

Interactive comment on “Contributions to local and regional-scale formaldehyde concentrations” by L. Bastien et al.

Parrish (Referee)

david.d.parrish@noaa.gov

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Summary:

The paper presents an interesting analysis of formaldehyde sources in the San Francisco Bay area. This research is relevant because 1) formaldehyde is an air toxic to which significant health impacts have been attributed, and 2) the modeling methods presented here may well have wider applications. The study is well conceived and executed, and the paper is well written, with the procedures and results concisely and clearly explained. I recommend that the paper be published when the following comments are addressed. It is most important to address the major comments that question if everything is done correctly (major comments 1, 3, 6, 7) and less important to

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address the comments related to more discussion of formaldehyde sources and sinks.

Major issues and comments:

1) Section 2, which describes the model, the procedures for conducting the modeling, and the interpretation of the model results, is largely outside my area of expertise, so I can neither support nor critique most of that material. Section 3.1 provides the only evaluation of the model performance that is accessible to me, and I expect that this is true of most readers of the paper. The evaluation of the forward model performance is only through comparisons of monthly average diurnal cycles of mixing ratios of O₃, NO and NO₂ (Figures S2-S7) for the July and December simulation periods. However, the discussion is qualitative (e.g., “Agreement is good for O₃ mixing ratios in July and December . . .”), and in my view, not entirely accurate. Some large errors in the O₃ simulation are evident, so that I am not confident that the model simulation can be accurately used for its intended purpose. I recommend a more thoughtful evaluation be conducted that can provide some quantitative information regarding how well the model actually performed. In this regard, I have the following suggestions.

The three species O₃, NO and NO₂ are closely coupled in the atmosphere due to rapid interconversion: $\text{NO} + \text{O}_3 \Rightarrow \text{NO}_2 + \text{O}_2$; $\text{NO}_2 + h\nu + \text{O}_2 \Rightarrow \text{NO} + \text{O}_3$. Hence, it makes sense to base the model-observation comparison on $\text{NO}_x = \text{NO} + \text{NO}_2$ and $\text{O}_x = \text{O}_3 + \text{NO}_2$ (which are not affected by the above interconversion) rather than on the separate species, whose concentrations are more difficult to interpret.

For O₃ at any low elevation site in the Bay Area in the absence of continental (natural or anthropogenic) effects, I would expect a constant average diurnal profile at about 25 ppb in summer and 40 ppb in winter (see Parrish et al., 2009). The utility of the model is to simulate how concentrations differ from this zero-order expectation. To objectively evaluate the model performance, one should quantitatively compare how the simulated and observed O_x concentrations differ from this expectation. A qualitative examination of the figures suggests that the model may be substantially overestimating O₃ (and

therefore Ox) production in the SF Bay area in summer. If there is a quantitative overestimate in the simulated photochemical production of ozone, then the implications for the accuracy of the simulation of the photochemical production of formaldehyde must be discussed.

The observed NO_x concentrations are expected to reflect anthropogenic emissions, so disagreements in a quantitative comparison of the simulated and observed NO_x (or CO) concentrations may indicate errors in the emission inventory or in the simulation of vertical transport and horizontal advection. If the comparison is poor, then the reasons for the poor comparisons, and the implications for the conclusions of this paper must be discussed.

For the carbonyls, I cannot recommend an approach superior to that taken in Figures S8-S10, but the results can be more informatively summarized. Since one goal of this paper is to understand formaldehyde concentrations, any bias in the model simulations of the aldehydes should be quantitatively discussed. A qualitative examination of the figures suggests that there is no significant bias in the formaldehyde results, but that acetaldehyde simulations may be biased high; these conclusions should be put on a quantitative basis. The model underestimate of acetone mixing ratios should also be put on a quantitative basis (i.e., something like a factor of 3 or 5), and the possible reasons discussed (i.e., the primary emissions may be underestimated as has been found by McDonald et al., 2018).

Once a quantitative comparison is in hand, the authors should discuss how the comparison supports (or brings into question) the conclusions of the study.

2) The evaluation of the adjoint of the forward model through the comparisons illustrated in Figure 2 is quite compelling.

3) Pg. 9, lines 29-31: The statement given here seems to present a conundrum: “In other words, even though the population-weighted formaldehyde mixing ratio is larger in summer, scaling emissions uniformly year-round would result in a larger mixing ratio

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change in winter.” However, if emissions were reduced by 100%, then I would expect formaldehyde mixing ratios to be reduced to the small methane photochemical oxidation steady-state of 0.1 to 0.2 ppb (McCarthy et al., 2006) in both seasons. Does this imply that the secondary production of formaldehyde, which dominates in the summer, is very non-linear? Please fully discuss this apparent conundrum; a compelling explanation of the quoted statement is necessary for this result to be accepted as really representative of the atmosphere, and not an indication of a shortcoming of the modeling approach.

4) It would be useful to give an explanation for the cause of the result reported in the last sentence in Section 3.2. Why do formaldehyde mixing ratios increase when NO_x emissions are decreased? Is this related to VOC sensitive-NO_x saturated photochemical ozone formation? Is this possibly related to the conundrum mentioned in point 3 above?

5) Can Table 2 be expanded to give a complete budget for formaldehyde? Include additional columns for primary emissions, total sources and total losses. I would guess that the total sources and total losses should come close to balancing, with the difference due to net transport out of the modeling domain. This would then give the reader a useful summary of the relative magnitudes of sources and sinks of formaldehyde in the two seasons.

6) Pg. 11, lines 7: “Removal by dry deposition decreases by a factor of three between July and December.” Other factors being equal, I expect dry deposition to simply scale with formaldehyde concentration, but this difference is larger than can be explained by the concentration differences in Table 1. Please explain how the “other factors” account for this finding.

7) Last paragraph, Section 3.3 – A much better description of exactly what is going here is required. I don’t think that all “chemistry has been turned off”, since that would turn off photochemical production of formaldehyde as well as photochemical loss pro-

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cesses, and result (I guess) in large negative sensitivities in summer. Please clarify.

8) Pg. 12, lines 3-5 state “Secondary formation of formaldehyde is enhanced by NO₂ to NO conversions associated with the photolysis of NO₂, and is inhibited by NO to NO₂ conversions associated with the reaction of NO with ozone . . .” This is an interesting finding, but the reason for and implications of this sensitivity is not discussed. Is this possibly related to point 4 above? Please discuss.

9) Pg. 12, lines 8-10 note “In Section 3.2, ISOPRENE, ETHENE, OLE1, and OLE2 were identified as the main contributors to secondary formaldehyde in July, yet none of the reactions that directly involve any of these species appear in Table 4.” This is again an interesting observation, but it is not discussed further. What is the reason for this? Please discuss how this fits in the overall picture of formaldehyde sources and sinks that you all are developing.

10) The discussion in the last paragraph of Section 3.4 is not entirely correct. In particular the sensitivities of many of the reaction rates are similar between the two seasons. This discussion should be improved. Also, what is the cause of the opposite effects on formaldehyde of two competing fates for peroxy acetyl radicals (CH₃C(=O)OO•)? It seems many of my comments (3,4,8,10) all involve the role of NO_x in formaldehyde formation. Can a coherent discussion of all of the NO_x related issues be added in a separate section? In this regard, it would be useful to explicitly discuss the effect of reducing NO_x emissions on population weighted formaldehyde exposure; if I understand correctly, reducing NO_x emissions would worsen the formaldehyde health effects, but this is not explicitly discussed in the paper.

Minor issues:

1) Paragraph on Pg. 2 and 3 – In the discussion of the approaches used to estimate the relative importance of direct emissions versus secondary formation of formaldehyde, it may be useful to point out that the results for Houston are not expected to be similar to those from other urban areas (such as Mexico City) given the vast petrochemical

industrial activities in Houston.

2) Pg. 9, line 18: “Figures 3a and 3c” should be “Figures 3a and 3b” I guess.

3) Pg. 9, lines 28-29: I have a difficult time fully understanding and remembering the quantities discussed. I suggest that the sentence on these line be changed to more fully emphasize the quantities: “The air basin-wide response (Table 1) decreases by a factor of 1.6 between summer and winter, while its sensitivity to emissions (Figure 3) almost doubles.”

References

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