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Interactive comment on "Shipborne measurements of total OH reactivity around the Arabian Peninsula and its role in ozone chemistry" *by* Eva Y. Pfannerstill et al.

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Dear Referee,

We thank you for your constructive and helpful comments. They are addressed below and in the new version of the manuscript (attached together with the updated Supplement):

Page 5 L15, what is the exact frequency to change the PTFE filter? It should be stated.

The frequency has been added to the text: "*A PTFE (polytetrafluoroethylene) filter*, *changed weekly (and additionally after intense particle contamination events such as dust storms), prevented contamination of the sub-sampling line by particles or sea spray."*

2. Page 5 L17-21, The interference by NO, NO2 and O3 toward the total OH reactivity (kOH) measurements determined in the lab on average seems to be quite different from those of the total OH reactivity comparison experiments presented by Fuchs et al., 2017. Details of the lab experiments shall be presented in this paper (maybe partly in the supporting materials) so that the measurement quality of the data is with higher transparency. The highest correction 7.4 s-1 at high NOx is actually comparable to the observed values. In this case, it might be useful to present a frequency distribution of the corrected kOH as the high Nox conditions seems to be frequently encountered during this ship campaign as shown by Figure 1.

The corrections for NOx and ozone are, for the same pyrrole/OH ratios and NOx/ozone concentrations, comparable to those during the intercomparison described in Fuchs et al. (2017). However, the conditions during AQABA were usually different from that chamber based study, which naturally leads to differences in the resulting corrections. Ozone values were in the Arabian Gulf larger than ever tested during the intercomparison. A frequency distribution of the fraction of total OH reactivity due to this correction can now be found in Fig. S1 (attached). A description of the laboratory experiments has been added to the Supplementary Information as well. The following additions to the text were made:

"Ozone, NO and NO2 interferences were quantified in the laboratory (details of the experiments can be found in Sect. S1). NO2 loss and conversion to NO in the mass flow controller during tests was monitored by an NO/NO2 analyzer (Two-channel-chemiluminescence detector). The combined NO, NO2 and ozone corrections amounted to a median of ˜24 % of total OH reactivity or an average of 0.36 ± 0.19 ppb

of pyrrole over the whole campaign, which equals ≈ 1.9 s^{-1}, with a maximum absolute correction of 1.39 ppb (7.4 s^{-1} / 27 % of total OH reactivity) under the influence of closely located ship emissions (high NOx). A frequency distribution of the corrected fraction of total OH reactivity is displayed in Fig. S1."

The following addition was made to the Supplement:

" S1. Laboratory characterizations of NO, NO2 and ozone interferences

S1.1 NO interference

To quantify the NO interference, NO from a standard gas cylinder (Air Liquide, Krefeld, Germany) was added to the CRM system running in C2 mode at pyrrole/OH ≈ 2.0. The mixing ratios of the added NO were ˜0, 5, 10, 15, 20, 30, 90, 140, 170, 220, 350 ppb. The resulting decrease in pyrrole mixing ratio (ΔC3 in ppb) vs. the NO mixing ratio resulted in a polynomial relationship of the form $\Delta C3 = a[NO]^2 + b[NO]$. During AQABA: a ≈ -3E-4; b ≈ 0.17.

S1.2 NO2 interference

To quantify the NO2 interference, NO2 from a standard gas cylinder (Westfalen AG, Münster, Germany) was added to the CRM system running in C2 mode at pyrrole/OH ≈ 2.0. All tubes were flushed with NO2 for several hours and the contact of the NO2 with metal surfaces (pressure reducer, mass flow controller) was reduced to a minimum to avoid losses. To quantify the amount of NO2 lost/converted to NO in the setup used, conversion to NO was monitored by an NO/NO2 analyzer (Two-channel-chemiluminescence detector). 8−12 % of the NO2 was converted to NO depending on the flows and mixing ratios used. This loss was corrected for when calculating the NO2 mixing ratios in the reactor. The mixing ratios of the added NO2 were ˜0, 20, 40, 60, 100 ppb. The resulting decrease in pyrrole mixing ratio (ΔC3 in ppb) vs. the NO2 mixing ratio resulted in a polynomial relationship of the form $\Delta C3 = a[NO2]^2 + b[NO2]$.

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During AQABA: a ≈ -2E-4; b ≈ 0.08.

S1.3 Ozone interference

Using an ozone generator (Thermo 49C O3 Calibrator, Thermo Environmenal Instruments LLC, Franklin, USA), ozone was added to the CRM system running in C2 mode at pyrrole/OH ≈ 2.0. Ozone mixing ratios used were ˜ 0, 20, 30, 45, 90, 130, 180, 260, 350 ppb. The resulting decrease in pyrrole mixing ratio (ΔC3 in ppb) vs. the O3 mixing ratio resulted in a linear relationship of the form ΔC3 = a[O3]. During AQABA: a ≈ 0.0058. “

3. Page 5 L23-25, are these test hydrocarbons representative for the air masses characterized in this study?

We agree that it is important to use test hydrocarbons that are relevant for the air masses seen in the study area. This is why we carefully evaluated the use of the available gas standards for calculating the correction factor. It is especially important to cover the relevant range of reaction rate constants of trace gases with OH, because this strongly impacts the correction for deviation from pseudo first order. Therefore we included isoprene despite its low abundance in the area, as some alkenes with fast reaction rate constants towards OH were observed. The explanation of this correction was extended in the manuscript:

“The calculation of total OH reactivity with the CRM equation assumes pseudo-1st-order conditions inside the reactor, which can, however, not be met while preserving a reasonable sensitivity (C3–C2 difference). The correction for deviation from pseudo-1st-order conditions inside the reactor was derived from empirical test gas measurements adapted from the approach in Michoud et al. (2015). The deviation from pseudo-1st-order depends on the pyrrole/OH ratio and on the reaction rate con-

stant of the measured trace gas towards OH. Especially, trace gases with fast reaction rates (comparable to that of pyrrole) require the largest correction because their concentration inside the reactor decreases at a similar rate as that of pyrrole, leading to an underestimation of their reactivity. Such gases, namely alkenes, were present during AQABA (e.g. a C5H8-alkene which was not isoprene). This is why we did not use an average correction factor for all gas mixes as in Michoud et al. (2015), but we applied a correction where the composition of the air mass is taken into account.Test gases used were toluene (for aromatics correction), isoprene and propene (for alkenes correction), propane and cyclohexane (correction for other species). These test gases are representative of the relevant trace gases and ranges of reaction rate coefficients observed during AQABA. In test experiments, these trace gases were added to the CRM system in known amounts, i.e. known total OH reactivities, at pyrrole/OH ratios representative for the campaign. The correction factors resulting from comparing the observed reactivity with the expected reactivity were weighted according to the measured composition of the ambient air at the moment of observation (. . .)"

Full details of the method are available in the cited papers.

4. Page 10 L17, I don't quite understand how can be the ratio of the C3 carbonyls toward that of propane can be used as an indicator of oxidation state. The C3 carbonyls can be produced from larger NMHCs from propane and the degradation products can be C2 and C1 carbonyls. As the lifetime of C3 carbonyls and propane is different by one order of magnitude, the ratio is not good to characterize the oxidation state. It is probably still better to relay on the ratio of toluene to benzene or xylene to toluene for the analysis of the oxidation state.

On reflection we agree that only one indicator for the oxidation state of the air mass is not enough. Therefore, we now added two more: toluene/benzene as suggested by the reviewer, and C5 carbonyls vs. pentanes. The latter were chosen because a far weaker contribution to C5 carbonyls via the fragmentation of higher hydrocarbons is expected (see e.g. Master Chemical Mechanism), and the pentanes and their oxidation products have similar lifetimes. Even for C3, we consider the fragmentation a minor influence on the measured C3 carbonyls. We thank you for this suggestion because the two new ratios add information to the manuscript:

In Sect. 3.1.2: "*The C3 carbonyls vs. propane (C_3H_8), C5 oxidation products ($C_5H_{10}O$) vs. pentanes (C_5H_{12}) and toluene vs. benzene ratios (Table 1) were used here as indicators of the oxidation state (and, thereby, the extent of photochemical ageing) of the air. We note that this approach is based on the assumption that production of the carbonyls by oxidation dominates over direct emission, although some direct combustion emissions cannot be excluded. The toluene vs. benzene relationship is based on the assumption of simultaneous emission of both compounds. Notably, a distinct difference between northern (less oxidized, $[C_3H_6O]/[C_3H_8] \approx 1.9$ and $[C_5H_{10}O]/[C_5H_{12}] \approx 1.3$) and southern Red Sea (oxidized, $[C_3H_6O]/[C_3H_8] \approx 9.4$ and $[C_5H_{10}O]/[C_5H_{12}] \approx 1.9$) was observed.* "

In Sect. 3.2.1:

"Here, emission sources were closest to the point of observation, which was reflected in highest total OH reactivity (median: 18.8 s^{-1}, average $\pm$ standard deviation: 18.7 $\pm$ 7.9 s^{-1}) and low C3carbonyls/propane and high toluene/benzene ratio medians of 0.3 and 0.8, respectively. In contrast, OH reactivity in the air originating from Iran was lower (median: 9.8 s^{-1}, average $\pm$ standard deviation: 10.8 $\pm$ 3.4 s^{-1}), with a slightly higher C3carbonyls/propane and a lower toluene/benzene ratio (both 0.4). "

In Sect. 3.2.1:

"The upper part of the graph shows indicators of the photochemical age of the air mass. The $[C_3H_6O]/[C_3H_8]$ ratio decreases and the toluene/benzene ratio increases when getting closer to Kuwait, meaning that the research vessel was approaching the emission sources (refineries, oil platforms). Both these indicators show opposite patterns, as expected. The $[C_5H_{10}O]/[C_5H_{12}]$ ratio follows the $[C_3H_6O]/[C_3H_8]$ ratio

except for an increase towards Kuwait, which shows that the fresh emissions observed here were richer in propane than in pentanes, and indicates a mix of fresh emissions with aged air masses."

In Sect. 3.2.2: *"The toluene/benzene ratio was between 1 and 3, indicating fuel combustion emissions as a source in Suez City and/or from ships, rather than biomass burning which tends to be richer in benzene."*

5. Page 10 L29-30, what is the detection limit of the used total OH reactivity instrument?

We added this information to the text: " *Total OH reactivity measured over the Arabian Sea during AQABA was with a median of 4.9 s^{-1} (average ± standard deviation: 5.6 ± 2.0 s^{-1}) below the detection limit of 5.4 s^{-1}.*"

6. Sect. 3.5.1 the ozone production regime is analyzed using the ratio of the OH reactivities of VOCs to that of NOx. This is plausible but not accurate enough as the primary production rate of ROx radicals will influence the ozone production regime as well.

And since the NO2/NO ratio may be different for different VOCs/NOx ratio, the ozone production regime could still be different even under same VOCs/NOx ratio. So I suggest the influence of the ROx primary production rates (e.g. O3, HONO and carbonyls photolysis, etc) as well as the influence of the NO2/NO ratio shall be further analyzed.

The analysis of ozone production regimes as we present it here was developed by Kirchner et al. (2001). The authors of this method took into account the NO2/NO, HONO and ROx influences and extensively explain why the lifetime ratios of VOC/NOx (the inverse being daytime OH reactivities of NOx/VOC) are valid for distinguishing

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between the different regimes. They also characterized the method in a modelling study which showed that this indicator of ozone production regimes performs better than other commonly used ones (e.g. NOy, O3/NOz). To make this clearer, we added the following to the text: *"The method and underlying chemistry has been extensively evaluated for different conditions and compared to other methods in Kirchner et al. (2001). The amount of peroxy radicals produced by VOC oxidation is linked to the OH reactivity of VOCs (. . .). Only data at daytime (06:00–18:00 local time) was considered, because the method inherently is limited to daytime chemistry."*

Thanks to your comment regarding the NO2/NO ratio, we realized that we can only use daytime values to assess the ozone production in a meaningful way. Therefore we have updated Fig. 9 (attached) accordingly.

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