Response to Reviewer 2

We thank the reviewer for the insightful comments and suggestions. We have addressed the reviewer's concern by making the following modifications to the paper.

General comments:

The paper presents a wide range of topics and analyses. Little background is provided to bring the reader up-to-speed on the various analyses techniques or chemical mechanisms. I wonder if the paper should be split into two papers so more thorough discussions can be provided.

We thank the reviewer for pointing this out.

Because the main text of this article is already quite lengthy, we moved some analytical details from this article into the Supplement and referred to other published articles for the analytical details and uncertainty information. Samples for this work were analyzed in the same batch with Jen et al. (2019), and the quantification standards used are also the same.

We respectfully prefer not to split this article into 2 at this stage. We are preparing another manuscript that focuses on the PTR-TOF-MS data from these same fire periods. Further discussion of the oxidation mechanisms will be provided in that paper.

There is no mention of data quality or uncertainties in the paper. These are very low concentrations and especially when ratios are presented, I question the reliability of the values.

We thank the author for this comment. However, in the main text, we have written that:

"As estimated by Jen et al. (2019), compounds exactly matched with a standard compound have an uncertainty ~ ±10%. Compounds quantified by the nearest compound in the same class have an uncertainty of ~ ±30%. Compounds with unknown functionality have a systematic uncertainty of 200%. We expect compounds with second column retention time > 1.6 s to also have such high uncertainty because there were no standard compounds with that high polarity, and a surrogate standard with lower polarity was used for quantification. However, only 7 reported compounds were in that chromatographic region with extremely high quantitative uncertainty."

We will add the following sentence to this paragraph.

Calibration was performed down to 2-10 ng for most compounds, and 20 ng for very polar compounds such as 2,4-dinitrophenol, 5-nitrovanillin and 4-nitrocatechol. In such concentrations, these analytes were observed at 10-10000 times the chromatographic signal-noise ratio. We can very conservatively assume the detection limit to be 1 ng. When we took a 3-hour sample at 21 lpm, the limit of detection was equivalent to ~ 0.26 ng m^{-3}. That is far below the concentrations of most compounds measured.

Specific comments:

Line 33: Confusing sentence, suggest eliminating "primary and secondary" to simplify.

We deleted "primary and secondary" as suggested by the reviewer. Now the sentence reads:

We observed no net particle-phase organic carbon formation, which indicates an approximate balance between the mass of evaporated primary and secondary organic carbonaceous compounds to the addition of secondary organic carbonaceous compounds.

Line 135: Why does the temperature only go up to 320C?

The temperature of the GC oven can go above 320°C. However, the thermal desorption system we have cannot ramp to temperatures far above 320°C. The GC oven final ramp temperature was therefore set at 320°C. Also, by ramping to 320°C and holding there for 5 minutes, compounds having volatilities close to C36 alkane can elute, defining the lower volatility range of observable compounds by this method which is typical of GC-MS analyses for biomass burning particulate matter.

Lines 238-245: A comment on the accuracy of the forest inventories might be appropriate. I laughed at the 0.3% because these estimates have so much uncertainty.

This 0.3% is obtained by spatially joining the fire perimeter and the post-fire canopy damage databased provided by the Sonoma County authority. They did not specifically report the uncertainty of this survey. We cannot comment on potential uncertainties from the survey but refer the reviewer to the report of that survey for the details (https://sonomaopenspace.egnyte.com/dl/sJcDLWK7U5/?). We agree that stating 0.3% here is unnecessary. We changed the sentence to:

"Conifer vegetation accounted for less than 1% of the area within the perimeter of the Atlas Fire."

Line 270-271: This sentence seems out of place. I don't understand how it fits into the current paragraph. What is EI?

We thank the reviewer for raising this issue. We changed the sentence to:

"Based on the structures, most of these sugars (if underivatized) can fragment into $C_2H_4O_2^+$ (*m/z* 60) under electron ionization, which can contribute to the signal of $C_2H_4O_2^+$ when they are measured by aerosol mass spectrometers (Fabbri et al., 2002)"

Lines 279-288: This seems like introductory material since it is primarily on previous studies. Lines 288-289: This seems out of place, like a discussion or conclusion point.

We agree that some sentences here do not fit very well into the result and discussion section. However, the description of the toxicity of PAHs and other compounds here can support our argument that evaluation of more compounds' health effects in the fire aerosols is necessary. We shortened this paragraph to:

"In all samples, the fraction of PAHs remained below 0.3% of total quantified OA. The low PAH fraction in OA measured at UCB could be a result of both low PAH emission and photochemical loss. The emission, exposure, and health impacts of PAHs in biomass burning received a great deal of attention in previous studies (Shen et al., 2013; Sun et al., 2018; Tuet et al., 2019). However, other groups of compounds, such as monocyclic aromatic compounds including hydroquinone, catechol and cinnamaldehyde (Leanderson and Tagesson, 1990; Muthumalage et al., 2018), may also make substantial contributions to the toxicity of biomass burning smoke. The maximum concentrations of the most abundant positively identified compounds and most abundant PAHs observed at Berkeley and their possible hazards are listed in Table S1. Knowledge of the health impacts of inhaling compounds in this list are still lacking. For example, many nitroaromatic compounds were found to be mutagenic (Purohit and Basu, 2000). The nitro-compounds were found to be the main contributor to the mutagenicity of $PM_{2.5}$ in Northern Italy (Traversi et al., 2009). The sum of concentrations of (methyl-)nitrocatechols observed at Berkeley exceeded 1.2 μg m-3. However, no toxicological research of these compounds was found in PubChem."

Line 326-327: Suggest rewrite of this sentence, as written it sounds like this work showed that hydroquinone and two other compounds were shown to be good tracers, but that's not the case.

We changed the sentence to:

"Hydroquinone and two other compounds were also shown to be good tracers for manzanita burning in our previous work (Jen et al., 2018). They were present in most of the plumes, which is in line with our finding that manzanita is widely distributed in that region."

Line 336: Suggest replacing "reached peak" with "peaked" for clarity.

We changed it as suggested by the reviewer.

Line 339-340: This is a strong statement for what looks like a weak pattern in the figure. Suggest softening to something like "our observations were consistent with the hypothesis that 7-oxo-DHAA to DHAA ratio is a useful indicator…"

We changed this sentence as recommended by the reviewer. Now the sentence reads:

"Our observations were consistent with the hypothesis that 7-oxo-DHAA to DHAA ratio is a useful indicator for the formation of BB SOA."

Line 354: Suggest adding a sentence addressing the diel concentration differences expected for OH and NO3 to complete this argument.

We rewrote this part and added an important and recent reference by Palm et al. (2020) to substantiate our conclusion.

"Finewax et al. (2018) has shown that the molar yield of 4-nitrocatehcol when catechol reacts with OH and NO_3 are 0.3 ± 0.03 and 0.91 ± 0.06, respectively. **The dominance of NO_3 radicals as the nighttime oxidants can help to explain the higher nitrocatechols/OC ratio at night. It was recently reported that these nitrocatechols can be further oxidized by OH radicals, the major daytime oxidant (Palm et al., 2020).** The difference in oxidation mechanism is thus a more plausible explanation for the diel changes in the nitrocatechols/OC ratio **observed at Berkeley**."

Line 450: "OSc of compounds can be satisfactorily predicted" This statement was not made in the previous sections, and I'm not clear on how you know it is "satisfactory".

Although we did not explicitly draw this conclusion, we mentioned in line 206-207 that "The saturation vapor pressure model and the $\overline{OS_c}$ model achieved an R^2 of 0.93 and 0.96 between the modeled responses and the true responses, respectively (Figure S2)." In Line 202-295, we also mentioned the similarity of our prediction with Hatch et al (2018). But we understand that the word "satisfactory" may cause some concerns. We removed this word from the sentence. The revised sentence reads:

"We demonstrated that using easily obtained parameters from GC × GC measurements, the volatility and $\overline{OS_c}$ of compounds can be predicted."

Line 734: Instead of "label", I suggest using "symbol" in the caption

We thank the reviewer for this suggestion. We replaced the word "label" with "symbol".

Figure 2: It is hard to distinguish the colors in these figures.

The figure was changed to make the colors contrast more. We also changed two lines to dashed lines to make it easier to read. Now the figure appears as follows:

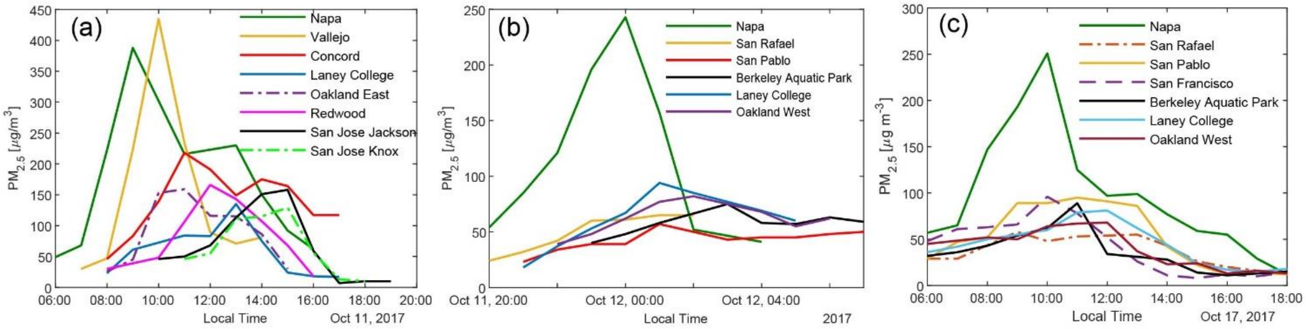

Figure 3: It would be easier to digest if the legend was in the same order as the stacked bars.

We thank the reviewer for this suggestion. We changed both Figure 3 and Figure 8 accordingly.

Figure 3

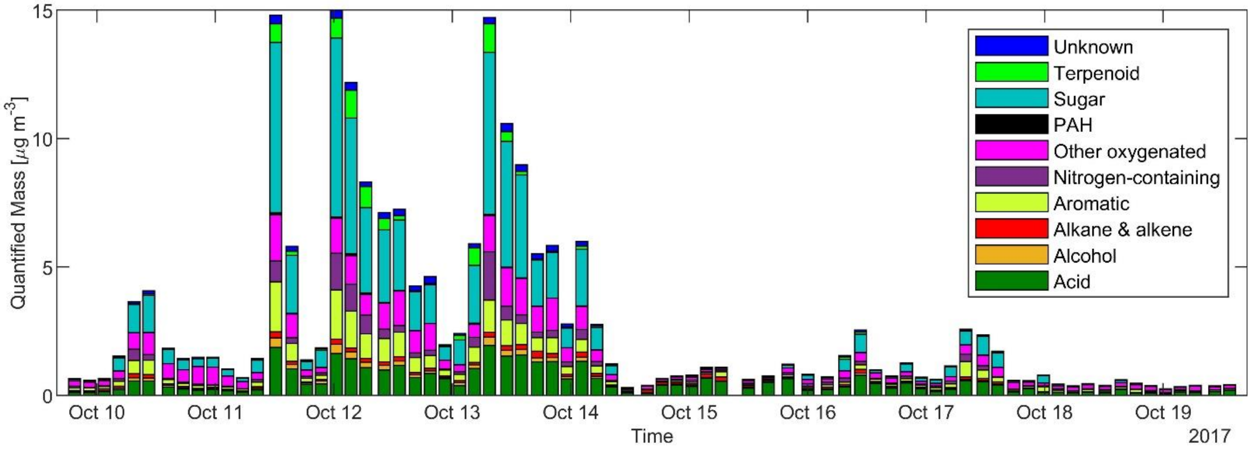

Figure 8