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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,

Thank you very much for your constructive and helpful comments. We addressed them in the new version of the manuscript (attached with tracked changes) and below (changes in green):

Page 1, line 30: Please state the measurement uncertainty. Does this result imply that oxidation products of primary emissions have been measured in this campaign or that contributions to the OH reactivity from oxidation products is

low in this region?

It is a good idea to mention the uncertainty early in the manuscript, so we added it to the abstract. The contribution of oxidized species was measured as comprehensively as possible by PTR-ToF-MS and was relatively large, as we state earlier in the abstract: "Due to the rapid oxidation of direct volatile organic compound (VOC) emissions, oxygenated volatile organic compounds (OVOCs) were observed to be the main contributor to OH reactivity around the Arabian Peninsula ($9-35$ % by region)."

Changes made: We now report the "*measurement uncertainty (50%)*".

Page 4, line 15: Is there any impact of the length or the heating of the inlet on the trace gases sampled? While wall losses of gases may be reduced by heating, are there any other effects that need to be considered? Have any experiments been performed to test that the length and heating of the sampling line do not impact the concentrations of VOCs?

While no inlet loss tests were conducted with this specific inlet, we discuss in Sect 3.4 the probable loss of larger, less volatile VOCs in the inlet line due to its length. A further sentence on this topic has now been added to the methods section as well.

Changes made: "*We assume that the length of the inlet prevented some of the larger, less volatile VOCs from reaching the instruments (see Sect. 3.4).*"

Page 4, line 28: Is the ratio of pyrrole to OH sufficiently high to ensure pseudo-first-order conditions?

No, it is not, as it never is in the CRM approach to OH reactivity. This is why we performed a correction for deviation from pseudo-first-order conditions as described in section 2.4. In order to make this clearer we added the following sentence on p. 4, line 31: *"Because this ratio deviates from pseudo-first order conditions, as is typical for*

CRM, a correction needed to be applied (see Sect. 2.4)."

Page 4, line 31: What was the variability in the measurements of C1?

To clarify the variability observed in C1, we added the average and standard deviation of C1 measurements to the sentence: *"C1 was determined every 5−7 days (average ± standard deviation over the whole campaign: 60.71 ± 1.18 ppb of pyrrole)."*

Page 5, line 5: Please provide a summary of the VOC measurements and limits of detection.

We added this information to the manuscript in Sect. 2.3: *"Average detection limits for the different NMHCs ranged from 1−25 ppt. The NMHC and methane measurements are described in detail elsewhere (Bourtsoukidis et al., 2019). The PTR-ToF-MS was deployed at 60 °C drift temperature, 2.2 mbar drift pressure and 600 V drift voltage (E/N = 137 Td). 1,3,5-trichlorobenzene was fed continuously into the sample stream for mass scale calibration. The time resolution of the measurement was 1 min and background measurements were performed every 3 h for 10 min. The PTR-ToF-MS was calibrated with a multicomponent pressurized gas VOC standard (Apel-Riemer Environmental Inc., Colorado, USA). Mass resolution (full width at half maximum) at 96 amu ranged between ˜3500 and ˜4500. Average detection limits for the compounds measured by PTR-ToF-MS ranged from 1−107 ppt. A full list of the trace gases measured by GC-FID and PTR-ToF-MS can be found in Table S1."*

Page 5, line 20: What is the typical percentage correction in the total reactivity? For the maximum correction of 7.4 s-1, what was the total reactivity?

We made the following addition to the manuscript and added a Figure S1 (attached): *"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."

Page 5, line 26: Please provide some further details explaining the basis for the corrections.

As requested we have now added further details explaining the necessity of the pseudo-1-st-order correction and hope this explains it sufficiently:

"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 constant 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.

Page 6, lines 8-13: Please consider providing supplementary information which includes further details of which species were calibrated using gas standards and which masses have estimated concentrations.

We agree that this is important information and therefore included it into our Supplementary Information in Table S1 even in the initial submission: As indicated at the top of the table, grey shaded compounds were calibrated with gas standards and non-shaded compounds were calibrated with the theoretical approach. To make this clearer, we now added "specified in Table S1" to the text: *"Out of a total of 120 chemical species that were considered for the calculation of speciated reactivity, 42 chemical species (specified in Table S1), including many of the known important contributors to OH reactivity, were calibrated with gas standards and therefore have low uncertainties in their concentrations as well as in their reaction rate coefficients (5−15 %). A further 78 exact masses (specified in Table S1) monitored by PTR−ToF−MS were attributed to molecular formulae "*

Page 6, line 12: 'Formulas' to 'formulae'.

We changed this in the text.

Page 6, section 2.5: Can an estimate of the total uncertainty in the calculated reactivity be provided?

This information is already given in this section: "*The uncertainty of the resulting speciated (i.e. calculated)OH reactivity depends on the fraction of gas-standard calibrated*

compounds in the ambient air at any given point of time and varies between 10 % and 92 %, with an average and median of 45 % over the whole campaign." To further clarify that "speciated" reactivity is the same as calculated reactivity, we added *"(i.e. calculated)"* behind the word "speciated".

Page 10, lines 12-19: The use of the ratio between C3 carbonyls and propane to determine the age of the air mass must assume there are no direct emissions of C3 carbonyls. Please provide some comments on the validity of this assumption.

We agree that we cannot exclude direct emissions of carbonyls. However, when they are emitted together with propane, due to their longer lifetime they will remain present longer, contributing to the ubiquitous carbonyl "background" concentration and therefore later causing a larger C3 carbonyls/propane ratio. Due to the lifetime difference, we still expect a larger ratio in aged air masses than in freshly emitted ones.

Following the reviewer's comment we decided that a single ratio is not enough to indicate the oxidation state of an air mass. Therefore have added two more indicators (toluene/benzene and C5 carbonyls/pentanes). These both show the same general trends from more oxidized to less oxidized, with short sections where some direct emissions are apparent; see Table 1 and this addition to the text: *"The C3 carbonyls (C3H6O) vs. propane (C3H8), C5 oxidation products (C5H10O) vs. pentanes (C5H12) and toluene vs. benzene ratios (Table 1) are used here as an indicator 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, [C3H6O]/[C3H8] ≈ 1.9 and [C5H10O]/[C5H12] ≈ 1.3) and southern Red Sea (oxidized, [C3H6O]/[C3H8] ≈ 9.4 and [C5H10O]/[C5H12] ≈ 1.9) was observed."*

Page 14, section 3.4: Does the extent of missing reactivity correlate with the estimated age of the air masses?

No, there is no trend visible (neither in fraction nor in absolute missing reactivity). We added this information to the text: "*The unattributed reactivity fraction does not correlate with the indicators used for estimating the air mass age.*"