Responses to Referee 1 Comments

1. *Line 139: I would like a little more discussion on how close to or far away from Lagrangian sampling each flight was. If this has been well characterized, perhaps an SI table is appropriate. 'Semi-Lagrangian', while often used in the BB literature, is vague*.

   We thank the reviewer for the suggestion. We have added details on the emission time of the plume center smoke for each fire plume sampled. Emission time is calculated by subtracting the estimated smoke age from the sample time. The spacing of Twin Otter plume intercepts were close to Lagrangian sampling. The difference of emission times of smoke sampled by the Twin Otter at plume center is < 10 min. The difference of emission times of smoke sampled by the DC-8 at plume center is between 30 and 60 min. The differences between each aircraft are due to air speed. The Twin Otter flies at ~70 m s^{-1} compared to the DC-8 air speed of ~170 m s^{-1}.

   We added SI Table 2, shown below, along with additional text to the manuscript.

Estimated Emission Time at Plume Center (UTC) ± uncertainty (min)

Transect	WF 1 (Aug 7 2019)	WF2	Castle (Aug 22 2019)	Cow (Aug 29 2019)
1	23:01:04 ± 5.0 min	Aug 8 00:36:01 ± 8.0 min	**01:01:41 ± 1.2 min**	**01:30:59 ± 71.5 min**
2	22:46:13 ± 6.6 min	Aug 8 00:18:18 ± 7.7 min	**00:59:58 ± 1.4 min**	**01:27:45 ± 68.1 min**
3	22:43:11 ± 3.8 min	Aug 8 00:09:45 ± 6.2 min	**00:59:55 ± 1.7 min**	**01:30:34 ± 55.6 min**
4	22:33:25 ± 8.6 min	**Aug 7 23:53:59 ± 7.2 min**	**00:52:11 ± 3.8 min**	
5	22:13:04 ± 13.7 min	**Aug 7 23:29:05 ± 12.8 min**		
6	21:58:06 ± 12.8 min	**Aug 7 23:24:59 ± 8.2 min**		
7	**21:51:34 ± 16.5 min**	**Aug 7 23:14:38 ± 6.2 min**		
8	**21:37:17 ± 15.6 min**	Aug 7 22:50:45 ± 11.4 min		
9	**21:13:38 ± 19.9 min**	Aug 7 22:41:39 ± 22.5 min		
10	**20:55:25 ± 30.2 min**			

SI Table 1: List of estimated emission times (UTC) with uncertainty (min) for each plume. Emission times for transects used to constrain the model are bolded.

Added to section 2.1.1

> "Even so, estimated emission times (calculated from estimated plume ages) suggest smoke sampled on successive intercepts at the Castle and Cow plume centers were emitted within 3- and 10-min time periods, respectively. However, plume age uncertainties for the Cow plume are large (SI Table 1)."

Added to section 2.1.2

> "However, smoke emission times for the plume center of WF1 and WF2 covered a larger time period (~30 – 60 min) compared to the NOAA Twin Otter (SI Table 1)."

2. *Sect 2.1: It's no secret that UHSAS have struggled with saturation in high-aerosol environments such as wildfire plumes. While not one of the most crucial measurements in this paper, I recommend including a brief discussion in the text or SI about its performance for the specific plumes used in this work.*

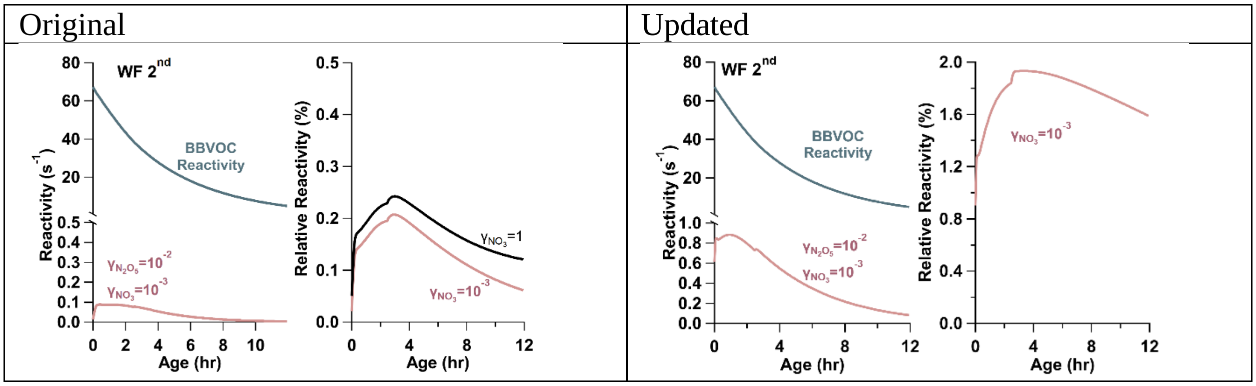
   Indeed, saturation can be an issue for the UHSAS, however we were able to correct for this in flight. The following text was added to the manuscript in section 2.1.1.

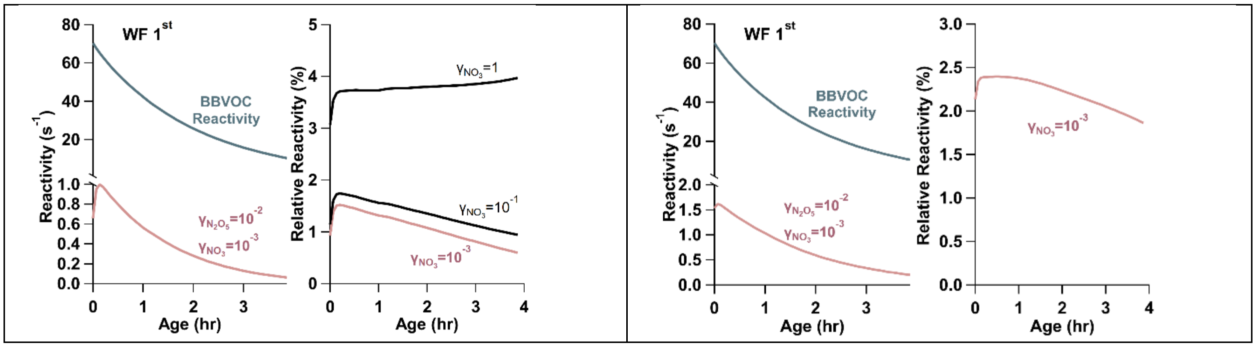
   > "The UHSAS data were corrected for coincidence up to a factor to 1.4, following the method described in Kupc et al 2018. The sample for the UHSAS was diluted up to a factor 2.9 for part of the flights to increase accuracy at higher concentrations."

3. *Related, the UHSAS (Twin Otter) and SMPS (DC-8) are on 1 Hz vs 60 s timescales. How did you account for this difference in your analysis? (Especially since you assumed center-line modeling and the SMPS almost certainly did not capture only the center of a plume in 60 s).*

   To account for the lower time resolution of the SMPS, we took a conservative approach by using the maximum observed aerosol surface area. Related to this, we have realized that the SMPS does not capture larger aerosol (> ~250 nm) and therefore we have instead used the Laser Aerosol Spectrometer (LAS) to calculates surface area. Doing so has resulted in a change in surface area of a factor of up to 100 in the WF1 and WF2 box model runs. Even so, the resulting N_2O_5 heterogeneous reactivity accounts for < ~2.5% of total NO_3 and N_2O_5 combined reactivity. The increase is small because of the substantial NO_3 reactivity found in the wildfire plumes we study.

   In response to this change, we have updated SI Figure 11 and related text. The cases for $\gamma_{NO_3} = 0.1$ and $\gamma_{NO_3} = 1$ were removed from the figures because they are unrealistically large NO_3 uptake coefficients.





4. *Section 2.1.1-2.1.2: (Twin Otter and NASA DC-8 descriptions) Were there any opportunities during FIREX to characterize instruments (specifically, instruments measuring the same species) from each aircraft against each other? If yes or no, could you briefly detail. Is it anticipated that 'real' individual differences in a given species present at each fire studied greatly outweigh differences (uncertainty) between two different instruments and platforms measuring said species?*

   The Twin Otter and NASA DC-8 were based at the same airfield for a period of time during FIREX-AQ, but they unfortunately did not execute coordinated flights sampling the same fires on the same day to provide direct comparison between the different sets of instruments.

   Among the relevant instruments that could have been directly compared, the stated uncertainties are < 3 % for CO, < 10 % for NO and NO_2, <3 % for O_3, and < 10 % for j_{NO2}. Calibrations for HONO have larger uncertainties (30 % for the UW I^- CIMS and 15 % + 3 pptv for the NOAA I^- CIMS). As shown in Figure 2 (which includes the above uncertainties), the calibration and stated measurement uncertainty is typically smaller than any differences between transects, and certainly smaller than differences across sampled fire plume. Therefore we anticipate that the actual individual differences in a given species present at each fire studied greatly outweigh differences (uncertainty) between two different instruments and platforms measuring said species.

5. *Line 202: Why only one "Dark" case? Please provide a brief justification, including why you chose the WF2 case as the dark case's template.*

   We chose only one "Dark" case as to not lengthen the analysis and paper further than it already is. Further "Dark" model runs were outside the scope for this analysis and therefore were not included. The WF2 case was chosen as a template for the "Dark" case because the smoke was emitted near sunset (unlike WF1), provided sufficient emissions such that chemistry would continue throughout the night (unlike Castle), and the observations were not already in the dark (unlike Cow).

   In response, the first paragraph of section 2.3 was modified as shown below.

> "We modeled smoke plumes from three fires (Castle, Cow, and WF). We present four model cases (Castle, Cow, WF1, WF2) constrained by aircraft observations and one case (Dark) identical to the WF2 case except all modeled photolysis frequencies are set to zero. We consider the dark model run only for the WF2 case and not the others since it is a hypothetical exercise intended to illustrate the evolution of smoke emitted after dark, a case for which there were no available observations from the 2019 campaign. ~~The Dark case simulates oxidation of the WF2 plume if it was emitted after sunset.~~ The Dark case is used to understand the effect of photolysis on the WF2 model run."

6. *Lines 236-7: what qualifies as "small" uptake coefficients and aerosol diameters here? Are the aerosol diameters appropriate for this equation (3) appropriate for the (non-coarse) mode/s observed?*
   We thank the reviewer for the questions. We have added the following text to the manuscript to clarify.

   > "For large particle diameters or large uptake coefficients, the simplified heterogeneous uptake equation requires a correction for gas phase diffusion (Fuchs & Sutugin, 1970; Kolb et al., 2010). For accumulation mode particles of order 100 nm and uptake coefficients of order 0.01, this correction is not important."

7. *Some of the discussion between Sect 2.3.1 Chemistry and Emissions and Sects 2.3.2-3 seem a little disconnected. Are you using the ER inventory (Sect 2.3.1) only for compounds not measured directly that are still important to MCM mechanisms? Also it seems that Eq 1 does not care about background (out-of-plume) concentrations of species. Is that the case, and if so can you briefly justify using total rather than background-corrected concentrations (mixing ratios)?*

   We thank the reviewer for the comment.

   For clarity, we have modified the text in section 2.3.1 to inform the reader that further details of how emission ratios are used will be given in section 2.3.3, shown below.

   "We initiate the model, as discussed in section 2.3.3., using an emissions inventory of 302 BBVOCs in the form of emission ratios (ERs)."

   The reviewer's question about our use of the ER inventory for model initiation is answered by the two excerpts from section 2.3.3 below.

   > "In all plumes except the Castle plume, our first transect sampled smoke 36 min – 2 h old and therefore we implemented an iterative method (McDuffie et al., 2018; Wagner et al., 2013) to estimate initial emissions (at age = 0). We began with best-guess estimates of CO, NO, NO_2, HONO and O_3 then systematically changed these initial conditions to minimize the differences between model output and observations downwind."
   >
   > "Initial conditions in the Castle run were taken directly from observations of NO, NO_2, O_3, CO, HONO, phenol, catechol, cresol, and methylcatechol in the first transect where the plume age was 3 $\pm$ 1 min, and therefore was close

> to age = 0. We initiated the remaining 298 BBVOCs by using CO and Eq. (1).”

However, these excerpts are separated by text describing the iterative method. We have modified the manuscript by combining the above paragraphs at the beginning of section 2.3.3 and making clarifying additions, as shown below.

> “In all plumes except the Castle plume, our first transect sampled smoke 36 min – 2 h old and therefore we implemented an iterative method (McDuffie et al., 2018; Wagner et al., 2013) to estimate initial emissions (at age = 0). We began with best-guess estimates of CO, NO, NO_2, HONO, O_3 and all BBVOCs (determined by CO and our emissions inventory by Eq. (1)) then systematically changed these initial conditions to minimize the differences between model output and observations downwind. Initial conditions in the Castle run were taken directly from observations of NO, NO_2, O_3, CO, HONO, phenol, catechol, cresol, and methylcatechol in the first transect where the plume age was 3 ± 1 min, and therefore was close to age = 0. We initiated the remaining 298 BBVOCs by using CO and Eq. (1). Initial conditions for all cases are shown in SI Table 5.”

It is correct that Eq. (1) does *not* include background (out-of-plume) concentrations of species. This is by definition since emission ratios describe an initial (age=0) emission relative to another emission, in this case CO. In other words, emission ratios are specific only to a fuel type and are independent of background conditions. Alternatively, Normalized Excess Mixing Ratios (Eq. 5) account for background conditions and are used to describe observations when age>0. To clarify this point, the following text was added immediately after Eq. (1).

> “Note that an ER is used to describe an emission (when smoke age = 0) and is different than a Normalized Excess Mixing Ratio (defined in section 2.4.1) used to describe observations when smoke age >0.”

8. *Relatedly, it’s slightly unclear to me exactly what the box model used consists of. It uses the MCM and a NOAA F0AM BB mechanism. Are those the only components to it (along with the dilution rate discussed)? Has this exact model been used elsewhere?*

All of the components of this model have been used in other applications, but their combination is specific to this paper. To clarify this point to the reader, we have added the following text to the end of section 2.3 Box Model Description

> “Components of our model have been used for other applications (Decker et al., 2019; McDuffie et al., 2018; Robinson et al., 2021; Wagner et al., 2013). However, the combination of the components is specific to this work.”

9. *Line 320: make sure to note that you are using 'delta' notation to denote background-corrected (I don't think this notation was previously defined).*

The following text was added

> "(where Δ indicates background-corrected)"

10. *Line 326-329: briefly justify why you're using the latter transects of the WF2 fire rather than the former.*

We use the latter transects of the WF2 Fire plume because only the later transects show a monotonic decrease in CO (most easily seen in SI Figure 3), which was one criterion we used for selection observations to be used in the model. This is described in section 2.3.2 shown below.

> "We chose transects that showed a monotonic decrease of CO with distance from the fire, cover an age range of at least one hour, and have similar emission times as shown in SI Figure 2 – 3 and SI Table 1."

We have edited the lines in question to direct the reader to section 2.3.2, as shown below.

> "In order to avoid these changes, we use only observations from the latter to constrain our model, as discussed in section 2.3.2."

11. *Line 381 & elsewhere: Why is formaldehyde separated from other BBVOCs in the analysis?*

Formaldehyde is a simple aldehyde and therefore does not fall into one of the general BBVOC categories shown in the top pane of Figure 3 (i.e. furans, terpenes, etc.). However, it has a substantial contribution to OH reactivity. Therefore, we specify HCHO separately. We have added the following text to clarify.

> "In this analysis we do not specify an aldehyde group, and therefore separate HCHO from the general BBVOC groupings."

12. *Lines 409-411: Why do BB plume have more pronounced reactivity for NO3 than for OH or O3? If discussed elsewhere, point to that discussion.*

We thank the reviewer for this suggestion. The increased reactivity of NO_3 is due to the specific emissions from biomass burning, such as oxygenated aromatics and furans that have substantial reactivity towards NO_3.The concept of increased NO_3 reactivity in BB plumes is introduced in section 1 Introduction and copied below.

> " This is the result of elevated concentrations of several highly reactive BBVOCs within the plume. Specifically, directly emitted aromatic alcohols (phenolics) react with NO_3 at near the gas-kinetic limit to form nitrophenolics, a subset of nitroaromatics, and secondary organic aerosol (Finewax et al., 2018; Lauraguais et al., 2014; Liu et al., 2019; Xie et al., 2017)."

To emphasize this point, we have added the following sentence after the lines in question.

> "The increased reactivity of NO_3 is due to the specific emissions from biomass burning, such as phenolics and furans that have substantial reactivity towards NO_3. The compounds greatly increase NO_3 reactivity compared to urban VOC profiles, but do not increase OH reactivity to the same degree."

13. *Line 496: Akherati et al., 2020 also an appropriate citation here: Oxygenated Aromatic Compounds are Important Precursors of Secondary Organic Aerosol in Biomass-Burning Emissions: Ali Akherati, Yicong He, Matthew M. Coggon, Abigail R. Koss, Anna L. Hodshire, Kanako Sekimoto, Carsten Warneke, Joost de Gouw, Lindsay Yee, John H. Seinfeld, Timothy B. Onasch, Scott C. Herndon, Walter B. Knighton, Christopher D. Cappa, Michael J. Kleeman, Christopher Y. Lim, Jesse H. Kroll, Jeffrey R. Pierce, and Shantanu H. Jathar, Environmental Science & Technology 2020 54 (14), 8568-8579, DOI: 10.1021/acs.est.0c01345*

    We thank the reviewer for their suggestion. The reference has been added.

14. *Line 588-593 (paragraph) be careful with wording here. For example- "Further, the nitrocatechol yield changes to 27 % – 50 % (Figure 9 D) when varying total BBVOC emissions by a factor 0.5 – 4." Change the order of one of these number pairs--from Fig 9D the yield is 50% at a BBVOC factor of 0.5 and drops to 27% by a BBVOC factor of 4.*

    We thank the reviewer for their suggestion. The following text was altered

    > Original: "Further, the nitrocatechol yield changes to 27 % – 50 % (Figure 9 D) when varying total BBVOC emissions ~~by a factor 0.5 – 4."~~
    >
    > Revision: "Further, the nitrocatechol yield changes to 27 % – 50 % (Figure 9 D) when varying total BBVOC emissions **from 4 to 0.5.**"

15. *Lines 606-609 (paragraph): If the reactions & temperature dependence are uncertain, how did you obtain an estimate of phenolics/NO2 for 268 K?*

    The estimate at 268 K is determined by using the $k_{NO_2+O_3}$ rate coefficient at 268 K, but using the k_{O_3} rate coefficient at 298 K. The text was altered, as shown below, to clarify.

    Original:

    For example, the above calculated ratio could be much lower in cold lofted plumes, but knowledge of temperature dependent O_3 + phenolic rate coefficients are unavailable. Using temperatures observed in the WF2 plume (~268 K) for $k_{NO_2+O_3}$ the phenolics to NO_2 ratio at which NO_3 and O_3 oxidation is equal would be ~ 4.

    Revision:

For example, the above calculated ratio could be much lower in cold lofted plumes, but knowledge of temperature dependent O_3 + phenolic rate coefficients **(k_{O_3})** are unavailable. Using temperatures observed in the WF2 plume (~268 K) for $k_{NO_2+O_3}$ **(but using k_{O_3} at 298 K)** the phenolics to NO_2 ratio at which NO_3 and O_3 oxidation is equal would be ~ 4.

16. *Line 640-41: citation for these estimated PNA and PAN lifetimes?*

    The PAN and PNA lifetimes are determined from the model directly. The temperature dependent rate coefficients for each are taken from IUPAC recommended rates (Atkinson et al., 2006). This citation is now included in the main text, as shown below.

    > "The WF2 plume is lofted, and therefore cold (~267 K), which results in a long PAN and PNA lifetime (~150 h, and ~0.4 h, respectively, calculated from the model directly (Atkinson et al., 2006))."

17. *Line 643 & associated figure caption: define CH3O2NO2 (methyl peroxy nitrate?).*

    This is now defined in the main text as shown below.

    > "The increase in NO_2 after sunset promotes methyl peroxy nitrate ($CH_3O_2NO_2$) as well as NO_3 chemistry products, which grow steadily overnight."

Figures/Tables

18. *Figure 2: while useful for Sect 2 discussion, I suggest considering whether this figure could be moved to the SI. It is quite large and there are already an extensive number of detailed figures.*

    We thank the reviewer for the suggestion. After careful consideration, we have decided to keep Figure 2 in the main text. Comments 1 and 2 from reviewer 2 are concerned with a lack of model and observation comparisons as well as making the comparisons clear to the reader. To address these comments from reviewer 2, we have decided to keep Figure 2 because it is the only model and observation comparison presented in the main text.

19. *Figure 3 caption: I suggest reminding the reader what 'all model runs' means in "Average (all model runs).." .*

    We thank the reviewer for the suggestion. The text within the parentheticals was altered as follows

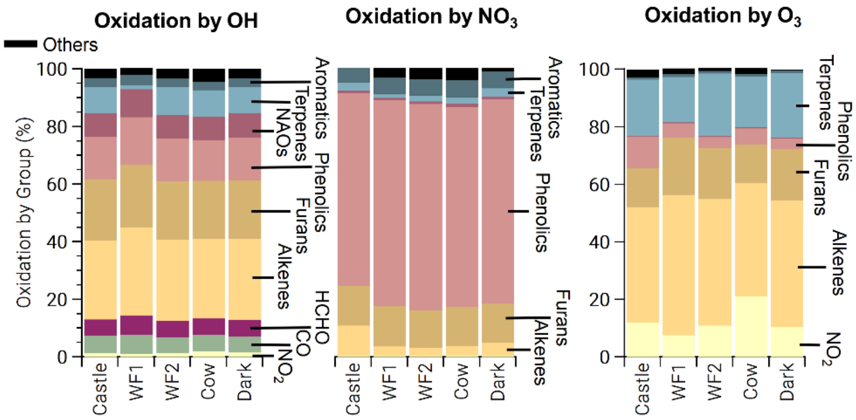
    Original: (of all model runs)

Revision: (of all five model runs)

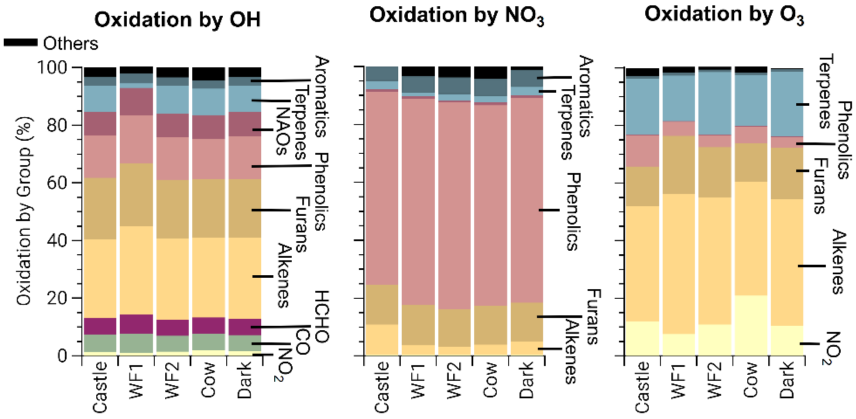
20. *Figure 4: I suggest increasing whitespace between the OH and NO3 bar clusters just a bit to make the distinction between the two more clear.*

    We thank the reviewer for the suggestion. Additional white space was added. Also, the y-axis of O_3 and NO_3 was modified to match the y-axis of OH. The Original and revised figures are below.

    Original:



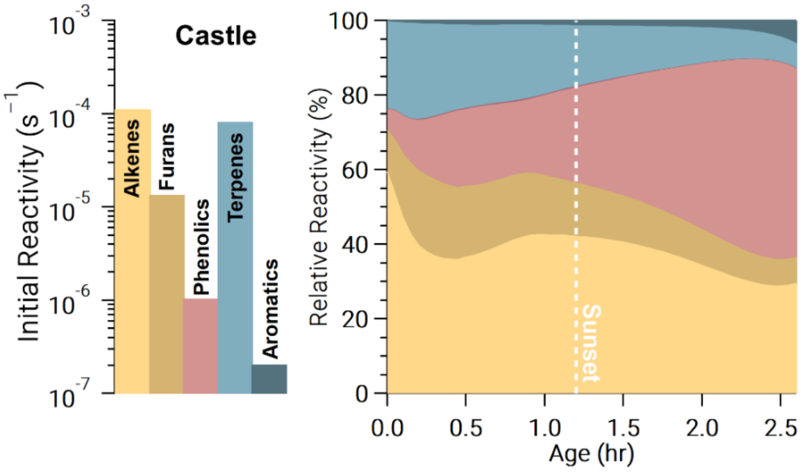
    Revision:



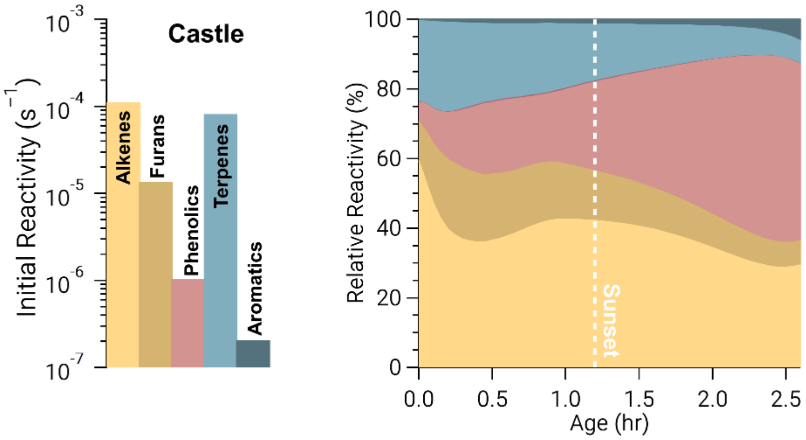
21. *Figure 5: same comment, please space the ‘subpanels’ out a little more (that is, add more whitespace in between each subplot).*

    Additional whitespace was added.

    Original:



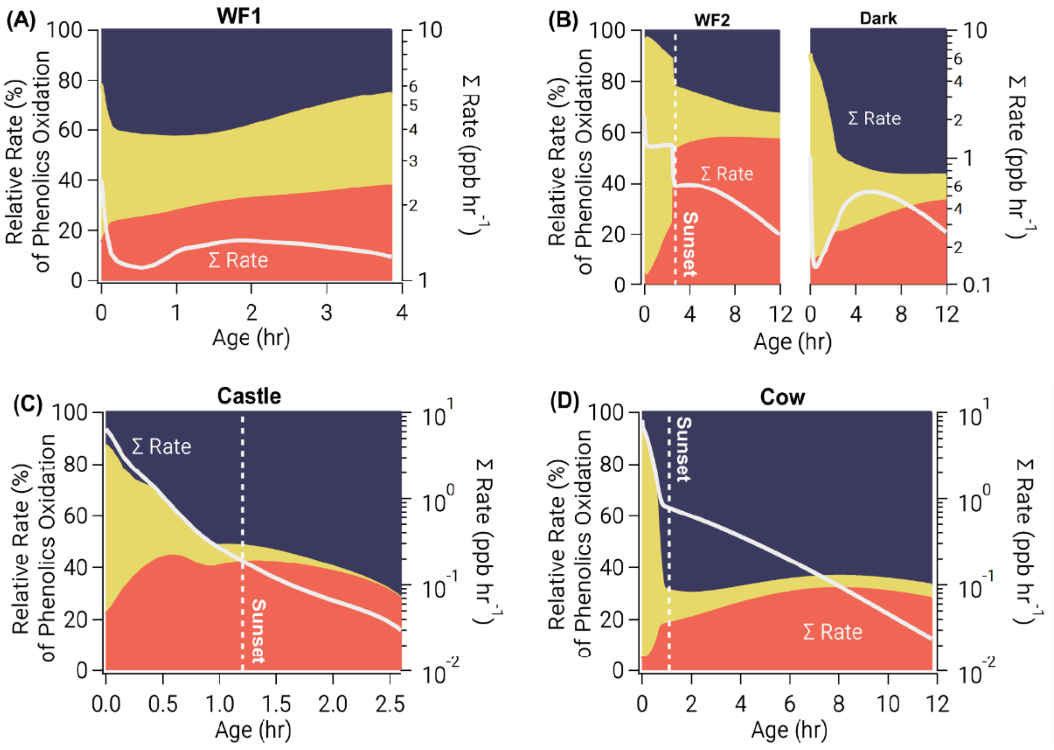
Revision:



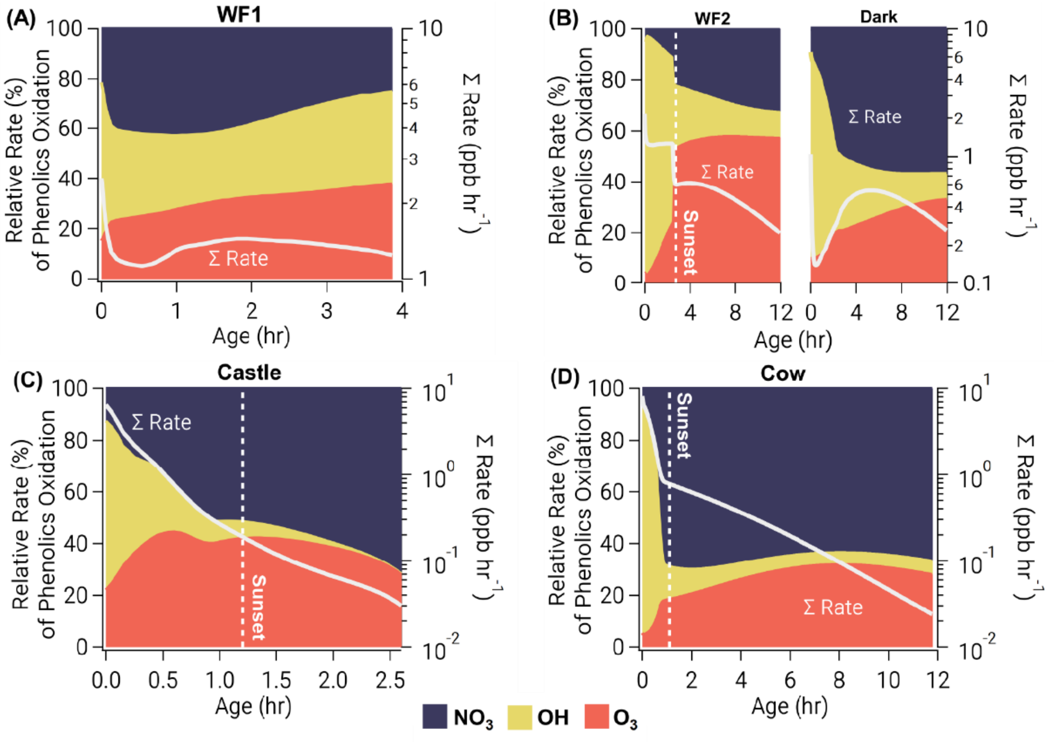
22. *Figure 7: note for final publication that the right-hand line on panel D got cut off. I suggest adding a legend for the different colors (O3, NO3, OH) within the figure to make it more easily interpretable to the reader (rather than having to repeatedly refer to the figure caption). Could copy over legend from Fig 6.*

We thank the reviewer for the suggestion. We have updated Figure 7 as shown below.

Original:



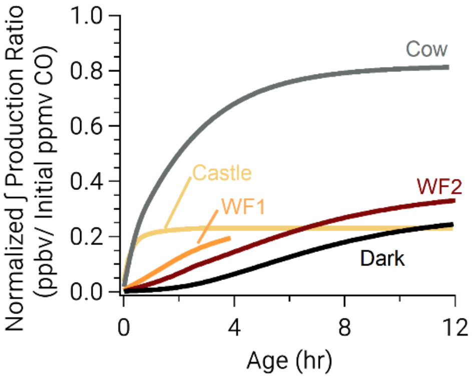
Revision:



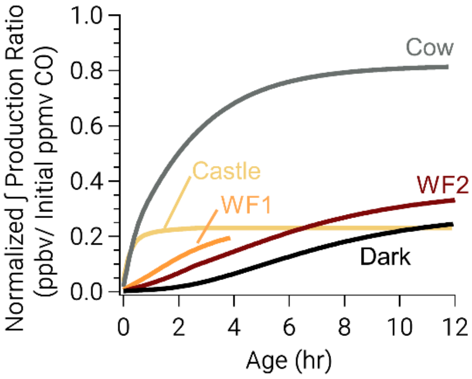
23. Figure 8: it's a little difficult to read 'Castle'-- could consider enlarging all fire names on this.

We thank the reviewer for the suggestion. We have increased the font size of all fire names

Original:



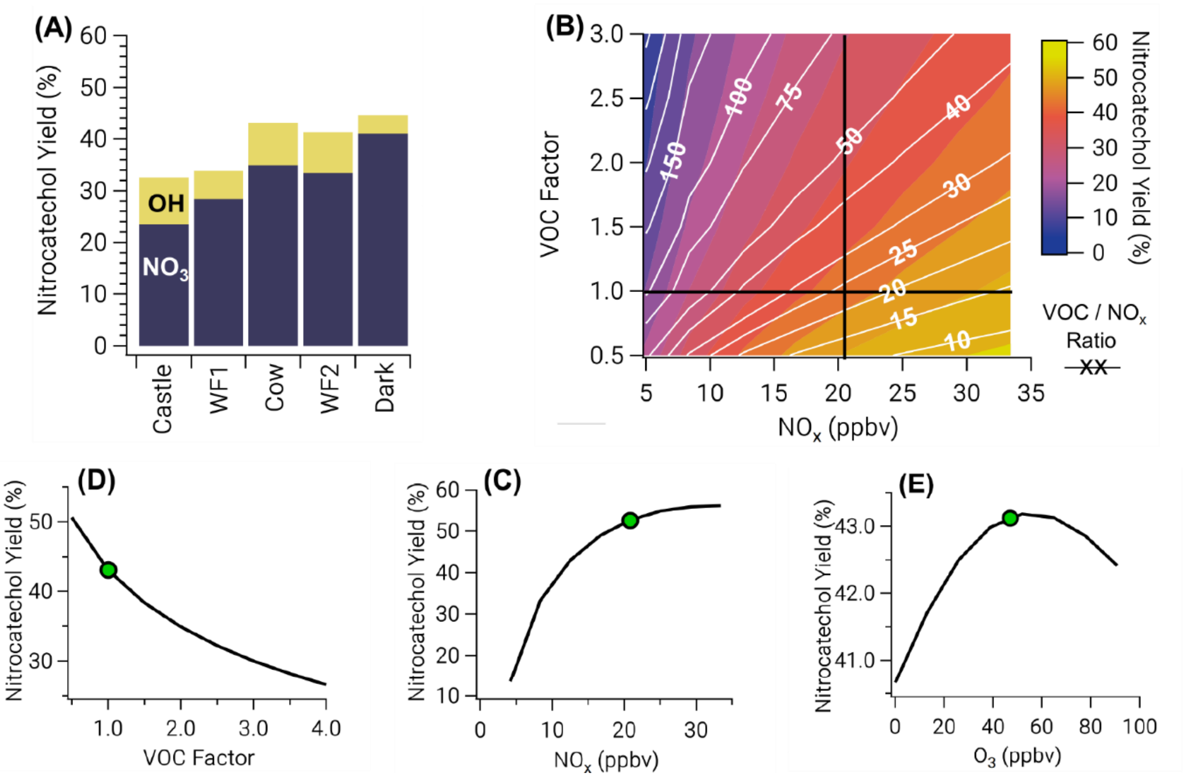
Revision:



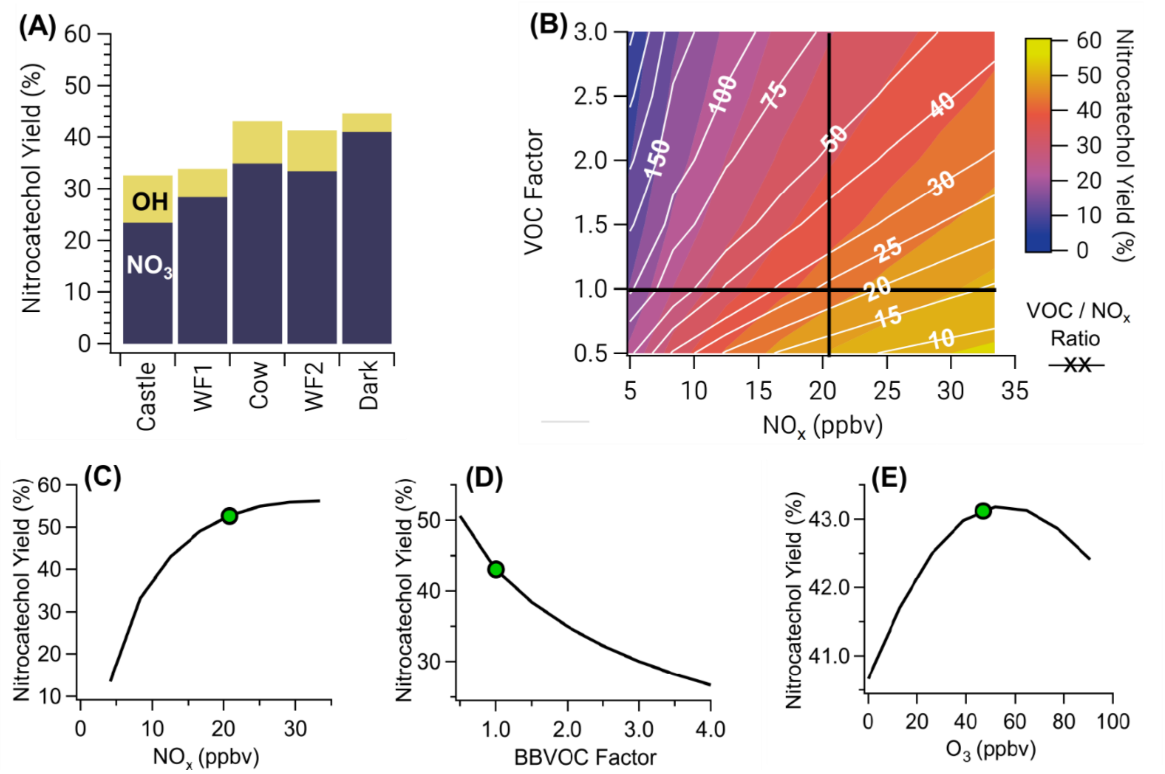
24. *Figure 9: Panels C and D appear to be out of order (not going from left to right) . Also 'BBVOC' is used throughout in the text-either update figure captions from VOC or note in caption that you are using 'VOC' for "BBVOC" here, if that's correct. Or note why you use VOC instead of BBVOC here if it's for another reason.*

We thank the reviewer for the comment. We have updated the figure and caption to read "BBVOC" as shown below.

Original:


(A)
Nitrocatechol Yield (%)
0
10
20
30
40
50
60
OH
NO_3
Castle
WF1
Cow
WF2
Dark
(B)
VOC Factor
0.5
1.0
1.5
2.0
2.5
3.0
NO_x (ppbv)
5
10
15
20
25
30
35
150
100
75
50
40
30
25
20
15
10
Nitrocatechol Yield (%)
0
10
20
30
40
50
60
VOC / NO_x Ratio
XX
(D)
Nitrocatechol Yield (%)
30
40
50
1.0
2.0
3.0
4.0
VOC Factor
(C)
Nitrocatechol Yield (%)
10
20
30
40
50
60
0
10
20
30
NO_x (ppbv)
(E)
Nitrocatechol Yield (%)
41.0
42.0
43.0
0
20
40
60
80
100
O_3 (ppbv)

Revision:


(A)
Nitrocatechol Yield (%)
0
10
20
30
40
50
60
OH
NO_3
Castle
WF1
Cow
WF2
Dark
(B)
VOC Factor
0.5
1.0
1.5
2.0
2.5
3.0
NO_x (ppbv)
5
10
15
20
25
30
35
150
100
75
50
40
30
25
20
15
10
Nitrocatechol Yield (%)
0
10
20
30
40
50
60
VOC / NO_x Ratio
XX
(C)
Nitrocatechol Yield (%)
10
20
30
40
50
60
0
10
20
30
NO_x (ppbv)
(D)
Nitrocatechol Yield (%)
30
40
50
1.0
2.0
3.0
4.0
BBVOC Factor
(E)
Nitrocatechol Yield (%)
41.0
42.0
43.0
0
20
40
60
80
100
O_3 (ppbv)

Supporting Information

25. *I'm fine with having multiple short tables on the same page, but I suggest increasing the whitespace between each paper. Since the title and caption are in the same font, page 11 of the SI is hard for me to quickly parse. Also, isn't it ACP convention to put table captions at the top of the table? (Or is that just what most people have done previously.)*

    We have increased the white space between the table on page 11. We have also moved the table captions to the top of the table to align with ACP convention.

26. *Page S2, Mechanism section (line 1202)-I'm a little confused by the comment "reactions in red are already in the MCM and will need to be replaced when used in conjunction with an MCM mechanism." Maybe the meaning here is clear to regular MCM users, but by "replace" do you mean "remove"? Could you expand on this note a little more to make the meaning more clear?*

    Remove would be most accurate. We have modified the yields for phenolic oxidation by NO_3 and OH. Therefore, our mechanism duplicates these reactions in the MCM, but changes the yield. As a result, a user will need to remove the original reactions in the MCM mechanism. The following text was changed to clarify.

    > Original:
    >
    > "Note: reactions in red are already in the MCM and will need to be replaced when used in conjunction with an MCM mechanism."
    >
    > Revision:
    >
    > "Note: reactions in red are already included in the MCM with a different yield. When using the below mechanism in conjunction with the MCM, the red reactions will need to be removed from the MCM to avoid duplicate reactions."

Technical comments

27. *Line 186: looks like the WF1 and WF2 fires should be referred to as Fig 1B and 1C. Note that in discussing the Cow fire (lines 195-199) you don't refer to Fig 1E.*

    These changes were made.

28. *Line 376: switches between X and x, are these meant to be consistent (X or x)?*

    Yes, these are meant to be consistent. Instances of lower case x were changed to capital X.

29. *Line 424: missing parentheses around Decker citation.*

    Parenthesis have been added.

Responses to Referee 2 Comments

Major Comments:

1. *Length: The article is too long and I recommend that the authors try to summarize the key findings and arguments at the beginning of section 4 in a bulleted format. At the same time, they should also lay down the discrepancies discovered in the modeling as they wouldn't want the reader to assume that the model agreed with the measurements perfectly for all fires and instances. Researcher studying this topic will be more interested in the interpretation of the nuanced model-measurement comparison.*

   We thank the reviewer for the suggestion. We have converted the conclusion section (section 4) into a bulleted format. We also added a summary of the model and observation comparison section (2.4), which includes additions discussed in comment 2. Specific changes are below.

   Original:

   Our model suggests OH is reactive to most BBVOCs, while NO_3 is most reactive to phenolics, and O_3 to alkenes and terpenes. We find that initial reactivity is a good indicator for subsequent oxidation by OH, but not for NO_3 and O_3. For example, unlike urban plumes, we find that NO_3 loss to NO, photolysis and heterogeneous uptake are negligible loss pathways, and that most (≥98 %) of NO_3 loss occurs through BBVOC oxidation.

   Phenolics are the only BBVOC group for which oxidation by NO_3, OH, and O_3 is competitive. Specifically, NO_3 is responsible for 26 – 52 % of phenolic loss and leads (36%) phenolic oxidation in an optically thick mid-day plume. In addition, all phenolic oxidation after sunset is dependent on O_3, whether through direct oxidation by O_3, production of NO_3 by NO_2 + O_3, or ozonolysis of unsaturated hydrocarbons and subsequent decomposition to OH radicals.

   We find NO_3 chemistry is responsible for 72 – 92 % (84 % in an optically thick mid-day plume) of nitrocatechol formation and controls nitrophenolic formation overall. Ultimately, nitrophenolic formation pathways account for 58 – 66 % of NO_x loss by sunrise the following day. Formation of nitrophenolics by NO_3, as opposed to OH, is the largest NO_x sink and accounts for most of the inorganic and organic nitrogen at the end of the night. While both PANs and PNA account for most of the NO_x loss shortly after emission, they decompose overnight providing a NO_x source for nitrophenolic formation and increase nitrocatechol yield.

   Revision:

   - **Section 2.4: Observations and Model Comparison**
     - Our model achieves agreement with observed CO and O_3 typically within a difference of 10 %. However, strong O_3 gradients between

plume center and edge can cause larger differences, specifically in the WF2 model run.

  - Absolute differences between the model and observations of NO_x and HONO are generally < 1 ppbv, but can be as large as 3.4 ppbv.
  - In most cases, BBVOC comparisons show that the model and observations agree within a factor of ~2, if not within observation errors.
  - Model and observation agreement for phenolics and nitrophenolics is only available for two model runs (Castle and Cow) and most comparisons agree within observation errors, but some disagree by as much as a factor of 60.

- **Section 3.1: Reactivity**
  - Our model suggests OH is reactive to most BBVOCs, while NO_3 is most reactive to phenolics, and O_3 to alkenes and terpenes.
  - Unlike urban plumes, NO_3 loss to NO, photolysis and heterogeneous uptake are negligible loss pathways. Most (>97 %) of NO_3 loss occurs through BBVOC oxidation.
  - Reactivity of OH and O_3 is similar to, or greater than urban plumes, but NO_3 reactivity is a factor of $10 – 10^4$ greater than typical urban plume reactivity.
- **Section 3.2: Oxidation Rates**
  - Initial reactivity is a good indicator for subsequent oxidation by OH, but not for NO_3 and O_3.
  - Phenolics are the only BBVOC group for which oxidation by NO_3, OH, and O_3 is competitive.
  - The nitrate radical is responsible for 26 – 52 % of phenolic loss and leads (36%) phenolic oxidation in an optically thick mid-day plume.
- **Section 3.3: Phenolic Oxidation and Nitrophenolic Production**
  - All phenolic oxidation after sunset is dependent on O_3, whether through direct oxidation by O_3, production of NO_3 by $NO_2 + O_3$, or ozonolysis of unsaturated hydrocarbons and subsequent decomposition to OH radicals.
  - Yields of nitrocatechol vary between 33 – 45 %.
  - Nitrate radical chemistry is responsible for 72 – 92 % (84 % in an optically thick mid-day plume) of nitrocatechol formation and controls nitrophenolic formation overall.

- **Section 3.4: Fate of NO_x in Dark BB Plumes**
  - Formation of nitrophenolics by NO_3, as opposed to OH, is the largest NO_x sink and accounts for most of the inorganic and organic nitrogen at the end of the night.
  - Nitrophenolic formation pathways account for 58 – 66 % of NO_x loss by sunrise the following day.
  - While both PANs and PNA account for most of the NO_x loss shortly after emission, they decompose overnight providing a NO_x source for nitrophenolic formation and increase nitrocatechol yield.

2. *VOC measurements: How did the individual BBVOCs as measured by the various gasphase trace instruments compare against the time-resolved model predictions? It seems to me that several instruments in this list (https://csl.noaa.gov/projects/firexaq/dc8/payload.html) could have easily measured the reduced and lightly-oxygenated VOCs described in this paper (alkanes, single-ring aromatics, alkenes, biogenic VOCs)? These comparisons, assuming if they are found to be reasonable, would provide additional evidence for the oxidant-resolved decay of the VOCs driving the oxidation chemistry inside the plumes. A very related point is also why these same measurements were not used to initialize the BBVOCs. How do the lab measurements (e.g., during FIREX-2016) compare against these field measurements? Is it appropriate to use a lab-based emissions profile to initialize the model. Either these measurements need to be included in the analysis or a strong reason needs to be provided for why these were not included. I would consider this a major limitation of this study.*

We thank the reviewer for the question. Below are responses to each part of comment 2.

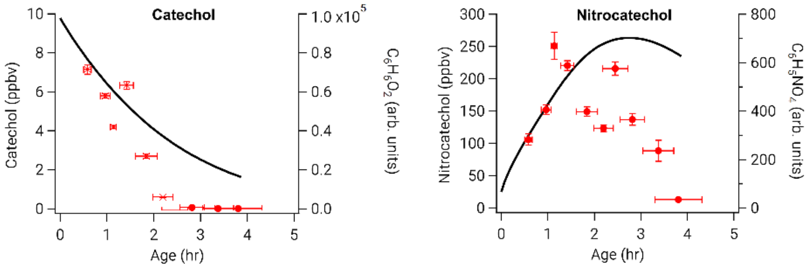
Comparison of model to more observations: We agree that additional model and observation comparisons would be beneficial. We used all high time resolution (~1 Hz) data that was available at the time of submission. We chose to exclude measurements with lower time resolution, and integrated measurements, because our analysis focuses on the plume center only. Measurements with insufficient time resolution may only capture a plume edge or capture a mixture of plume edge and center chemistry that would be inappropriate for our plume center analysis.

The link provided in comment 2 above refers to the DC-8 payload. This is relevant to the Williams Flats first and second plume samplings on Aug 07, 2019, that were used in our box model (referred to as WF1 and WF2 within the manuscript). On this flight, the NOAA H_3O^+ Time of Flight Mass Spectrometer was inoperable. The University of Innsbruck Proton Transfer Reaction Time of Flight Mass Spectrometer (PTR ToF MS) was operating, but at the time of manuscript submission the data were uncalibrated and had not been released for use. These data are now available. Therefore, we have added 11 new model and observation comparisons to the manuscript. These additions include a brief description in the main text (see below), as well as a revision of SI Figure 7 and 8 and two additional figures (SI Figure 11 and 12). Generally, the comparisons show that the model and observations agree within a factor of ~2, if not within observation errors. All comparisons made in the manuscript only take observation errors into account and neglect model errors. Model errors include variability in laboratory derived emission ratios, which can vary by a factor of 10 or more. Therefore, we consider a factor of 2 agreement to be acceptable.

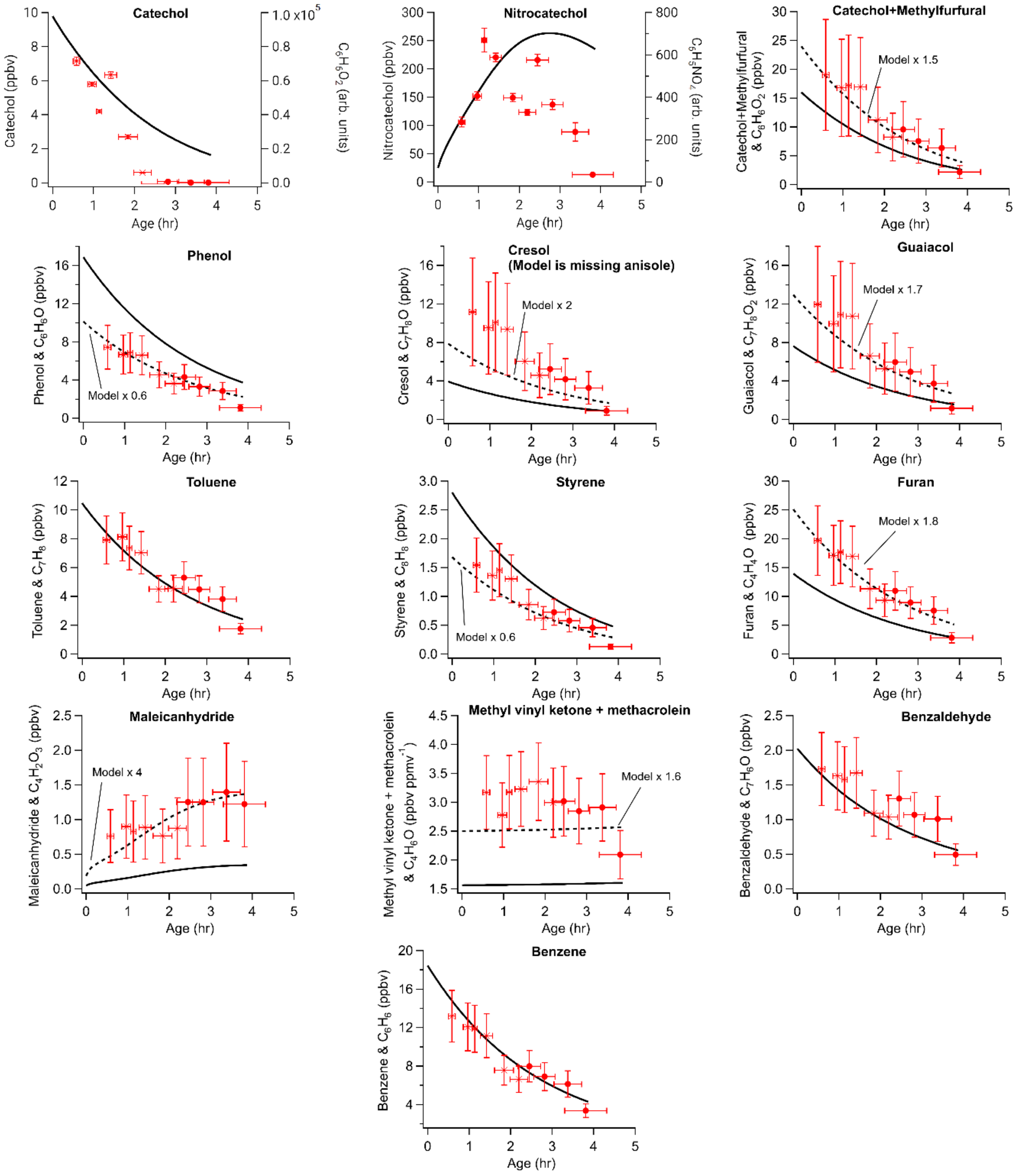
Added text to section 2.4

> “Additional model and observation comparisons of BBVOCs, including phenolics (discussed in detail below) are included in SI Figure 5 – SI Figure 12. In most cases, the comparisons show that the model and observations agree within a factor of ~2, if not within observation errors.”

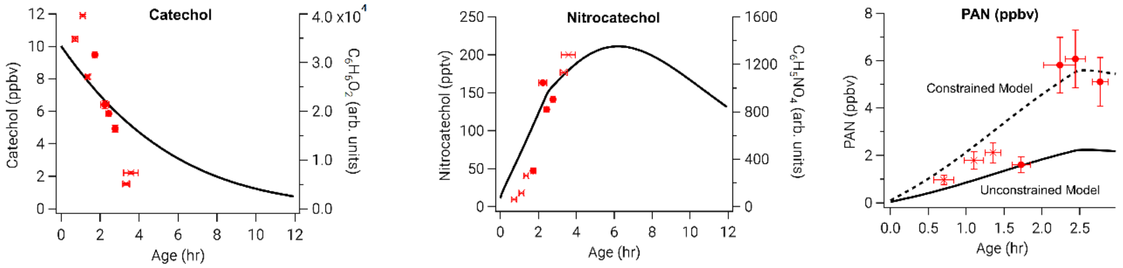
Original of SI Figure 7



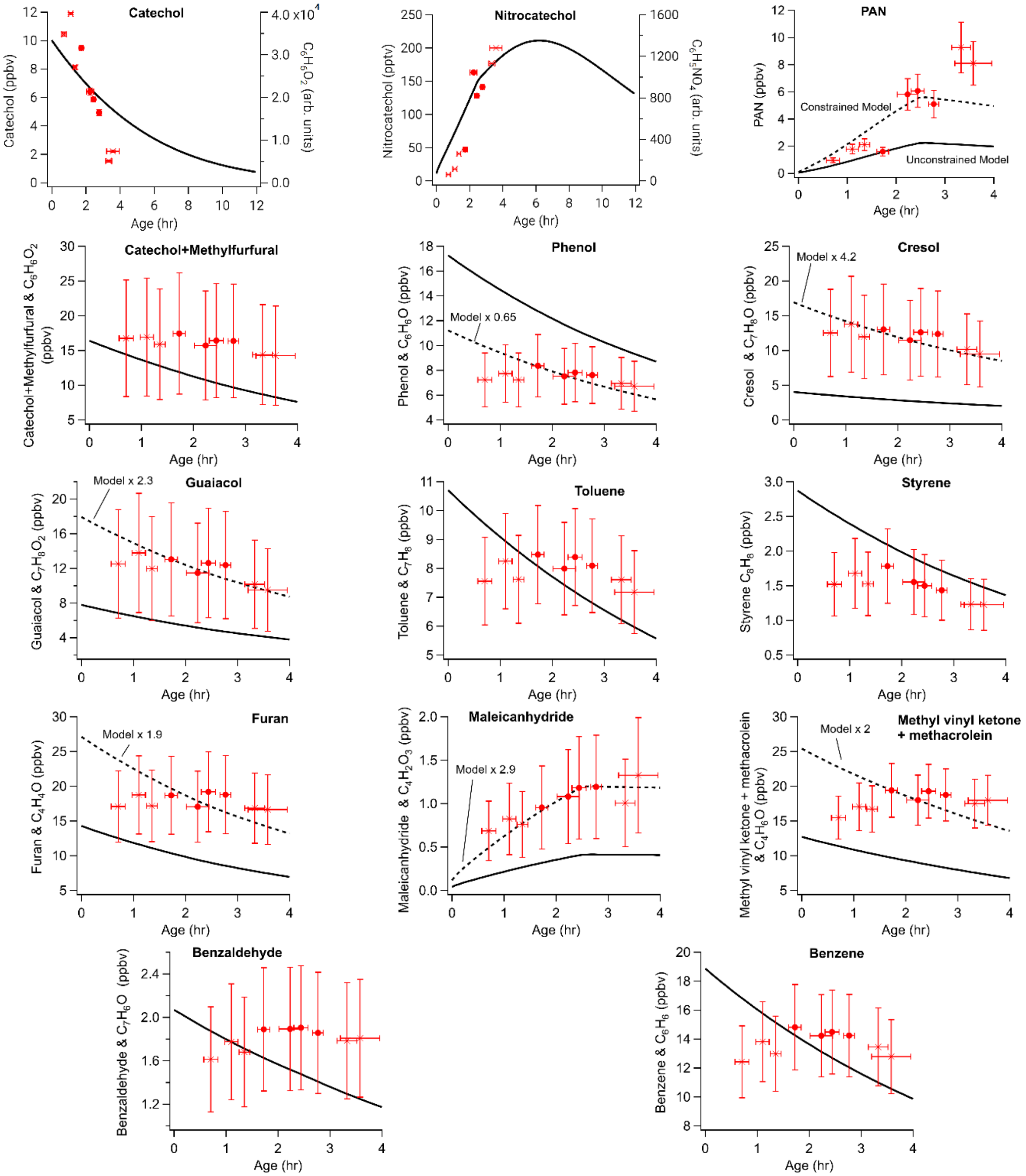
Revision of SI Figure 7



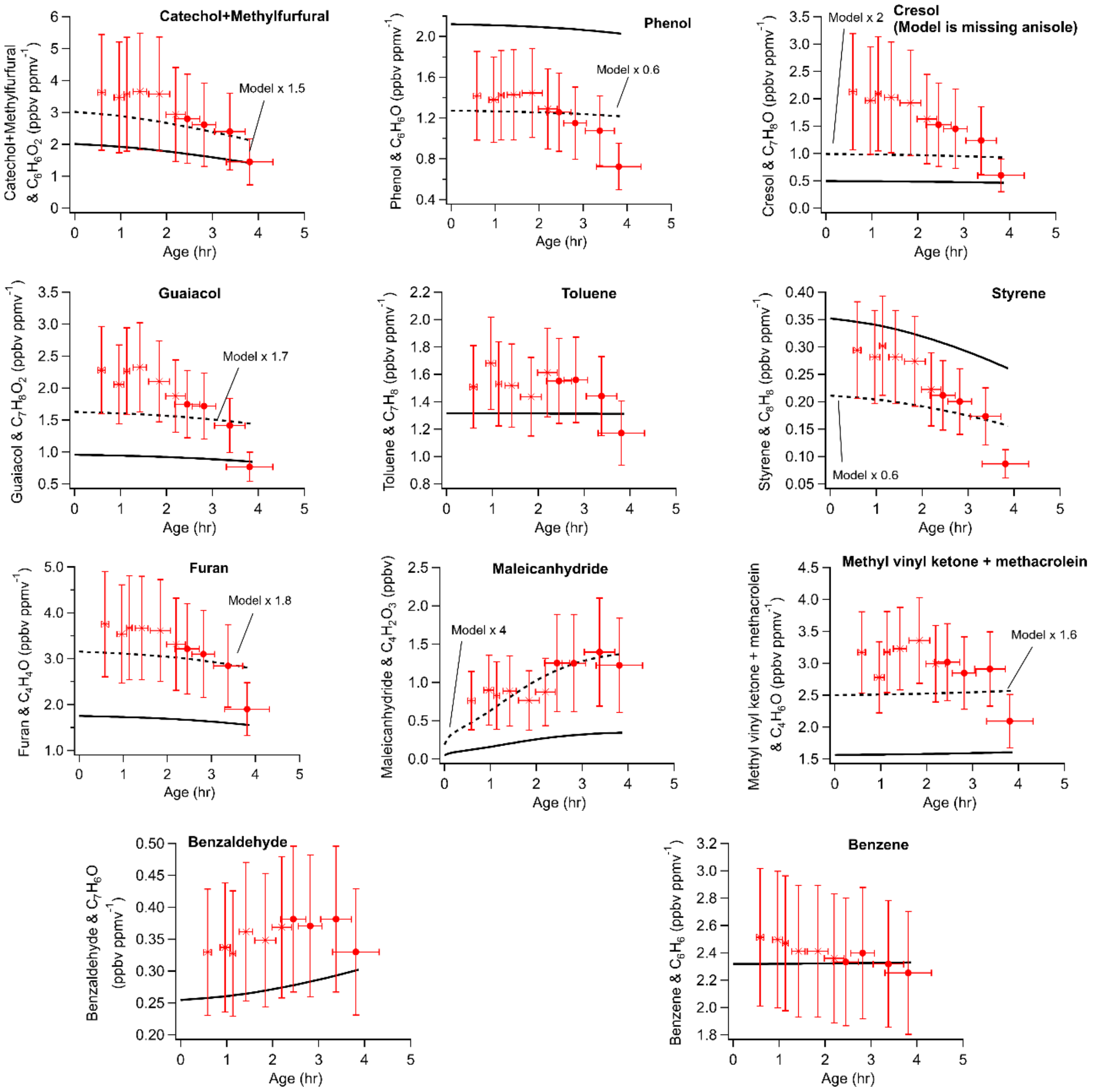
Original of SI Figure 8



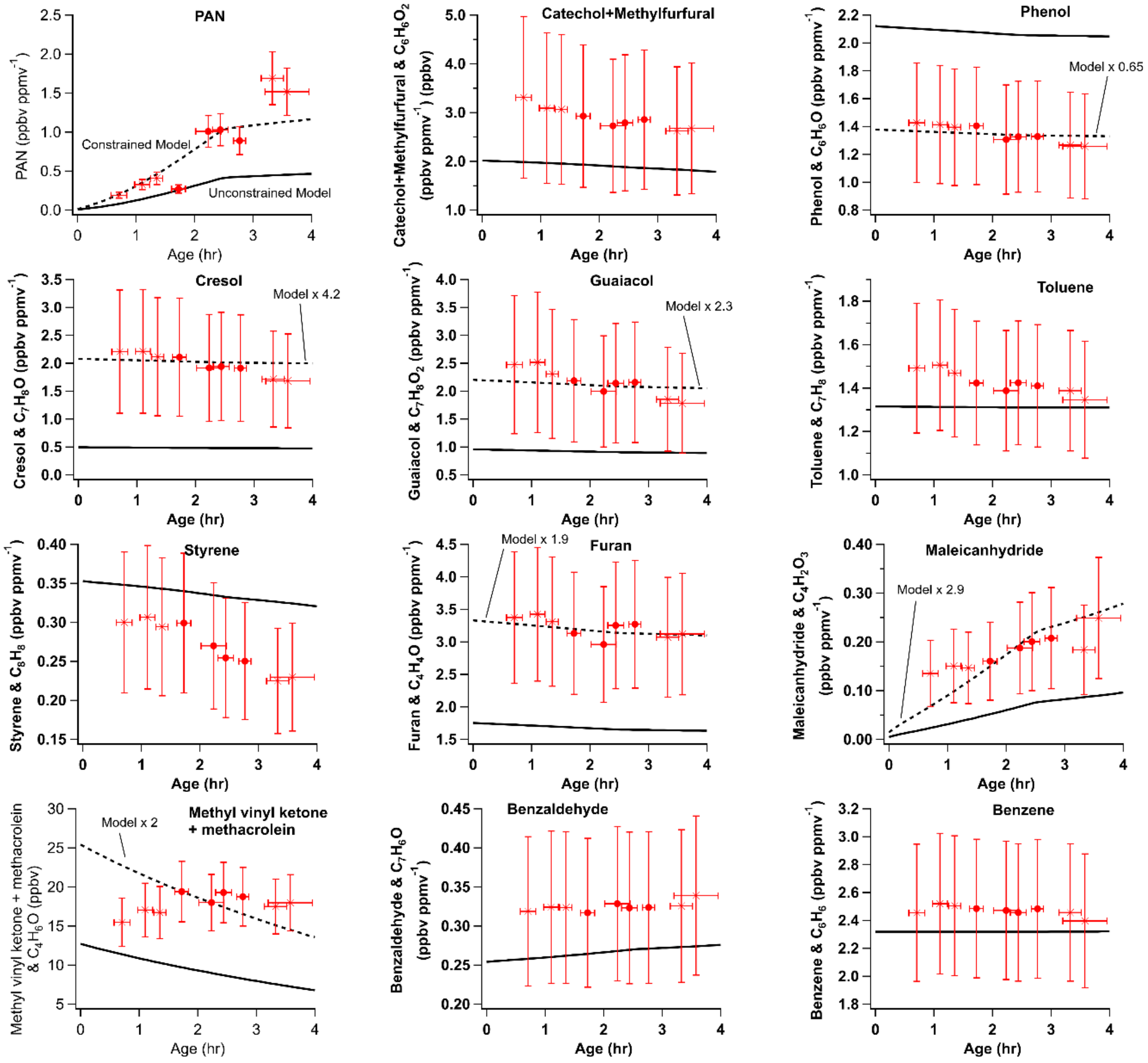
Revision of SI Figure 8



New SI Figure 11



New SI Figure 12



BBVOC initialization and comparison to lab measurements: As discussed in section 2.3.3, except for the Castle model run, we do not initialize our box model with observations due to older smoke age. Our model is initiated at the time of smoke emission (t = 0), which is always earlier than the first plume sampling. This requires us to use an iterative method to constrain our model with a small number of compounds (CO, NO, NO_2, HONO and O_3). Even so, we can use the model results to understand how well the laboratory derived emissions compare to observations. Generally, the model and observation comparison suggest the laboratory derived emission ratios agree with observations within a factor of ~2 (seen in SI Figure 5 – 12). As described in Decker et al. 2019, this is well within the expected variability for laboratory derived emission ratios.

3. *Qualitative comparisons to day time: I mostly understand the novel contributions of this work in understanding the detailed nighttime evolution of BBVOCs and NOx in wildfire plumes. However, this nighttime evolution needs to be placed in context of the global (i.e., day+night) evolution by comparing to the daytime evolution. How are the lifetimes of NOx and BBVOCs different during the day versus night? What fraction of the total oxidation is happening between day and night? How important are daytime versus nighttime processes to the formation of certain oxidation products (e.g., nitrophenolics)? This day versus night perspective is missing to highlight the relative importance and uniqueness of nighttime chemistry to plume evolution. Perhaps this could be added to Section 4.*

   We thank the reviewer for this comment and agree that a general comparison between daytime and nighttime oxidation processes and rates is relevant. However, the question is complicated since it depends not only on the chemistry, but also on the diel cycle of fire emissions and the ability of aircraft to sample plumes emitted at different times of day. As described in section 2.1, it was not possible with the fires in 2019 to sample smoke that was emitted after dark.

   "However, due to a less active fire season in 2019 (NIFC, 2019) and to the decreasing smoke injection height with time of day for the sampled fires, smoke emitted after dark proved difficult to sample reliably within the altitude range of the NOAA Twin Otter. While the NOAA Twin Otter sampled over a dozen plumes after sunset, plume age estimates (described below) suggest these plumes were emitted before or at sunset."

   Therefore, the comparisons made in this paper are for processes characteristic of daytime emitted smoke only, and aside from the theoretical "dark" model, we do not provide a general comparison of day to night emitted smoke. Such a comparison might be possible with a different sampling strategy than was possible with the Twin Otter or DC-8 in 2019.

   From a purely chemical (rather than dynamical, fire cycle) perspective, comparison of oxidation processes requires defining a day to night threshold. However, as we show in the manuscript, "daytime" and "nighttime" oxidation can happen regardless of the time of day and the transition between primarily "daytime" to/from "nighttime" can be complex. Further, we find that oxidation conditions can vary significantly depending on other factors, such as background O_3, that cannot be easily categorized as a daytime or nighttime condition. Therefore, we have chosen to describe the oxidation conditions in context of actinic flux and O_3 conditions throughout the text.

   How are the lifetimes of NOx and BBVOCs different during the day versus night? We believe this question is quantitatively addressed in section 3.4.2. Specifically, lines 659 – 667 copied below. Even so, we have added a qualitative summarizing statement (bolded below) to make the day vs. night comparison clear.

   "Model runs with relatively large photolysis and O_3 at emission (Castle, Cow, and WF1) have near emission τ_{NO_x} that range from 1 – 3 h (Figure 11), which are accompanied by larger total oxidation rates for all BBVOCs (SI Figure 13 – SI Figure 15). These model runs also exhibit the fastest nitrophenolic formation rates (section 3.3.2 and Figure 8). In contrast model runs with low or zero photolysis and near zero O_3 (WF2 and Dark) exhibit near emission τ_{NO_x} = ~10 – 16 h and τ_{NO_x} = 20 – 150 h, respectively. The absence of photolysis in the Dark model run explains the large difference in τ_{NO_x}between the WF2 and Dark model runs as the WF2 model run has greater O_3 and P(NO_3) that promotes NO_3 chemistry as well as OH radical that promotes PANs formation. **In short, we find that daytime conditions have shorter NO_x lifetimes, greater rates of BBVOC oxidation, and greater rates of nitrophenolics formation when compared to nighttime conditions.**"

What fraction of the total oxidation is happening between day and night? Providing a fraction is not straightforward. Instead, we discuss oxidation of three main BBVOC groups in the context of actinic flux as well as time of day. This discussion is found in section 3.2.2.

> "To study the competition between all oxidants, we focus on three main BBVOC groups: phenolics, furans/furfurals, and alkenes/terpenes. Generally, furans/furfurals and alkenes/terpenes groups are mainly oxidized by OH and O_3, while NO_3 plays a small role (Figure 6). Oxidation of furans/furfurals and alkenes/terpenes by OH (18 – 55 %, 11 – 43 %, respectively) and O_3 (39 – 76 %, 54 – 88 %, respectively) can vary widely depending on the plume. We find this is due to the variability of actinic flux. In model runs with less photolysis at emission, OH oxidation is low compared to model runs that are more optically thin. This reduction of oxidation by OH appears to be replaced by O_3 rather than NO_3. For example, relative furan/furfural oxidation by OH in the WF1 model run (relatively large integrated jNO_2) is 31 % less than that in the Cow model run (comparatively lower integrated jNO_2), yet O_3 oxidation is 32 % greater. … Generally, NO_3 oxidation of phenolics increases with O_3 availability and decreases with available actinic flux, but these relationships are coupled and complex. One example is seen in the WF2 model run, which has the second lowest integrated jNO_2 value, and large emissions of NO that keep O_3 low during sunlit hours. Therefore, P(NO_3) is reduced, NO_3 is present at lower mixing ratios within the first hour of oxidation, and phenolics are less subject to NO_3 oxidation when compared to the other model runs.
>
> As actinic flux increases so does OH and O_3 production, and therefore oxidant competition. One example is shown by the Castle model run where OH leads phenolic oxidation (41 %) with O_3 second (33 %). The Castle model run demonstrates the greatest observed background O_3 (90 ppbv). Further, the Castle model run has significantly smaller total emissions (based on CO) than the other model runs and the greatest integrated jNO_2. Due to the increased background O_3 and photochemical production of OH, NO_3 plays a smaller role in the oxidation of phenolics (Akherati et al., 2020)."

How important are daytime versus nighttime processes to the formation of certain oxidation products (e.g., nitrophenolics)? The answer to this question is touched on in the sections referenced above but is discussed in detail in section 3.3.2 for nitrophenolics.

> "Nitrophenolic formation increases with O_3 and photolysis, which promotes formation of NO_3 and OH. For example, the Castle and Cow model runs have relatively large O= and jNO_2 at emission and therefore form nitrophenolics rapidly (0.6 – 1.4 ppbv h^{-1} within the first 15 min). In contrast, the WF and Dark model runs have near zero O_3 due to large emissions of NO and relatively low or zero jNO_2 and therefore form nitrophenolics more slowly (<0.1 – 0.7 ppbv h^{-1} within the first 15 min).
>
> Despite the rapid formation of nitrophenolics in the Castle model run, it has the least (excluding WF1) total nitrophenolic formation relative to total emissions as seen in Figure 8. Figure 8 shows integrated nitrophenolic formation per emitted ppmv of CO, which allows us to compare total nitrophenolic formation across varying plume sizes. In contrast to the Castle model run, the Cow model run has the greatest nitrophenolic formation. These differences are the result of differing phenolic oxidation pathways. The Castle model run has a large (90 ppbv) O_3 background, which results in O_3 accounting for ~40% of phenolic oxidation between 30 min – 2 h of age (Figure 7 C). At the end of the Castle model run (2.6 h) O_3 oxidation accounts for 33% of total phenolic loss, the largest of any model run (Figure 6). This is markedly different than the Cow model run where OH and NO3 chemistry control phenolic oxidation before sunset, and NO3 after. While O_3 accounts for only 16 % of phenolic loss at the end of the model run (~12 h). In our model, the reaction of O_3 + phenolics forms a ring opening product (SI Figure 14), but the rate coefficients and mechanisms are largely uncertain as discussed in the following section."

Minor Comments:

4. *Line 206: Did the other fire cases not run into near-background levels if run for 12 hours?*

   The reviewer is correct. We have updated the line in question to clarify.

   > "<u>There were sufficient emissions for the WF1, WF2, Dark, and Cow model runs such that there were emissions remaining above background levels after 12 h of model time.</u> The Cow, WF2, and Dark cases are run from emission until sunrise the following day (about 12 h). The Castle case is run for 2.6 h until all BB emissions are near (<<1%) background levels. We run the WF1 case until the age of the oldest sampled smoke (~4 h) because we do not have any observations of photolysis rates with which to constrain the model past that point."

5. *Line 209: How is the 'earliest smoke transect' define? Shouldn't this be at 't=0'?*

The earliest smoke transect is defined as the aircraft transect that sampled the youngest smoke (typically the first transect performed) which had a smoke age > 0, as stated in the manuscript (line 210) "between 2 min and 2 h".

We use age to refer to smoke age and, by definition, the model time and smoke age are equivalent. In other words, we initiate the model at age = 0, as stated in the manuscript (line 209 – 210) "We start the model at the emission time (age = 0) of the earliest smoke transect (the youngest sampled smoke)". This means we initiate the model smoke before it is sampled by the aircraft.

> *Line 282: An average of all outside-plume data for a given fire or was a transect specific background used instead? If the former, it should be pointed out that the background would be evolving as well.*

In all models we use a constant background value ("an average outside of the plume", line 282). We found that only O_3 has a significant change in background mixing ratio between transect. This is discussed in the manuscript in lines 307 – 311 copied below:

> "Ozone median differences vary from 0.3 – 6.3 ppbv with a median difference of 0.8 – 27.2 % across all runs. For the WF1 and WF2 plumes we found that a significant increase (38.5 ± 0.4 and 35.3 ± 7.5 ppbv, SI Table 2 and SI Table 5) in model background O_3 compared to the upwind leg was required to capture the observed plume-center O_3. This is due to photochemical O_3 production at the plume edges, where O_3 was as much as a factor of ~2 greater than the background O_3. The increased plume edge O_3 is not captured in our plume-center model, and thus requires an increase in model background O_3."

6. *Section 2.3.3: I anticipate that similar modeling exercises will be executed to study the gas/particle evolution in wildfire plumes given the data generated by FIREX-AQ and other similar field campaigns focused on fires (e.g., WE-CAN). The paper could benefit from a flowchart that explains the iterative process of constraining dilution and chemistry.*

   We thank the reviewer for the suggestion. Considering that the manuscript is already long, as stated by the reviewer in comment 1, with 11 main text figures and, now, 18 SI figure we have decided not to expand the figure count. We believe the written description conveys the iterative process clearly.

   > "We began iteration with CO and k_{dil} by increasing best-guess estimates of CO and varying k_{dil} within the fit errors until we minimized the differences between observed and modeled CO. This in-turn determines the emissions of BBVOCs by Eq. (1). Next, we iterated NO_x, HONO and the NO/NO_x ratio such that the sum of NO_x and HONO did not exceed the observed NO_y and the initial NO/NO_x ratio remained between 0.6 – 1 (Roberts et al., 2020). Lastly, we iterated the initial and background O_3. As explained in section 2.4, we were required to iterate on background O_3

> in some model runs in order to achieve agreement between model and observations. We repeated the above process to minimize the differences between model and observations. In an attempt to avoid finding a local solution, as opposed to the "best" solution, we reversed the order of iterating O_3, NO_x and HONO when repeating the above process."

7. *Line 324-328: How does this reactive nitrogen evolution compare to observations during the WE-CAN campaign (Juncosa Calahorrano, JGR, 2020)?*

The WE-CAN NO_y budget presented by Calahorrano et al. generally agrees with the budget presented in our manuscript. A detailed comparison to Calahorrano *et al.* is beyond the scope of this paper since a more specific manuscript on the FIREX-AQ NO_y budget is currently in preparation. We have made the following additions to this paper, however.

First, note that the budget presented by Calahorrano et al. is for NO_y, while the budget presented in this manuscript is NO_z ($=NO_y-NO_x$). The fraction of PANs in both budgets may be the most straightforward compound to compare. Generally, our maximum fraction of PANs (~50 %) agrees with Calahorrano et al. (~40%) within our model uncertainties for PAN (described in lines 629 – 636) during sunlit hours. Our model begins to deviate from the NO_y budget trend seen by Calahorrano et al. once the sun sets, as expected.

The NO_y budget by Calahorrano et al. is divided into measurement categories such as pNO_3 (particulate nitrate) and Σ Org $N_{(g)}$ (sum of gas-phase organic nitrogen species). These are difficult to compare with our model. We find that nitrophenolics account for a large fraction of the NO_y budget. The nitrophenolics are expected to be in the gas-phase and particle phase. The amount in either phase varies widely based on the nitrophenolic (nitrophenol vs nitrocatechol, for example). Our model does not include particle phase partitioning of the nitrophenolics because the parameters needed to determine this is currently not well known. Instead, the model assumes the nitrophenolics remain in the gas-phase (as discussed in the manuscript in lines 358 – 361).

Further, inorganic nitrate likely accounts for a large fraction of pNO_3 in the NO_y budget by Calahorrano et al. Our model does not account for these particle phase losses. One way to make a rough comparison of our budget to the NO_y budget by Calahorrano et al. would be to compare the sum of Nitrophenolics, HNO_3, and PNA (~40 %) to the sum of Σ Org $N_{(g)}$ and pNO_3 (~45 %) after ~2 h of smoke age. This comparison finds rough agreement within the model and measurement errors. However, as stated earlier, there are large uncertainties associated with this type of comparison.

We have added a brief description of this comparison to the text at the end of section 3.4.1.

> “Our NO_z budget generally agrees with the NO_y budget of western U.S. wildfire smoke sampled during the 2018 Western Wildfire Experiment for Cloud Chemistry, Aerosol Absorption, and Nitrogen (WE-CAN) presented by Juncosa Calahorrano et al., 2020. Generally, the maximum fraction of PANs in our budget (~50 %) agrees with Juncosa Calahorrano et al. (~40%) within our model uncertainties. Comparisons of particulate nitrate and organic nitrogen (gas or particulate) between our model run and the analysis of Calahorrano et al. are uncertain since our model does not account for gas-particle partitioning of nitrophenolics. Our model begins to deviate from the NO_y budget trend seen by Calahorrano et al. once the sun sets, as expected.”

8. *Figure 2, 3, and elsewhere: As most of the changes in the absolute concentrations and reactivity are being driven by dilution/mixing with background, it’s hard to see the role of chemistry on the trace gas evolution. Wouldn’t it be better to present these data with respect to a chemically-inert tracer (e.g., as a ratio to dCO or dAcetonitrile)?*

   We agree that dilution plays a dominant role for mixing ratio and reactivity change with respect to time. Below we respond to this comment separately for mixing ratios and for reactivity.

   Mixing Ratios: The main goal of Figure 2 in the main text is to provide a comparison of the model and observations, which requires a comparison of dilution. We also provide dilution corrected (as normalized excess mixing ratios relative to CO) versions of Figure 2 in SI Figures 4 – 12, which are discussed throughout the text.

   Reactivity: Figure 3 includes a time series plot in the lower most panel, which is affected by dilution. We chose to keep this figure in absolute reactivity (as opposed to relative reactivity) in order to communicate the large scale of the smoke reactivity. Further, as stated in lines 424 – 431, the absolute reactivities are determined by our BB emissions database, which is relative to CO. Therefore, normalizing these figures by CO would eliminate this absolute reactivity comparison. We argue that differences in chemistry are seen when comparing each time series in the bottom of Figure 3 against each other. That is, comparing the absolute change in reactivity for NO_3 against OH and O_3. This comparison is made in the main text beginning on line 393.

9. *Line 446: NO2?*

   This line is correct as written. The main loss for NO_3 in urban plumes is indeed reaction with NO or photolysis of NO_3.

10. *Line 528: This suggests that the lifetime of phenolics during the night are likely to be much longer than those during the day. This day versus night distinction needs to be provided to communicate and quantify that the nighttime/dark chemistry is much slower than during the day.*

    Yes, that is correct. To make this distinction clear, and to quantify it, we have added the following text to the end of the referenced paragraph.

> “Generally, the phenolic lifetime increases with decreasing actinic flux. The contrast between day and night phenolic oxidation is best seen by comparing the WF2 and Dark model runs. Phenolic lifetimes in the Dark model run are, on average, a factor of ~2 greater than phenolic lifetime in the WF2 model run.”

11. *General question: would it be more appropriate to refer to phenolics as oxygenated aromatics? I am not trained as a chemist so I don’t know the answer to that question.*

There is not clear nomenclature for these compounds, however we have tried to be as consistent as possible with our language. We argue that oxygenated aromatics would also include compounds such as furans and furfurals. While these are also important compounds in BB, we are referring to 6-membered benzene rings with attached alcohol(s). The simplest form is phenol, and we generally use “phenolics” to refer to phenol and its higher order cousins. To clarify this point for the reader, we have added the following text after the first instance of phenolics.

> “Specifically, directly emitted aromatic alcohols (phenolics, <u>i.e. 6-membered aromatic rings with an alcohol functional group, which are distinct from the broader class of oxygenated aromatics that also includes furans, furfuals, etc.</u>) react with NO_3 at near the…”

12. *Section 3.3.2: The nitrophenolic oxidation products are presumably semi-volatile so they should partition into the particle phase to some degree. How does this affect the model-measurement comparisons shown (SI Figures 5-10)?*

We agree that nitrophenolic compounds are semi-volatile and most, if not all, of some nitrophenolics are expected to partition to the particle-phase. The MCM includes gas-phase losses of nitrophenolics, only, through further nitration. These gas-phase losses are expected but have yet to be presented in peer-reviewed literature. Therefore, the loss processes for gas-phase nitrophenolics in our model are incomplete. We discuss this caveat in section 2.4.3.

> “Overall the model recreates the relative time evolution of nitrophenolics well. Disagreement between the model and observed compounds could be caused by many factors including, but not limited to, interfering isomers measured by the UW I^- HR ToF CIMS or the NOAA I^- ToF CIMS, variable fire ERs, and loss or production of nitrophenolics not captured by our mechanism. The MCM includes several gas-phase loss processes of nitrophenolics, but no gas to particle partitioning. Nitrophenolics readily partition to the aerosol phase (Finewax et al., 2018). Further, the MCM does not include photolytic loss of nitrophenolics, despite some evidence to the contrary (Sangwan and Zhu, 2016, 2018). Therefore, when analyzing gas phase nitrophenolic evolution we only consider integrated formation, as discussed in section 3.3.2.”

SI Figures 5 – 10 compare gas-phase measurements (both calibrated and uncalibrated) of nitrophenolics to modeled gas-phase nitrophenolics mixing ratios. Generally, the model either agrees with observations or is greater than observations. Omitting the aerosol loss pathway may be the cause for some discrepancies. However, precisely how these differences affect the model and observation comparison is uncertain. To clarify this point to the reader, we have added the following text to the above section.

> "Further, the MCM does not include photolytic loss of nitrophenolics, despite some evidence to the contrary (Sangwan and Zhu, 2016, 2018). Omitting the aerosol loss pathway may be the cause for these discrepancies. However, precisely how these differences affect the model and observation comparison is uncertain. Therefore, when analyzing gas phase nitrophenolic evolution we only consider integrated formation, as discussed in section 3.3.2."

13. *SI Figure 3: Why were early CO values for WF1 not included to model dilution? What's happening with the low CO values around 1 hour of age for WF2?*

These values were removed according to our transect selection criteria described in the main text (lines 246 – 248) and copied below:

"Fire emissions and photolysis conditions can change rapidly, therefore we constrain the model to a subset of plume transects. We chose transects that showed a monotonic decrease of CO with distance from the fire, cover an age range of at least one hour, and have similar emission times as shown in SI Figure 2 – 3 and SI Table 2."

It is likely that the differences in CO decay seen in WF2 near 1 h are the result of sampling smoke emitted under significantly different fire conditions, or the aircraft sampled a different part of the smoke plume (e.g. transecting the upper boundaries of the plume as the smoke was still rising).

14. *Figure 11: Can similar comparisons be done for the various NOz species (other than the nitrophenolics) as undertaken for CO, NO, NO2, etc. in Figure 2 and phenolics in SI Figures 5-10? It looks like some of the NOz species were measured as per SI Table 1.*

Figure 11 is a comparison of NO_x lifetime as a function of age for each model run, as well a comparison of how much NO_x remains at the end of the model run. Figure 2 and the SI Figures 5 – 10 are direct observation and model comparisons in mixing ratio space, or uncalibrated arbitrary units and mixing ratio space. It is not possible to make direct observation and model comparisons of lifetimes.