

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 #1

Received and published: 27 January 2017

Comments on B. Baier et al. Higher measured than modeled ozone production at increased NO_x levels in the Colorado Front Range

Overall this paper is interesting but not entirely convincing. However, it is the authors staking their reputation on this and I will not stand in their way. However, I hope that the many co-authors are sufficiently convinced that they will not also agree to be co-authors any paper using their data that comes to a different conclusion about high NO_x photochemistry.

There are three major issues the authors should address:

1) They dismiss large negative values but not large positive values as unphysical. It is

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not clear that both types of errors shouldn't be treated as representative of the random error of the method used.

2) Much is made of the linear NO_x dependence of the model observation mismatch. A figure showing this should be presented.

3) The authors dismiss HONO and VO_{CR} as a potential source of discrepancies too easily. It would be better to instead assume the entire discrepancy is due to HONO or to VO_{CR} that is correlated with NO and show the reader the relationships between NO, HONO and VO_{CR} that would be required to explain the results. Then the reader can judge whether those ideas are plausible.

Other comments

Page 2 Line 27: Only the formation of peroxyacyl nitrates, and not alkyl nitrates, is a form of O_x loss. The reaction RO₂ + NO → RONO₂ does not produce or consume either O₃ or NO₂.

Page 2 Line 27: Equation 3 includes the production of nitric acid via OH + NO₂ - this should also be included in the description of ozone chemical loss processes.

Page 4 Line 1- 3: It would be useful to understand which of these references are from ambient field studies and which (if any) are from chamber studies. Some of the proposed explanations of the MOPS v. Modeled PO₃ in this paper should exist in both field and chamber studies (e.g. OH + NO₂ + O₂) while others (e.g. ClNO₂) are unlikely to be a factor in chamber studies.

Page 4 Line 13 - 20: It is unclear what this paragraph is actually describing. Are these results all from a single study, or are these similar results from a variety of MOPS deployments?

Page 8, Line 22: Were time periods selected for removal based on the humidity or of the MOPS measurement itself? It is unclear from the description in this paragraph and should be clarified.

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Page 9, Line 17-19: While Figure 1 shows several days where the MOPS peak PO₃ value is between 10-20 ppb/hr greater than the modeled value, it also shows several days where the MOPS minimum PO₃ value is between -10 and -20 ppb/hr (e.g. Jul 21, 23, 24, Aug 6). Since these large negative values are explained as non-physical, why is it not equally plausible that the large positive values are a measurement artifact as well?

Page 11 Line 12 & Page 12 Line 5: The claim that the difference between MOPS and Modeled PO₃ is linear with NO is difficult to evaluate from the figures provided. Since the NO dependence of the MOPS-Model disagreement is an important part of the analysis, the authors should include a figure that directly shows the difference in PO₃ during the morning as a function of NO.

Page 12, Line 8-9: This sentence appears to contradict section 2.2, where median diurnal values of VOCs are said to be used in the model calculation. The authors should clarify how the model includes the dependence of VOC reactivity on NO.

Page 12, Line 15-17: As written, the proposed $\text{OH} + \text{NO} + \text{O}_2 \rightarrow \text{HO}_2 + \text{NO}_2$ reaction seems to be an OH loss as well as an HO₂ source. The authors should clarify why the argument here against a missing VOC source do not also apply to this proposed reaction.

Page 12, Line 27-Page 13, Line 5: I am uncertain whether the mechanisms listed in this paragraph are candidates for the $\text{OH} + \text{NO} + \text{O}_2$ reaction mechanism or not. Rewording this paragraph to clarify what some possible forms of this reaction are, and whether it might involve additional species such as acetylene would be useful.

Section 3.3.6: Given the known difficulties models have in capturing HONO concentrations, this section feels overly brief in dismissing HONO as a HO_x source. I would appreciate at least brief consideration of what magnitude HONO source would be necessary to make the modeled PO₃ values match the MOPS values.

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Figure 5: If the disagreement between measured and modeled PO₃ is strictly a function of NO_x, why is the disagreement so much worse on plume days, even though plume and non-plume days both have average morning NO concentrations of approximately 2 ppb? Are there other significant differences between plume and non-plume days, or is there significantly more variability in the amount of NO_x on plume than on non-plume days?

Technical Corrections Page 12, Line 12: If this number is a rate of HO₂ production, then the units on this are incorrect (perhaps intended to be radicals cm⁻³ s⁻¹?) Page 13, Line 1-2: In this sentence, the phrase "the formation of" appears to be extraneous. The accent on FRAPPÉ is inconsistent. Sometimes the campaign is incorrectly written as FRAPPÈ.

Interactive comment on Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2016-1089, 2017.

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