and 32 ppb<sub>v</sub> day<sup>-1</sup>, respectively, which is in agreement with previous studies that predicted net photochemical O<sub>3</sub> formation conditions in the region. Net ozone destruction
- 595 was only observed for a few days with clean conditions over the Arabian Sea and the Southern Red Sea. Based on HCHO/NO<sub>2</sub>ratios our analysis suggests tendencies towards NO<sub>x</sub>-limitation over the Mediterranean, the Southern Red Sea, the Arabian Sea

and the Arabian Gulf and VOC-limitation over the Northern Red Sea and the Oman Gulf, which reproduces the trends observed by Pfannerstill et al. (2019).

NO<sub>x</sub> results from the atmospheric chemistry – general circulation model EMAC underestimate the measurement data by 10 % whereas median modeled O<sub>3</sub> overestimates the measurement by 23 %, the latter being related to limitations in model resolution in coastal proximity and near shipping lanes. Although EMAC generally reproduces regional NO<sub>x</sub> and O<sub>3</sub> medians, the scatter when comparing both data sets is large. NO<sub>x</sub> is generally too low as it does not resolve local point sources and too high for clean regions. Lowest NO<sub>x</sub> of less than 0.1 ppb<sub>v</sub> found in the in situ measurements is not reproduced by the model as emissions are averaged over a large area (1.1°). Median noontime RO<sub>2</sub> retrieved from the EMAC model are ~ 5 % higher than RO<sub>2</sub>

605 estimates based on measurement data, however, the RO<sub>2</sub> sum deduced from EMAC is sometimes about a factor of 2 higher than the regional RO<sub>2</sub> estimate based on the Leighton Ratio and measured tracer data. NOPR estimates based on modeled data reproduce the tendencies derived from the measurements very well. However, the model does not reproduce observed net ozone destruction along some clean parts of the ship cruise.

#### Data availability

610 Data used in this study is available to all scientists agreeing to the AOABA protocol at https://doi.org/10.5281/zenodo.3693988.

#### **Author contributions**

IT, HF and JL designed the study. UP and IT performed the CLD NO and  $NO_2$  measurements and processed the data. JC and PE performed the  $O_3$  measurements, JS performed the actinic flux measurements. JS performed cavity ring-down spectroscopy

615 measurements of NO<sub>2</sub>. DD and BH performed the HCHO measurements. HH, MM, RR, ST performed the OH and HO<sub>2</sub> measurements. J-DP was responsible for the H<sub>2</sub>O measurements. Model simulations were made by AP. All authors have contributed to writing this manuscript

#### **Competing interests**

The authors declare no conflict of interest.

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625 like to thank the whole AQABA community for a successful campaign.

## Appendix: Acronyms and abbreviations

## General

630	AQABA	<u>A</u> ir <u>Q</u> uality and Climate in the <u>A</u> rabian <u>Ba</u> sin campaign
	CyI	The <u>Cy</u> prus <u>Institute</u>
	KAUST	King Abdullah University of Science and Technology
	KISR	Kuwait Institute for Scientific Research

## Regions

635	AG	<u>A</u> rabian <u>G</u> ulf
	AS	<u>A</u> rabian <u>S</u> ea
	Μ	Mediterranean Sea
	NRS	Northern <u>R</u> ed Sea
	OG	<b>O</b> man <u>G</u> ulf
640	SRS	<u>S</u> outhern <u>R</u> ed <u>S</u> ea

## Scientific

	CLD	Chemiluminescence detector
	CRDS	<u>Cavity</u> ring-down spectroscopy
	ECHAM5	Fifth generation <b>E</b> uropean <b>C</b> entre <b>Ham</b> burg general circulation model
645	EMAC	ECHAM/MESSy Atmospheric Chemistry model
	FWHM	<u>F</u> ull <u>w</u> idth at <u>h</u> alf <u>m</u> aximum
	GC-FID	<u>Gas chromatography – flame ionization detector</u>
	HORUS	$\underline{\mathbf{H}}$ ydr $\underline{\mathbf{O}}$ xyl $\underline{\mathbf{R}}$ adical measurement $\underline{\mathbf{U}}$ nit based on fluorescence $\underline{\mathbf{S}}$ pectroscopy instrument
	HO <sub>x</sub>	$OH + HO_2$
650	LED	Light emitting diode
	LIF	Laser induced fluorescence
	MBL	<u>M</u> arine <u>b</u> oundary <u>l</u> ayer
	MESSy	<u>M</u> odular <u>E</u> arth <u>S</u> ubmodel <u>Sy</u> stem
	NOPR	<u>Net ozone production rate</u>
655	NO <sub>x</sub>	$NO + NO_2$
	PFA	<u>P</u> er <u>f</u> luoro <u>a</u> lkoxy
	PSS	Photostationary steady state
	PTFE	Polytetrafluoroethylene
	SLM	<u>S</u> tandard <u>l</u> iter per <u>m</u> inute
660	STEAM3	<u>Ship</u> <u>Traffic</u> <u>E</u> mission <u>A</u> ssessment <u>M</u> odel 3
	TMU	<u>T</u> otal <u>m</u> easurement <u>uncertainty</u>
	VOC	<u>V</u> olatile <u>o</u> rganic <u>c</u> ompounds
	UV	<u>U</u> ltra <u>v</u> iolet

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