

Comments to the Author:

Thanks for your attention to the reviewers' comments. There are still some issues and unanswered questions that I would ask you to attend to.

You did not answer Reviewer #1's question about what fraction of OH reactivity is represented by these pyrolysis emissions.

Reviewer #1's question, "I don't have a good sense of how important the pre-flame pyrolysis emissions are compared to total emissions from a fire. Do the authors have a metric of what fraction of VOCs (or OH reactivity) is emitted in this process?"

- This is a good question. The fraction of VOCs (or OH reactivity) represented by pre-flame pyrolysis emissions compared to total emissions from a fire can be determined if the total emissions are also measured. Given the present measurements exclusively sampled pre-flame pyrolysis emissions (and not total emissions), the fraction of VOCs (or OH reactivity) cannot be calculated for this particular data set. That said, we have explored this question further using data available in the literature to give the reviewer a sense of the proportion of VOC emitted via pre-flame pyrolysis. It should be noted that the pre-flame pyrolysis period may be quite short in length compared to the other stages of a fire, all of which depend on fuel type and other variables. Using the time profile VOC emissions (including nitrogen and oxygen containing VOCs) provided in the SI by Akagi et al. (2014), the fraction of pre-flame pyrolysis emissions was estimated using measurements from Block 22b and assuming that the time period from 13:40:48–13:45:31 associates with pre-flame emissions (VOC sum of 2.21 ppm) and 13:40:48–16:48:03 for total emissions (VOC sum of 69.8 ppm). The fraction obtained is 0.032, which suggests that the emissions represented by pre-flame pyrolysis are relatively low compared to total emissions. In the study by Akagi et al. (2014), the OPAG was not orientated in such a way as to optimally distinguish and detect pre-flame pyrolysis emissions from other emissions (in that study, the OPAG was specifically set up to capture downwind smoke). For the present manuscript, language has been included suggesting that emissions via pre-flame pyrolysis may be relatively low compared to total emissions from a fire.

Figure 5 is redundant and does not add to the discussion, it should be eliminated.

- The editor is correct. Figure 5 and the associated text have been deleted and remaining text has been reworked.

It seems clear that NH₃ will be lost in the analytical system, but the authors are incorrect that other nitrogen species could be lost too, (line 525 revised text). In fact HCN and CH₃CN are quite well transmitted by stainless steel sampling components. But the authors are correct that amines will also be readily lost in their system.

- The editor is correct that it is really only NH₃ and the amines that are susceptible to this (notorious) sticking problem in such sampling devices. We have revised the text to better reflect the sticking being limited to only NH₃ and its amine cronies.

The authors quote the arithmetic mean is given in Table 2, but the Authors' reply says the geometric mean is the most appropriate - why was it not given instead?

- Indeed, after several internal discussions we report only the arithmetic mean in the manuscript. This is because the geometric mean is far less intuitive and understood by fewer folks, including many of the authors on this paper. It would require a few extra sentences to explain and since the paper is already too long we left it out.

The emphasis on peat content is still in the manuscript (line 548), it doesn't seem like these fuels have any peat content. What the authors' did not explain is that the magnitude of nitrogen compound emissions depends on the N-content in fuels, and did not connect their emission measurements with the fuel nitrogen measurements - are there dependencies there that shown up in the data?

- The editor raises an important point about the fuel content, and any correlations between the fuel nitrogen measurements and gas phase emissions. For the N-species it would be especially challenging as both NO and NO₂ are largely flaming species, and both are partially obscured by water lines in FTIR analysis, so our NO_x data is somewhat lacking here. We do have fairly extensive fuel characterization data coming from our USFS partners, but these data have not been work up yet, and such a study could involve many months of research. It is planned to investigate the fuel content v. emission profiles in an upcoming but separate paper.

Lines 62-66. These two sentences seem at odds with each other.

- Good point. This sentence has been revised.

Line 238. It seems in appropriate to call these ERs discrete since they are averages of a number of aliquots. The sampling scheme is intended to one set of combustion conditions, but the samples are not really discrete.

- Good point. This sentence has been revised.

Lines 312-315. This is a virtual repeat of material in lines 305-308.

- This is indeed redundant and has been eliminated.

Lines 416-418. This material is repetitious, and Figure 5 does not add anything new to the discussion, it can be eliminated and the text tightened up.

- The editor is correct. Figure 5 and the associated text have been deleted and remaining text has been reworked.

Line 421. How does point d) lead to this effect. Doesn't calibration account for this? Or are you saying you are missing entire compounds or classes because they are not detected?

- We have revised the text to indicate that the latter point that the ER relative to other OVOC for e.g. acetaldehyde may be biased high by the fact that other species have IR spectral band strengths or IR spectral interferences that make them appear anomalously low.

Line 582-583. I suggest rephrasing this, as it is hard to follow all the negatives.

- The sentence has been revised. We work in the Department of Redundancy Department.