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Interactive comment on "Higher measured than modeled ozone production at increased NO$_x$ levels in the Colorado Front Range" *by* Bianca Baier et al.

Anonymous Referee #2

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General comments

The manuscript describes a comparison of P(O3) measured using a second generation MOPS instrument and P(O3) modelled using a detailed chemistry mechanism (MCMv3.3.1) and lumped chemistry scheme (RACM2). A higher measured than modelled P(O3) is reported during the morning hours and the authors postulate that this discrepancy could be caused by a model under-estimation of HO2 under high NOx conditions and present a possible reaction which cycles OH to HO2 via NO that could rectify the discrepancy. The manuscript concludes with a discussion on how these model uncertainties may influence ozone reduction strategies in the region. From reading this manuscript in detail, I have not been convinced that the differences reported between

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modelled and measured P(O3) are not, in part, caused by instrumental issues (I have detailed my specific concerns below) and to a smaller extent, caused by uncertainties in the model constraints (e.g. the interpolation of the VOC measurements and the use of a constant, median VOC value for certain VOCs). I cannot recommend publication in ACPD before the specific comments I have raised below are adequately addressed.

Specific comments

Throughout the manuscript, the authors argue that the higher observed P(O3) than modelled P(O3) at high NO is supported by observations of higher (than modelled) HO2 under high NO conditions. Only recently, however, have HO2 measurements been reported in the literature that have not been influenced by artefact signals induced by the fast decomposition (within instruments) of certain RO2 species. The authors do not discuss recent observations and model comparisons made in China (Tan et al., 2017) where interference-free HO2 observations agree well with model predictions under elevated NO conditions. The authors need to provide a more balanced discussion of modelled and measured HO2 comparisons under high NO conditions which includes a review of the possible problems relating to HO2 measurements as well as the more recent HO2 modelled and measured comparisons.

Pg 5, line 8 -16: The authors discuss the influence of humidity on the O3 analyser used in the MOPS instrument and cite previous papers which have reported large changes in O3 concentration as RH is rapidly changed. How fast and by what percentage did RH typically change during these ambient measurements made in Golden? Did the authors attempt to correct for this RH dependence?

Pg 5, line 23: ‘some excess HONO was measured..’ how much and how did this vary with RH, T, [NO2] and actinic flux? Would this excess HONO be expected to be greatest during the morning hours when NO2 concentrations were high? Details like this need to be provided so the differences reported between modelled and measured P(O3) during the morning hours can be fairly assessed.

Pg 5, line 24: '..actions were taken'. Some details on the actions that were taken should be provided here.

Pg 6, discussion of model constraints: I have some concerns over how well the model constraints represent the local conditions in Golden. How many WAC samples were collected between 0700 – 1200? I worry that interpolating these canister samples may lead to underestimations in peak VOC concentrations. In table S1 the authors state that constant, median values of various species measured on board the aircrafts were used to constrain the model. How can this be a valid approach given the high variability of some of these species, e.g. the biogenics? Would this variability bias the model predictions as a function of time of day? I.e. were VOC concentrations highest during the morning when the boundary layer was lowest? It is unclear if the sensitivity analysis conducted (presented in Fig S1) included varying VOC concentrations by the observed variability or varying by the uncertainty in the VOC measurement only?

Pg 7, line 1: '..integrated for 24 hours..' I would be surprised if the reactive intermediates and, more importantly, modelled HO2 and RO2 are in steady state after 24 hours. By what percentage did the modelled peroxy radical concentrations change from day 1 to day 2?

Pg 8, line 19: How does the diel measured P(O3) change if the negative P(O3) points are not omitted? By omitting these negative points, does this not positively biased the P(O3) measurements in the morning when these negative points are most frequent? Were the modelled P(O3) calculated at the same time also removed? Could the authors be more quantitative when they discuss the O3 analyser RH dependence – what do they class as a 'drastic change' in RH?

Section 3.2 would benefit from Rate of Production Analysis. This would help to reveal what is driving the high modelled P(O3) on certain days. It would also reveal the cause of the differences that were observed between RACM and MCM at times rather than rely on speculation '..perhaps due to more explicit treatment of VOCs..'

Pg 9, lines 6-16: The authors give some reasons as to why they have confidence in the MOPS measurements during the morning hours when the model and measurements do not agree. I am not convinced, however, that the MOPS measurements are not positively biased at this time: By removing the negative P(O3) values which most frequently occurred during the morning hours, I would expect this to positively bias the measurements at this time even if a median rather than the mean value is used. Furthermore, I would expect heterogeneous HONO production to be greatest when NO2 concentrations are high, and, this would also artificially positively bias the measurements during the morning most.

Pg 10, lines 1-5: The measurement bias reported due to photolytic HONO production is of the same magnitude as the discrepancy between model and measured P(O3) observed during the morning (Fig 2). Although the authors argue that individual modelled and measured P(O3) deviations are often larger than the bias caused by photolytic HONO production, there seems to be, from studying figure 1, a similar number of positive and negative deviations of the MOPS P(O3) from the modelled P(O3) suggesting that many of these deviations are caused by noise rather than missing or uncertain model chemistry.

Section 3.3.4: A rate of 9 -15x10-11 cm3 molecule-1 s-1 for the postulated reaction ‘OH+NO (+O2) → HO2 + NO2’ cannot be justified given that the known reaction rate for OH reacting with NO is two to three times slower. The impact of this highly speculative reaction is presented as positively influencing the modelled P(O3) in line with the MOPS observations - this is misleading, however: Figure S2 highlights that although inclusion of this reaction, proceeding at a rate of 9 -15x10-11 cm3 molecule-1 s-1, improves the modelled and measured agreement in the morning, it actually worsens the agreement between the modelled and measured P(O3) during the afternoon; there is no comment about this in the text, however. How does this reaction influence other modelled species, e.g. OH?

Section 3.3.6: Some discussion of the modelled HONO sources is needed here. If only gas-phase sources, i.e. OH+NO are considered, the model likely under-estimates the actual HONO that was present.

Reference Tan et al., Atmos. Chem. Phys., 17, 663-690, 2017

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