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# *Interactive comment on* "Measurements of carbonyl compounds around the Arabian Peninsula indicate large missing sources of acetaldehyde" *by* Nijing Wang et al.

**Anonymous Referee #1**

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In this work, Nijing Wang and colleagues presented ship-borne measurements of a number of atmospheric carbonyl compounds around the Arabian Peninsula. During the AQABA campaign in 2017, a comprehensive suite of scientific payload provided the simultaneous measurements of an array of trace gases, including the carbonyl compounds measured using a PTR-MS system. The impacts of oceanic emissions and the oil and gas industry in this region are discussed. The manuscript is aligned with the scope of ACP, and the topic is of interest to the community.

A clear focus is given to acetaldehyde in this manuscript. It has been recognized that in situ measurement techniques of acetaldehyde may be subject to substantial inlet

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artifacts, especially in remote environments. Such artifacts may be related to tropospherically relevant ozone levels and have been reported for the PTR-MS system on research aircraft platforms (e.g., Northway et al., 2004). Compared to airborne measurements, in situ instruments onboard research vessels usually require much longer sampling lines due to logistic reasons; and the ship may had frequently encountered organic-rich air masses (e.g., polluted air, ship exhaust, and marine air with sea spray aerosols and possibly unsaturated organic compounds). The potential inlet artifacts for the ship-borne trace gas measurements have not been thoroughly discussed in many previous ship-borne studies. In this work, the authors presented fairly detailed results and discussion regarding the potential inlet artifacts, and concluded that the inlet artifacts, although cannot be fully ruled out, are unlikely to be significant in this dataset. I do appreciate the efforts the authors have invested in the potential inlet artifacts. Based on the results presented in this manuscript, I cautiously agree with the authors that the inlet artifacts are probably not a huge concern in this work. More thorough inlet tests would provide more information, which should be considered in future cruise deployments.

In addition, a global chemical transport model (EMAC) is used to examine the sources and sinks of these compounds in this region. The modeling component of this work certainly provides valuable insights. A more thorough model evaluation should also be carried out for some of the key precursors of these carbonyl compounds, such as ethane, propane, butanes, etc.

However, the empirical analysis presented in Section 3.2.1 is largely based on fundamentally flawed assumptions, especially for formaldehyde, acetaldehyde, and acetone. I will elaborate this later. This is one major drawback of this study. For this reason, it is my opinion that major revision is needed before publication in ACP. I would recommend the authors remove this section entirely. Or, perhaps some sort of box modeling (e.g., diurnal steady state model constrained to observed hydrocarbons and other measurements available) may be useful.

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The following comments should also been addressed:

Page 1, line 14: "In this study we examine carbonyl compounds (CxHyO), . . ." Clearly the formula CxHyO can be an alcohol, an ether, or an epoxide. I do not think a general formula is useful here.

Page 2, line 47: ". . .important source of free radicals (HOx)" should be hydroxyl radicals here. Also x should be in subscript. Unless the authors have other radicals in mind, in which case it should be more specific.

Page 2, line 48: NOx: please define all abbreviations the first time it appears in the main text. Also x should be in subscript.

Page 2, line 56-57: for the sake of completeness, should cite a few more previous studies here (e.g., Yang et al., 2014; Wang et al., 2019), in which tens of ppt of acetaldehyde were reported in the remote troposphere.

Page 2. Line 59: ". . . in those regions" this can be confusing. Please revise.

Page 4, line 100: VOC container might be misleading here. I'm guessing this is one of the lab containers loaded aboard, but it could be confused with some sort of container for volatile organic compounds.

Page 5, line 144: please provide a bit more info about this spectral radiometer, such as manufacturer, model, etc.

Page 5, line 145: since NMHCs provide vital constraints on the budget analysis in this work, please provide a bit more information here. For example, is this an online or canister-based GC-FID?

Page 5, line 156: I understand that EMAC is a well established model and many key components are archived elsewhere. Given the importance of oceanic emissions in this work, I am sure the readers would appreciate a bit more details, especially how the oceanic emissions are setup/configured for the compounds discussed in this work,

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such as acetaldehyde, acetone, etc.

Page 8, line 210-223: are these carbonyl compounds (i) directly emitted from the oil & gas facilities; (ii) produced from precursors emitted from these facilities; or (iii) associated with other anthropogenic activities in this area?

Page 10, Table 2: I am not entirely sure about the purpose of this table. I understand that the overarching goal here is to put the measurements obtained in this study into the context of previous studies. However, this table itself certainly does not cover the comprehensive characteristics of any of the category. For example, some of the studies cited in the marine category contains clear influence from anthropogenic emissions/biomass burning; none of the cited studies in this category reflects the pristine marine environments, such as tropics, Southern Ocean, etc. For this reason, this table may create wrong impression to the audience. I understand that this is not a review paper, but a more thorough review of the literature is always appreciated. Therefore, I would suggest that the authors compile a slightly more exhaustive list, and be cautious when quoting/discussing the numbers in the literature. I myself find some of the categories are less relevant for this work (e.g., urban, rural, forest), and the marine category can certainly use more details (e.g., coastal vs open ocean, northern vs southern hemisphere, high latitude oceans, natural vs influenced by anthropogenic/biomass burning emissions). I would also recommend the authors add relevant info (e.g., lat/lon) to this table.

Page 9, line 236-237: why do the authors compare the ship-borne measurements obtained in this work to the measurements from a rural site in Cyprus? The numbers may be similar for vastly different reasons. Or do the authors imply a connection with Cyprus? If yes, please clarify & elaborate.

Page 9, line 247-248: note that acetone may deposit into the ocean, especially in the continental outflow from polluted regions (e.g., Marandino et al., 2005; Schlundt et al., 2017; Yang et al., 2014).

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Page 9, line 253: Again, the authors compare the results in Red Sea to that from the other side of the planet (Thompson Farm, a rural site in the US). What is the point of the seemingly random comparison?

Page 11, line 269: are these numbers the sum of all measured unsaturated and aromatic carbonyls?

Page 11, line 293-295: these very general descriptions belong to the introduction section.

Page 11, line 298-299: The first two assumptions do not hold, for the following reasons: (1) Photolysis can be a significant sink for certain carbonyl compounds, such as acetone (Fischer et al., 2012); for formaldehyde it's even the dominant sink (Anderson et al., 2017). (2) Primary emissions contribute substantially to many carbonyl compounds in the atmosphere, such as acetone (e.g., Fischer et al., 2012), acetaldehyde (e.g., Millet et al., 2010). Biomass burning contribution to many of these carbonyl compounds is also substantial, and the authors even discussed the impacts of biomass burning in Section 3.2.2. Therefore, primary emissions certainly cannot and should not be ignored. (3) Dilution (mixing with background air) can lead to rapid decrease of tracer concentrations in freshly emitted plumes. Uptake by the terrestrial vegetation and the ocean may also affect the carbonyl budget on the regional and global scale. The impact of mixing may be cancelled out by scaling the mixing ratios of hydrocarbons and carbonyls to a long-lived compound, such as CO or ethylene, but I cannot think of a simple way to overcome other impacts as I listed above. In addition to the flawed assumptions, the carbonyl yields are not constant and depend on other variables (e.g., NOx levels, oxidation pathways). Table S4 did not clarify how the yields were derived.

Page 12, line 314-319: This exercise is only valid when the ratio in the source region is well understood, which is clearly not the case here. Figure S3 cannot rule out the possibility that there may be air masses with different initial toluene/benzene ratios mixed together. It certainly looks like there are multiple clusters in Figure S3. This

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comes back to my previous question regarding the oil and gas industry in this region: do these measurements reflect (i) direct emissions from the oil & gas facilities; or (ii) co-located (anthropogenic) emissions in this area? This type of photochemical clock does not work without a thorough understanding of the source characteristics.

To sum up, the OH exposure calculation may be useful, provided that the source contributions are well understood. The empirical analysis based on Equation 1 and 2, however, does not really provide scientifically valuable information, definitely not for acetone, acetaldehyde, and formaldehyde.

Page 14, Figure 4: Units for j_NO2 and OH exposure are missing. Same for Figure 5.

Page 14, line 366: "As mentioned before, photochemical oxidation contributed a large fraction to acetone and the larger aliphatic carbonyls over the Arabian Gulf and Suez areas" I think this statement needs stronger support. The terrestrial biosphere may emit a large amount of acetone. Moreover, the acetone yield from terpene oxidation is quite high, and the acetone production from terpenes may not be a huge source globally, but could well be in certain regions. Similarly, some of these compounds may be from anthropogenic sources or biomass burning.

Page 14, line 374-376: The authors concluded that the carbonyls are co-produced via photochemical oxidation because they show strong correlation with ozone. I am not totally convinced. It is plausible that these carbonyls may be co-emitted with ozone precursors.

Page 14, line 358: I noticed that the spatial distribution oil fields and refineries is from the year of 2007, while this cruise campaign was conducted in 2017. Is it possible to obtain more recent information on this?

Page 15, line 405: "The biomass burning emissions were probably transported by on the prevailing northerly wind above Northeast Egypt. . ." is this supported by backward trajectory analysis or meteorological conditions?

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Page 16, Figure 6: this is interesting. how are these not-assigned ions calibrated/quantified?

Page 17, line 449-452: any GC-FID measurements of isoprene during this period?

Page 17, line 460-462: "The model considers direct emissions (such as anthropogenic, biogenic, biomass burning etc.), atmospheric transport and mixing, photochemical production of carbonyls (by OH, O3 and NO3), and physical and chemical removal processes." This belongs to the method section where the model is introduced.

Page 17, line 465-466: "acetone was overestimated by a factor within 1.5 over the Arabian Sea, Gulf of Aden and Gulf of Oman, and underestimated by a factor within 2.5 over the other regions." Note that previous studies reported downward oceanic fluxes of acetone (ocean being a net sink) in the continental outflow from polluted regions (e.g., Marandino et al., 2005; Schlundt et al., 2017; Yang et al., 2014). How does the model treat the air-sea exchange of acetone? This key information is missing.

Page 19, line 504-505: "This indicates that the source of acetaldehyde was probably not from direct biogenic production..." this sentence is confusing. I think "direct oceanic acetaldehyde emissions are probably insufficient to explain..." might be more accurate?

Page 19, line 513-514: "To our knowledge, there is no clear experimental evidence showing the ocean to be a sink for acetaldehyde." This is probably true, but the language is vague (I think "direct" is a better choice than "clear" here), and several important studies are missing here. Schlundt et al. (2017) reported net downward fluxes of acetaldehyde in the polluted marine boundary layer (ocean is a net sink), which is inferred from measurements in the atmosphere and the surface ocean (so not "direct" evidence). Yang et al. (2014) reported oceanic fluxes of acetaldehyde using eddy covariance method (this is direct flux measurements). Indeed the fluxes were mostly upward for acetaldehyde (ocean is a net source), there appears to be a few points indicative of net downward fluxes, although are probably close to the limit detection of

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that system.

Page 21, line 549-554: can the authors please provide new plots like Figure 7 but for other major acetaldehyde/acetone precursors, such as ethane, propane, butanes, and perhaps ethanol as well? This would certainly make the case stronger, and may provide key insight into the acetaldehyde budget in this region. Even “remote” regions in this work are not really that far from the source regions. Therefore it remains unclear to what degree the underestimation/overestimation of carbonyls is due to their precursors. Emission inventories often have a hard time capturing the anthropogenic emissions, especially from the oil and gas industry.

Page 21, line 570: what biomass burning emission inventory is used in this work?

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