Referee 2:

We would like to thank the referee for the detailed review of our manuscript and the highly valuable feedback. The referee's comments (black) our replies (blue) and the resulting modifications to the manuscript (red) are listed below.

The manuscript titled "Measurement report: Observation-based formaldehyde production rates and their relation to OH reactivity around the Arabian Peninsula" reported the shipborne observations of HCHO, OH, and OH reactivity from the Air Quality and Climate Change around in the Arabian Basin (AQABA) campaign in summer 2017. The authors calculated the effective yield of HCHO with total HCHO loss rates, OH and OH reactivity, by assuming a photochemical steady-state of HCHO and analyzed factors (e.g., NOx, VOC speciation, OH reactivity) that potentially impact the effective yield of HCHO. The measurements in the unique environment and the simultaneous measurements of HCHO, OH and OH reactivity will add value to the community but the analysis is not clear and needs major modifications. I'll recommend publication of this manuscript after the authors address my comments below.

Page 1 Line 28: Biogenic is the natural emission from living organisms such as plants and does not include biomass burning. Most HCHO from biogenic sources is secondary produced.

We rewrote the introduction:

P1 L27 – P2 L3:

Formaldehyde (HCHO) is a ubiquitous trace gas that can help provide insight into the dynamical and chemical processes controlling atmospheric composition as an important source of hydroperoxyl radicals (HO_2) (Volkamer et al., 2010; Whalley et al., 2010; Anderson et al., 2017). The global atmospheric distribution of HCHO is dominated by in situ production during the oxidation of volatile organic compounds (VOCs) (Fortems-Cheiney et al., 2012; Anderson et al., 2017), although primary emissions from biomass burning (Akagi et al., 2011; Coggon et al., 2019; Kluge et al., 2020), vegetation (DiGangi et al., 2011), the industry sector (Parrish et al., 2012), shipping (Marbach et al., 2009; Celik et al., 2020) and agriculture (Kaiser et al., 2015) can contribute significantly to the local HCHO abundance.

Page 3 eqn 3 and eqn 4: If you did not use eqn3 to calculate p(HCHO), please state it clearly especially when you provide the detailed information about each term. when you used L(HCHO) in eqn 4 to calculate P(HCHO), would the steady-state assumption hold at zero OH? It is not clear that the intercept can represent additional HCHO sources to VOC oxidation by OH and major question 1 can be addressed. The intercept looks like to be the dry deposition term actually. Please also provide more information about the uncertainties in the dry deposition term.

Thanks a lot for this input, we hope the calculation is now explained more clearly in the manuscript.

In steady-state P(HCHO) = L(HCHO). For the assessment of PSS, we utilized scatter plots (fig.4), which represent the main loss and production processes in clean conditions. Scatter in these plots can be caused by direct emissions of HCHO, advection (transport) and due to deviation from photochemical steady-state (p 9 line 12-15). The additional scatter due to longer lifetime of HCHO (weak solar radiation) would be visible close to zero OH. Most of this data was removed anyway, since we only used daytime data. Some additional scatter is visible in e.g. AS Leg 2 and AG. In general, d(HCHO)/dt was quite small during AQABA as we experienced rather small diurnal variation of HCHO on most days (fig.2), which is also reflected in the total loss of HCHO (fig.3).

We compared the calculated deposition to the intercept b of the scatter plots (Fig. 4, P(HCHO) vs. R(OH)$_{eff}$ x [OH]):

Region	Deposition (average) pptv s^{-1}	Intercept b pptv s^{-1}	Deposition / Intercept %
AS1	0.0015 ± 0.0008	0.009 ± 0.002	16.6
GO	0.0088 ± 0.0046	0.058 ± 0.007	15.2
AG	0.0240 ± 0.0125	0.127 ± 0.050	18.9
AS2	0.0052 ± 0.0027	0.035 ± 0.004	14.8
GA	0.0049 ± 0.0025	0.050 ± 0.013	9.8
RS	0.0016 ± 0.0008	0.014 ± 0.003	11.4
RN	0.0042 ± 0.0021	0.051 ± 0.006	8.2
SU	0.0084 ± 0.0044	0.073 ± 0.015	11.5
MS	0.0053 ± 0.0028	0.038 ± 0.004	13.9

Using literature values for the deposition velocity, we calculate that dry deposition can account for only 8–19 % of the intercept. The deposition velocity would have to be underestimated by a factor of five or more or the BLH would have to be overestimated by a similar factor (or a combination of both).

It is more plausible that the intercept at zero OH is due to additional sources of HCHO such as the photolysis of OVOCs, reactions involving O$_3$ or direct emissions.

P3 L22–25:

In this study we used the PSS assumption to calculate P(HCHO) via its loss reactions:

$$P(HCHO) = L(HCHO) = \left(k_{OH+HCHO} \cdot [OH] + j_{HCHO} + \frac{v_d}{BLH} \right) \cdot [HCHO] \qquad (4)$$

P10 L3–6:

A compact linear relationship is expected under PSS conditions if chemical conditions do not change and the air mass is not affected by transport. While data points that do not fulfill PSS, (e.g. due to sporadic emissions from point sources, or advection of HCHO enriched or depleted air masses) are expected not to follow the regression line, yielding additional scatter.

P13 L22 – P14 L2:

Besides individual data points that do not follow the regression line, the intercept b of the bivariate fit can be interpreted based on Eq. 5 either as an additional loss of HCHO (e.g. wash out, deposition) or as a region wide attribution of additional HCHO sources not related to OH chemistry (P$_{add}$(HCHO), Fig 4). As mentioned above, the effect of wash-out should be negligible, since we only experienced a short rain event on the 12.08.2017 during the night. Using literature values for the deposition velocity in this study (Stickler et al., 2007), we calculate that dry-deposition can account for only 8–19 % of the intercept. The deposition velocity would have to be underestimated by a factor of five or more or the BLH would have to be overestimated by a similar factor (or a combination of both). While the elevated values representing the Arabian Gulf were influenced by the pollution event encountered at the center of the Gulf, the other regions representing enhanced concentrations of air pollution (SU, GO, RN) also show significantly elevated intercepts within their uncertainties (0.051–0.127 pptv s^{-1}) compared to the relatively clean regions (AS, MS, RS), where we determined smaller intercepts b (0.009–0.038 pptv s^{-1}). Additional HCHO production via the ozonolysis of alkenes, indicated by elevated levels of O$_3$ (Tadic et al. 2020) and ethene (Bourtsoukidis et al., 2019), seems very likely in AG and SU. Elevated levels of OVOCs (Wang et al., 2020) and CH$_3$OOH (Dienhart et al., 2021) were also detected in these regions

and thus it is more plausible to use the intercept b as an indicator for additional HCHO production (P_{add}(HCHO)) not related to OH chemistry, although it seems not feasible to use for quantification.

Page 3 line 18: Do you mean photochemical steady-state instead of photo-stationary state? I think photo-stationary state can mean recombination of the photolysis products to form HCHO. Please replace all "photo-stationary state" terms by "photochemical steady-state" throughout the manuscript.

We replaced all photo-stationary state with photochemical steady-state.

The lifetime of HCHO is 2.5 hrs or more in the study. What is the HCHO lifetime at sunset and sunrise? Are they short enough to assume to be in steady-state?

To ensure no great deviation from PSS, only data for which the HCHO lifetime was < 10 hrs were used, although the main production and loss pathways of HCHO both depend on solar irradiation (photolysis and OH production, see also Valin et al., (2016) Fig. 2). In addition, as discussed above we used the scatter plots (Fig. 4) to ascertain whether the PSS assumption is valid.

Page 4 eqn 5: Please define P0(HCHO)

P_0(HCHO) = P_{add}(HCHO); this was a typo from a previous version of the manuscript, thank you.

P4 Eq. 5:

$$\alpha = \frac{P(HCHO) - P_{add}(HCHO)}{[OH] \cdot R(OH)} \tag{5}$$

Page 8 line 17: No stickler et al. (2007) in the reference section

Stickler, A., Fischer, H., Bozem, H., Gurk, C., Schiller, C., Martinez-Harder, M., Kubistin, D., Harder, H., Williams, J., Eerdekens, G., Yassaa, N., Ganzeveld, L., Sander, R., and Lelieveld, J.: Chemistry, transport and dry deposition of trace gases in the boundary layer over the tropical Atlantic Ocean and the Guyanas during the GABRIEL field campaign, Atmos. Chem. Phys., 7, 3933–3956, https://doi.org/10.5194/acp-7-3933-2007, 2007.

Page 9 line 15-18: Is direct emission of HCHO very small compared to unsaturated hydrocarbons in the fresh pollution plume? Please specify the region and time when the fresh pollution plume occurred. The HCHO and ROH in AG leg seem to be high.

Bourtsoukidis et al. 2019 detected the highest mixing ratios of ethene during the pollution event (fig. S13, mean AG 0.788 ppb). At the same time the HCHO mixing ratios approached 12 ppb and O_3 (Tadic et al. 2020), acetaldehyde & acetone (Wang et al 2020) were enhanced. As already indicated in the text, we cannot differentiate between direct HCHO emissions, and HCHO that was formed as the plume was processed during transport from Kuwait / the western coast of the Gulf. The effect of the pollution plume is further discussed in section 4.

P10 L9-11:

The dataset covers a highly polluted event in AG (30.07.2017), although the high HCHO / R(OH) ratio, as well as enhanced Methanol, Acetaldehyde and O_3 mixing ratios (Wang et al., 2020; Tadic et al., 2020) indicate rather processed air masses which could also include primary emissions.

Page 9 line 18-20: Specify which region and time had rainout and which region and time had primary emission.

As already mentioned at page 3 line 30-31 no significant rain events occurred for this study during the AQABA campaign, only a minor precipitation event occurred in AS during night from 11. - 12.08.2017.

The primary emission of HCHO cannot be accurately identified, but we removed obvious pollution events (e.g. in plumes from ships or oil rigs) via co-variance with elevated NO_x, CO and SO_2 mixing ratios.

P10 L9-17:

The dataset covers a highly polluted event in AG (30.07.2017), although the high HCHO / R(OH) ratio, as well as enhanced Methanol, Acetaldehyde and O_3 mixing ratios (Wang et al., 2020; Tadic et al., 2020) indicate rather processed air masses which could also include primary emissions. Primary emission from point sources would likely shift data above the regression line due to the correlation with the HCHO mixing ratio (although this effect can be compensated depending on the OH concentration in emission plumes). The primary emission of HCHO cannot be accurately identified, but we removed obvious pollution events (e.g. in plumes from ships or oil rigs) via co-variance with with elevated NO_x, CO and SO_2 mixing ratios. Furthermore, rainout can affect the relationship, because it would result in data points shifted below the regression line, although this effect can be neglected in this study as only minor precipitation occurred in AS on the 12.08.2017 during night.

Page9 line20- page 10 line 1-2: The intercept may not represent additional HCHO sources because the steady-state assumption does not work at very long lifetime. The intercept can be equal to the dry deposition term.

The intercept (OH = 0) is the result of several processes including additional chemical loss and production, dry-deposition and may also be related to partial break-down of the PSS-assumption when OH is low (e.g. early morning, late evening). The intercept should thus not be overinterpreted and used to e.g. calculate deposition velocities. We only used it as in indicator for the possibility of additional HCHO sources, which is supported by covariance of the intercept with elevated levels of air pollution.

P10 L35 – P11 L4:

Non-zero P(HCHO) at zero [OH] × R(OH), corresponding to the intercept b of the linear regression, can be interpreted as the result of several processes including additional chemical loss and production, dry deposition and may also be related to partial break-down of the PSS assumption when OH is low (e.g. early morning, late evening). The intercept should thus not be overinterpreted and used to e.g. calculate deposition velocities.

Page 10 line 9: How do primary emissions and transport affect the alpha derived here?

Primary emissions of HCHO would result in data shifted towards the y-axis and thus may be partially responsible for the positive intercept on the y-axis. This would also bias the regression analysis and impact on α. Primary emissions of HCHO at low OH would tend to increase the intercept, whereas primary emissions at high OH would bias α to larger values.

P10 L24-31:

The highly elevated P(HCHO) values over the Arabian Gulf (Fig. S2) also include data during a pollution event on the 30.07.2017 in the center of the Gulf (Fig. 2, see also Tadic et al. 2020; Wang et

al. 2020; Pfannerstill et al 2019; Bourtsoukidis et al., 2019). The evaluated α in AG is thus likely influenced by primary emissions or transport of air pollution from the western coast of the Gulf. However, this pollution event seems to be representative for this unique region and thus we did not exclude the data from the study. Primary emissions of HCHO would result in data shifted towards the y-axis and thus may be partially responsible for the positive intercept on the y-axis. This would also bias the regression analysis and impact on α. Primary emissions of HCHO at low OH would tend to increase the intercept, whereas primary emissions at high OH would bias α to larger values.

Page 11 line 12-17 Can primary emission of HCHO also play a role in the highest calculated pHCHO on 30/07/2017 from figure 2?

Yes, as indicated above, primary emissions can bias the derivation of P(HCHO). We decided to keep the data from 30.07.2017 where we encountered air masses in the center of the Arabian Gulf, which included high mixing ratios of HCHO precursors e.g. acetaldehyde, methanol, acetone, ethene etc. NO_x mixing ratios were below 8 ppb and thus while the highly elevated HCHO mixing ratios are a result of photochemical formation, primary emissions can not be ruled out. We added additional information that this data was likely influenced by air pollution transported from the western coast of the Gulf.

P12 L11–13:

P(HCHO) varied between 0 and approximately 1.2 pptv s^{-1}, with values above 0.4 pptv s^{-1} only detected over the Arabian Gulf, which were likely influenced by air pollution transported from the west coast of the Gulf and Kuwait, where oil and gas industries are numerous (Pfannerstill et al., 2019).

Page 12 line 20: which are these three regions mentioned? Please be specific.

Removed this sentence from the manuscript and added additional information about wash out of HCHO.

P13 L22–25:

Besides individual data points that do not follow the regression line, the intercept b of the bivariate fit can be interpreted based on Eq. 5 either as an additional loss of HCHO (e.g. wash out, deposition) or as a region wide attribution of additional HCHO sources not related to OH chemistry (P_{add}(HCHO), Fig 4). As mentioned above, the effect of wash out should be negligible, since we only experienced a short rain event on the 12.08.2017 during the night.

Page 12: As mentioned before, the intercept likely cannot be interpreted as Padd(HCHO) because of the long lifetime at OH=0. Do the intercepts correlate with dry deposition?

See reply to comment above in which the contributions to the intercept are described in more detail.

Page 13 line 13-23. "individual trace gases (R(OH)x) from alkanes (R(OH)alkanes), alkenes (R(OH)alkenes), OVOCs without HCHO" is confusing. Does x represent individual group (e.g., alkanes) instead of individual trace gas? I would expect less VOC species and higher measured R(OH)x to total R(OH) ratio in cleaner or lower ROH environments. No information about the VOCs measurement methods is provided in Section 2. A table of the measured VOC species is needed to understand R(OH)x/R(OH).

Yes, R(OH)$_x$ represents the so-called 'speciated OH reactivity' towards a certain substance class (alkanes, alkenes, OVOCs, aromatics), which were calculated based on the findings of Pfannerstill et al. (2019), although we separated the Arabian Sea in 2 legs. Here we used it to sum up the contributions

towards certain compound classes to identify which regions covered a higher relative contribution of e.g. alkenes (Table 1, Pfannerstill et al. 2019).

We changed p13 line 13-15 to "individual substance classes ($R(OH)_x$, e.g. alkanes, alkenes, OVOCs, aromatics) based on the findings of Pfannerstill et al. (2019). We assume that the unmeasured VOCs are proportional to the measured compounds of a certain compound class, so that these values represent general trends for the VOC oxidation of the subdivided regions."

We also added the VOC measurements to section 2 and the measured VOC species are listed in table S2.

P6 L7–13:

Non-methane hydrocarbons (NMHCs) were measured with two coupled GC–FID systems (GC5000VOC and GC5000BTX; AMA Instruments GmbH, Germany). The GC5000VOC was used for the quantification of light hydrocarbons (C2–C6), while the CG5000BTX was used for the heavier hydrocarbons and aromatics (C6–C8). The NMHCs have average detection limits in the range of 1 – 25 pptv and a total uncertainty in the range of 6 – 13 % (Bourtsoukidis et al., 2019).

OVOCs were detected with a PTR-ToF-MS (8000, Ionicon Analytik GmbH, Innsbruck, Austria) with a total measurement uncertainty in the range of 6 – 17 %, an accuracy of ~ 50 % and 3σ detection limits (derived by background measurements) of 52 ± 26 pptv for acetaldehyde, 22 ± 9 pptv for acetone and 9 ± 6 pptv for methyl ethyl ketone (Wang et al., 2020).

Figure 5: Do you assume the unmeasured VOC groups are proportional to the measured R(OH)alkene, R(OH)alkanes, R(OH)OVOCs, and R(OH)aromatics? What about using the ratio R(OH)x / ROH on the x axis? This sounds the way to go if you want to evaluate the impact of the different VOC groups on HCHO yield alpha.

Thank you for this advice, we changed the x-axis to $R(OH)_x / R(OH)_{eff}$. We also color-coded the z-axis to identify certain regions during AQABA more easily and to check whether a trend with elevated NO_x is visible.

P14 L21–28:

For further analysis, we have recalculated mean OH reactivities ($\pm 1\sigma$ standard deviation) of the individual substance classes ($R(OH)_x$, e.g. alkanes, alkenes, OVOCs, aromatics) based on the findings of Pfannerstill et al. (2019). We assume that the unmeasured VOCs are proportional to the measured compounds of a certain compound class, so that these values represent general trends for the VOC oxidation of the subdivided regions (Table 1). Please note that we removed the reaction of HCHO with OH from the OVOC class, which is usually included when presenting speciated reactivity (see Table 1 in Pfannerstill et al., 2019). The ratio of $R(OH)_x/R(OH)_{eff}$ then represents the relative contribution of a certain compound class to the regional so-called effective reactivity, which reflects the measured VOC oxidation plus unattributed reactivity.

Page 15 line 19-page 16 line 1-2: I think the statement "the role of NOx in HCHO production is ambiguous" does not sound correct based on Wolfe et al. (2016) and Valin et al., (2016). Do you mean HCHO yield instead? The following explanation is also not clear. It is more evident that NO influencing the amount of OH radical can impact the production of HCHO. Explain how NO influencing the amount of OH radical can impact the yield of HCHO.

We improved the discussion about the NO_x dependence of the HCHO production by including the HO_x recycling and discuss the importance of the fate of RO_2 radicals. We also decided to remove fig. 6 from the manuscript, as the AQABA dataset mainly covers modest polluted air masses, covering sufficient levels of NO to induce HCHO instead of peroxide formation. Thus the HCHO

production was more likely limited by the abundance of oxidants and reactive VOCs rather than NO_x.

P17 L32 – P18 L10:

The yield of HCHO can also be interpreted as a function of NO_x levels if there are processes (at low NO) that lead to formation of e.g. peroxides rather than HCHO (Wolfe et al., 2016), this occurs when the recombination of CH_3O_2 radicals is prioritized instead of the reaction with NO to form the methoxy radical CH_3O (Stickler et al., 2006). NO also directly influences the abundance of OH, as it recycles HO_2 radicals to OH (Whalley et al., 2010; Wolfe et al., 2016) and thus elevated NO_x generally increases radical turnover. Valin et al. (2016) found that in isoprene rich regions, the influence of NO_x on HCHO production is primarily due to its feedback on the production of OH. Wolfe et al. (2016) showed that the NO_x dependence mainly affects the so-called prompt yield of isoprene oxidation as a non-linear function of NO_x. In general, the impact of NO_x on HCHO production can be reduced to two factors: radical recycling and the termination of RO_2 radicals (Wolfe et al., 2016). The fact that very clean background MBL air was rarely sampled during AQABA (lowest median NO_x of 0.16 ppbv over AS Leg 2) indicates that we rarely achieved conditions, in which the production of peroxides through the recombination of CH_3O_2 would dominate the production of HCHO through CH_3O_2 + NO. Tadic et al. (2020) also showed that most regions were in the O_3 production regime (signaling sufficient NO), which indicates that the production of HCHO was rather VOC and not NO_x limited.

Page 17 line 10-11: again "photochemical steady-state" instead of "photo-stationary state".

Correction made.

Page 17 Line 11-12: Could you provide potential reasons why the yield of HCHO depends largely on the presence of absolute VOCs levels? This does not have a clear physical meaning to me.

You are right, we removed this part.

P18 L25-27:

The region-wide yield of HCHO (α_{eff}) from reactions of OH differs along the various chemical regimes encountered with lowest values (less than 2 %) deduced over the Arabian Sea during the first leg and the southern Red Sea, and highest values (~ 32 %) over the Arabian Gulf.