Author's Response to Referee #1

In this response, the referee comments (in black) are listed together with our replies (in blue) and the changes to the original manuscript (in red).

Summary: The authors present reactive nitrogen measurements from the recent AQABA campaign, a ship-based summertime field campaign in the Mediterranean Sea, Red Sea, and the Arabian Gulf. Using a thermal dissociation cavity ring down spectrometer, they measure NOx (NO + NO2) and other reactive nitrogen species NOz (HNO3 + HONO + pNit + ClNO2 + N2O5 + others). Using these measurements and other auxiliary observations, they derive mean NO2 concentrations and lifetimes, cumulative NO2 losses during the day and night, and mean ozone production efficiencies. They also use back trajectories and ratios of NOz / NOy and NO2 / SO2 to attribute their observations to local ship emissions, near-coast industrial activities, and longer range transport.
This is a very well put together manuscript. The results are robust and thorough, and very useful for the community, especially given the lack of in situ data in the Red Sea and Arabian Gulf. I would recommend publication, following a few minor edits/suggestions for the authors first.

We thank the referee for the positive assessment of our paper and the helpful comments, which we address in the following responses.

General comments:

In the abstract (i.e. page 1 line 15) and in the methods section (i.e. page 5, line 18), the TD-CRDS instrument is presented as the primary instrument for both NOx and NOz, but it seems that the NOx measurements are all from the CLD instrument, which should be clarified. Also, were the NOz measurements derived from NOy – NOx(CRDS) or NOy – NOx(CLD)?

The lifetime and loss of NO_x sections (i.e. 3.1.3, 3.2.3, and 3.3.3) rely on the CLD measurements. We have clarified this by adding a statement to the abstract, and by dedicating a separate methods sub-section to the CLD instrument. NO_z mixing ratios, however, were always derived from NO_y – NO_x (TD-CRDS). The NO_x vs. SO_2 correlations are also based on the TD-CRDS measurements.

Abstract: Complementing the TD-CRDS measurements, NO and NO_2 data sets from a chemiluminescence detector (CLD) were used in the analysis.

Sect. 2.2: NO and NO_2 were measured with a chemiluminescence detector (CLD 790 SR, ECO Physics, 5 s time resolution) as described in Tadic et al. (2020), with total measurement uncertainties of 6 % (NO) and 23 % (NO_2) and detection limits of 22 pptv for NO and 52 pptv for NO_2, both calculated at a time resolution of 5 s and a confidence interval of 2σ. The CLD detection method is based on the chemiluminescence of electronically excited NO_2^* formed in the reaction of NO with O_3. Ambient NO_2 is photolytically converted to NO by exposure to UV light from LEDs emitting at wavelengths close to 398 nm. The CLD was calibrated very six hours using a 2 ppmv NO gas standard.

What was the methodology used to select the sub-regions in each Sea? Were they grouped together by eye? By some kind of filter? By similar HYSPLIT back trajectories? I ask because it looks like there is some data that is not considered in any of the sub-regions. If the sub-regions were selected by eye, I worry that it would bias the results in the paper to more “extreme” values, because that’s what stands out most. Was there any attempt to do some kind of statistical analysis to group together regions with similar chemistry/emissions influence?

For the Mediterranean Sea, the sub-regions were selected based only on having homogeneous NO_z/NO_y ratios. For the Red Sea and the Arabian Gulf, the definition of sub-regions was limited by the availability of TD-CRDS data, but also by other measurements of individual NO_z components (e.g. gaps in ONs data set).
The overall goal was not to draw up a NO_y budget for each point along the route, but to point out and contrast substantial changes in the chemical regimes in the different sub-regions. Concerning the sub-region definition, we added a short statement in Sect. 3.1.2:

The choice of these sub-regions was based on the existence of homogeneous NO_z / NO_y ratios over periods of hours to days. This approach enabled us to compare sub-regions with substantially different chemical regimes along the ship track, but does not lend itself to the derivation of a representative NO_y budget for the entire region.

Related to the previous comment, do those sub-regions include an entire diurnal cycle? Do each of the sub-regions capture the same segment(s) of the diurnal cycle? If not, have the authors considered how this may change the relative contribution to NOz of the various species?

Not all sub-regions cover an entire diurnal cycle, the time frames vary between 4 (M1) and 46 hours (RS1) in length, with an average of 16 hours. In none of the major NO_z components (pNit, HNO_3, ONs), were pronounced diurnal patterns observed. We therefore argue that any diurnal patterns in NO_z and the NO_z composition are overshadowed by the variability of air mass sources and the multi-component-nature of NO_z. We re-emphasize that the fractional contributions to NO_y are to be considered as coarse estimates.

The data availaible in each sub-region did not always cover an entire diurnal cycle, which will have an impact on the fractional contributions of individual NO_y species (see differences between day- and nighttime chemistry in Sect. 1). We argue however, that diurnal patterns in NO_y are likely overshadowed by the variability of air mass sources. The NO_y compositions presented are thus to be considered as coarse estimates.

Specific comments:

Page 4, Line 21: How long is the inlet upstream of the TD? Is there any concern about “sticky” gases such as HONO or HNO3 being trapped in the inlet walls before entering the TD?

The air samples reached the TD less than 30 cm behind the tip of the inlet.

Air samples reached the TD area less than 30 cm behind the tip of the inlet and we expect negligible inlet losses for NO_y species.

Page 5, Line 14: The authors later explain that PM1 comes from the AMS instrument, but since that's in the next section, it's a bit unclear here whether the PM1 measurement is coming from the OPC.

We have now clarified that both PM_{10} and PM_1 are derived from the OPC.

[…](both PM_1 and PM_{10} were measured with the OPC).

Page 5, Line 33: Does the CIMS instrument output a HNO3 or a HONO measurement, even if uncalibrated? Can that signal be correlated with the calculated HNO3 or the LOPAP HONO measurement?

No, during AQABA the CIMS was not configured to monitor HNO_3 or HONO.

Page 6, Line 11: What is the path length of the HONO instrument? Is it co-located with the other instruments?

We added these pieces of information:

The path length of the instrument was 1.9 m, and the inlet was also located on the foredeck of the ship in ca. 5 m distance to the TD-CRDS inlets.

Page 6, Line 26: Were HYSPLIT back trajectories calculated at all locations along the ship track, or just those representative locations shown in the figures?

The back trajectories start at the geographical centers of the sub-regions. We also generated back trajectories starting at the ship's location 4 hours before/after passing these points to confirm that no changes in the general directions of the air mass origins occurred. For clarity of the graphs we chose to include only one trajectory per sub-region. We added in Sect. 3.1.2:

For visual clarity, only the back trajectories starting at the geographical centres of the respective sub-regions are displayed in Fig. 3. Back trajectories starting at the ship's location 4 hours before or after confirmed that the air-mass origin was very similar.

Page 9, Line 23: Here and in a few other places, regions are described as being "influenced by land-based" pollution. However, it seems that depending on how populated the land is, "land-based" can either mean free from fresh emissions, or heavily influenced by fresh emissions. Can the authors clarify, or perhaps use terminology that describes the regions in terms of their influence from fresh emissions, either ship- or land-based?

When using this or similar terms, we refer to pollution sources. The text now reads:

[…] are influenced by ~~land-based pollution~~ fresh emissions from landbased sources […]

Page 17, line 12: […] the land-based emission sources of NO_x from urban/ industrialised areas gain in importance […]

Page 10, Line 11: Figure 4c doesn't really show the averaged NOx lost per day and per night, just the cumulative. Can the authors add those numbers to the figure, perhaps under the legend, or remove the reference to that figure in this line?

Average day- and nighttime losses have been added to the legends of Figures 4c, 8c and 12c.

Page 17, Line 20: How do the authors define "background mixing ratios of NOx" here?

We have added a definition. In this and in previous sections we also identified background conditions by filtering out data points where the NO_z / NO_y ratio was below a certain threshold.

Background conditions refer to NO_x mixing ratios found during periods when ship plumes were rarely encountered. "Background" NO_2 varied from region to region and was e.g. 50-150 pptv in the Mediterranean Sea).

Page 20, Line 5: How are OPE and NOPR defined differently here? It's a little unclear how these two parameters relate to each other.

We have added an explanation which distinguishes more clearly between the two metrics, at the place where we first compare OPE to NOPR results:

In contrast to the OPE, NOPR accounts for the total amount of O_3 produced in one day, considering production (governed by the formation of NO_2 via reactions of NO with HO_2 and RO_2) and loss (via photolysis and reaction with OH or HO_2). The OPE, on the other hand, focusses on the product side and assesses the competition between O_3 formation and sequestering into NO_z from a given initial level of NO_x. By approximating the O_3 production rate via the NO_2 formation from NO reactions with HO_2 and RO_2, the NOPR thus neglects the alternative branch leading to NO_z.

Figure 14: The fitted light for the Eastern Mediterranean (light blue) is very difficult to see over the experimental data.

The colour has been changed to a darker tone.

References

Tadic, I., Crowley, J. N., Dienhart, D., Eger, P., Harder, H., Hottmann, B., Martinez, M., Parchatka, U., Paris, J. D., Pozzer, A., Rohloff, R., Schuladen, J., Shenolikar, J., Tauer, S., Lelieveld, J., and Fischer, H.: Net ozone production and its relationship to nitrogen oxides and volatile organic compounds in the marine boundary layer around the Arabian Peninsula, Atmos. Chem. Phys., 20, 6769-6787, 10.5194/acp-20-6769-2020, 2020.