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Comment on acp-2022-580

Anonymous Referee #2

Referee comment on "Formaldehyde and hydroperoxide distribution around the Arabian Peninsula – evaluation of EMAC model results with ship-based measurements" by Dirk Dienhart et al., Atmos. Chem. Phys. Discuss., https://doi.org/10.5194/acp-2022-580-RC2, 2022

The manuscript by Dienhart et al. uses ship-based measurements of HCHO, H2O2, ROOH, OH, and HO2 as well as actinic flux measurements in order to assess the oxidative budget of the marine boundary layer (MBL) around the Arabian Peninsula in Summer 2017. With such limited measurements over the open ocean in the literature, the authors possess a valuable dataset to assess model performance over such regions. The authors use their measurements to assess the general circulation model EMAC and also report nighttime deposition velocity measurements of HCHO and H2O2 over the Mediterranean and Arabian Seas.

General comments: Ship-based measurements are difficult to perform, and so it is very impressive the authors were able to collect a dataset during AQABA of HCHO, H2O2, organic hydroperoxides (ROOH), OH, and HO2. A really decent job was done characterizing the uncertainty of their measurements given the circumstances of being on a ship. More will be discussed in the major revisions section below, but the lack of performing sensitivity tests with the EMAC model (such as by scaling VOC or other ship emissions to see impact on HOx and subsequently H2O2 and HCHO) made the model-measurement comparison of the paper weak. Additionally, several substantial questions arose while reading Section 3.3 when the authors use the net photochemical production/loss of H2O2 to evaluate the discrepancy between measured and modeled HOx. At times, the manuscript reads as a "Measurement Report" as opposed to a "Research Article" for ACP.

While the manuscript fits within the scope of ACP and presents a unique dataset for assessing oxidation chemistry in the MBL, major revisions are necessary when performing the model-measurement comparison, and so I would only recommend publication after the below issues are fully addressed. Authors could also consider turning the manuscript into a Measurement Report.

Major Revisions:

- Abstract: The abstract does not report any quantitative conclusions from the study with several sentences better suited for the introduction as opposed to an abstract. For example, the authors could report their determination of the nighttime deposition

velocities of H2O2 and HCHO over the Mediterranean and Arabian Seas since that would summarize their findings from Section 3.4.

- Line 141: Authors contradict themselves when they state that HCHO "is not removed heterogeneously via deposition" and then in Lines 158-159 say "heterogeneous losses via wet and dry deposition also significantly influence the HCHO distribution". Line 141 is simply incorrect and should be fixed.

- Section 2.7: Authors must mention how EMAC was initialized AND what was the spin up time used in their model runs. Additionally, since HCHO is the tracer generally used to assess recent VOC oxidation, I was surprised the authors had no plots of whether EMAC over or underestimated the VOCs measured during AQABA (Line 290 suggests VOC measurements exist from the campaign). Seeing the VOC data would be helpful when looking at the model-measurement discrepancies of HCHO.

- Lines 330-332: The logic is inconsistent. If it was deemed that HCHO data was contaminated by the ship exhaust plumes and thus should be filtered out, then the same filtering should apply to all other measurements. The authors mention that this contaminated airmass had high NOx levels, which would definitely have impacted the oxidative regime the instruments were sampling at that time. It would be an unfair comparison with EMAC to use measurement data that was known to be contaminated by Kommandor Iona because the model would not be expected to know those ship emissions.

- Line 455: It is vague and qualitative to just conclude that "VOC emissions in the Arabian Gulf need to be adjusted". How much do the emissions need to change? Is the necessary emission change even reasonable? Since the crux of the paper is the model-measurement comparison as stated in the title, then a sensitivity test should be performed and its results fully described by raising VOC emissions in EMAC by say 10% (or some number) and seeing whether that helps to close the discrepancy between the EMAC model and HCHO measurements and how the increased VOC emission impacts model oxidants like OH and HO2.

In fact, no sensitivity tests were performed with the model on any regions in the manuscript. Evaluation of model performance as implied by the title would imply that the model would be run with different initial conditions or settings to see the impact on oxidants.

Section 3.3: The authors are attempting to use H2O2 to evaluate the discrepancy between measured and modeled HOx since the production of H2O2 depends quadratically on HO2 and its photochemical loss linearly on OH. They want to do this by only looking at the effect of photochemistry on the H2O2 mixing ratio (Line 547), or said another way, completely ignoring H2O2 deposition (ignoring the last term in Equation 4).

While there's nothing intrinsically incorrect with Figure 6, I believe there's a grave error in Figure 7 when the authors have to multiply the loss rate constants by the H2O2 mixing ratio (Line 546). The moment a person multiplies by the H2O2 mixing ratio, the assumption that the authors are only looking at effect of photochemistry on H2O2 production and loss breaks down since the H2O2 mixing ratio is the net result of photochemistry, deposition, and transport. I'm not entirely sure if it's justified a priori to say H2O2 deposition is negligible (particularly when one looks at Figure 11; bottom panel for H2O2 nighttime deposition velocities).

There's also an interesting case with the Mediterranean Sea (MS) in Figures 7 and 8 where the net photochemical production agrees yet there are significant model-measurement discrepancies between H2O2, OH, and HO2 mixing ratios in Figures 4 and 5. The authors only say that overestimated model photochemical production of H2O2 in MS is

compensated by elevated losses via reaction with OH (Lines 548-549) so that both model and measurement agree, but could the authors elaborate more and specifically say what's wrong with the HOx budget in the model based solely on looking at MS in Figure 7? Related questions could be asked as well about the other regions.

Revisions:

- Lines 344-352: The reader would be greatly aided by a wind vector plot that shows the direction of where the airmass was coming from at each point for each leg of the campaign. For instance, when looking at points in the Arabian Sea (say in Figure 2), the reader would want to know whether the airmass that was being sampled originated from the open ocean or whether it was continental outflow that maybe was contaminated by other VOCs.

- Lines 354-358: I think more has to be said than just comparing the magnitude of the HCHO mixing ratio to other marine locations. Are the VOCs around the Arabian Peninsula generally larger than the central Indian Ocean (Wagner et al 2001) or the tropical Atlantic (Weller et al 2000)? HCHO is highly dependent on localized VOCs.

- Line 410: "most likely due to missing localized pollution events": It would be helpful to plot out the model-measurement differences along the ship tracks (similar presentation as Figure 2) since this would show whether there was a missing localized pollution event. Conversely, pointing out some examples in the SI plots would be helpful, but the spatial information is lost.

- Line 455 and Line 461: Avoid qualitative statements like "the agreement is quite good" or "even worse". It's completely subjective.

- Line 441: Instead of assuming, can it be shown that the airmass encountered in the Arabian Sea during AQABA originated from the continent, some industrial area, a ship plume, etc.? Can you run a Lagrangian model to get a back trajectory of the airmass? This is important since HCHO over the remote ocean is generally from CH4 oxidation.

- Line 582: Remove "transport" from the section title as it isn't discussed.

Technical Corrections:

- Line 150: Add "recent emissions from" right before the word "anthropogenic activity".

- Line 414: Change "Read" to "Red"

- Line 429: I think the authors meant "though" instead of "tough"?

- Line 507: 16.18.2017 is not a valid date

- Figure 6, 7, 8: Use of L(H2O2) notation. The use of this notation in these figures is not the same as defined in Equation 4 since it doesn't include the deposition term. Either change the notation in Equation 4 or somehow denote that this is photochemical only on the figures themselves.

- Figure 10: Legend needed on all subplots