

Interactive comment on “Atmospheric Evolution of Emissions from a Boreal Forest Fire: The Formation of Highly-Functionalized Oxygen-, Nitrogen-, and Sulfur-Containing Compounds” by Jenna C. Ditto et al.

Anonymous Referee #1

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Summary

The authors collected samples of functionalized organic compounds from a wildfire using an aircraft platform. Particles were collected on filters and sampled using LC and GC techniques offline, while gas phase compounds were collected in adsorbent tubes and sampled primarily using the LC method offline. The authors illustrate the importance of sulfide compounds, concluding that sulfides are formed through secondary chemistry and are a major contributor to CHONS compounds after plume aging. They discuss possible sources of these sulfur compounds. The measurements and analysis

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are quite interesting, and definitely of interest to others researching organic compounds (particularly lower volatility gases and particulate speciation). I have one major issue with how the authors quote numbers for relative contributions of sulfide and CHONS in the abstract, rather than using (dilution corrected) absolute concentrations to really prove that secondary formation is occurring. The data supporting abstract-level conclusions needs to be presented in the main paper, rather than the SI figures. This issue can be resolved through reorganization, and after addressing that along with my other comments, I would recommend for publication.

Specific Comments:

Abstract, Sect 3.1, 3.2, etc.: In several places in the main text and figs including the abstract, Sects. 3.1 and 3.2, you present data by relative abundance of each species. You present that the relative contribution of sulfides increases with plume age, and quote those numbers in the abstract in the context of saying sulfides are formed through secondary chemistry from S/IVOCs. However, the change in relative contribution alone could have several causes: sulfides could be being formed from chemistry in the plume (which is what you show with Fig. S6A with the CO-normalized plots), or sulfides could just be evaporating less than other functional groups and thus becoming relatively more important. Like I said, with Fig. S6A you show that the absolute concentration (when dilution corrected) is increasing, so there is some chemical formation, but you're not presenting your data or quoting the right numbers in the abstract to back up this conclusion. I believe this conclusion is really the main conclusion that you're trying to show with this work, and that's why you go on to a lot of discussion of possible secondary sources of sulfides in Sect. 3.5. But you're only showing it with an SI figure. This is a major issue with the organization of manuscript, in my opinion. And in the abstract, the quoted numbers seem potentially misleading to me. You present the numbers for relative increase (which on their own don't necessarily mean secondary formation, and might not quantitatively represent the amount of secondary formation), but the context is that sulfides are being formed through secondary chemistry. I think

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you need to be showing CO-normalized data in the main paper figs and quote those numbers in the abstract. As an imprecise use of data to back up conclusions in the abstract, I say it's a major issue, but it should be easy to resolve and it won't change your conclusions.

Line 180: Again, the increase in relative abundance of sulfides among CHONS species doesn't tell us whether sulfides are being formed, or if they're just evaporating/reacting more slowly than other functional groups. But the discussion here all assumes secondary formation. This is the same as my first comment, really.

Fig. S5 and elsewhere: What is the difference between abundance and occurrence? I don't see it explained anywhere, so I don't know what point you're trying to make by showing plots of occurrence.

Line 195: How are you estimating the volatility of the compounds? It looks like you might be explaining in line 201 (and Fig. S8, S9 captions), but it would be good to give that detail in the methods section before you start discussing volatilities here.

Line 82: Could you provide a little more info about the two-plume structure of the fire? Was it two spots of active burning/smoldering, and if so how close were they, or was it one spot that evolved two plumes with different ages? Mainly, I just want to know if both plumes in a given screen were sampled at approximately the same age. Maybe you could indicate an approximate location of the start of the second plume in Fig S1.

Line 87: What were the altitudes sampled in each screen?

Line 214: There are a lot of acronyms and methods involved in your analysis (not a criticism, just an observation!), so it can be a little tricky to follow that you're switching now from discussing the particle phase that was sampled via filters to discussing the gas phase sampled via adsorbent tubes. I'd recommend just adding a quick note here to say this more explicitly, that in order to try to understand the particle phase filter measurements presented earlier, you're now doing targeted analysis of the gas phase

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sampled via adsorbent tubes.

Line 300: Could you discuss whether or not there are any sulfur-containing compounds included in any fire suppressant materials that could have been deposited on this fire?

Sects. 3.4 and 3.5: Both of these sections are entirely 'discussion' of what could be explaining your data, and not presentation of your 'results'. Thus, they don't need to have their own sections under your 'results and discussion' header. You should either move them up into the previous sections where you actually present the results you're discussing, or change Sect. 3 to just 'Results' and have Sect. 4 be "Discussion" including these two sections (and make Conclusions be Sect. 5).

SI line 75: extra s in VOCs

Fig. S9: Should include a legend for screens 1-5, as in Fig S5, for completeness

Section S5: This whole section is great! Provides really nice context for interpreting all of the measurements you present throughout the manuscript. I'd advocate for moving Sect. S5 to the end of the main paper methods section.

Fig 1A along with Section S5: So Fig. 1A is really showing the relative abundance of the part of OA that could be sampled using the LC-ESI-MS method. You say LC is better for larger, more polar, more functionalized, less volatile compounds. How could this be biasing your percentages in Fig. 1A? E.g., maybe the sulfur compounds tend to be lower volatility and better sampled, while some less oxidized, less polar CHO compounds are poorly sampled? Some discussion would be useful, especially if you bring Sect. S5 to the main paper.

Title: It would be good to change the last word from "compounds" to "organic compounds" to make it more clear that organic compounds are the focus.

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