Reviewer 1

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 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.

> We thank the reviewer for their supportive comments. We modified our figure presentation and our discussion of the data in the abstract and manuscript to address both the absolute and relative contributions from CHONS and sulfide species. We discuss our edits in detail in the line-by-line responses below.

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 screen. 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 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.

We thank the reviewer for bringing up this important distinction. In Figure 1 and the associated discussion, we showed the contribution of CHONS and sulfide species in terms of their relative prevalence, to contrast changes in CHONS and sulfide contributions with other compound classes and functional groups in the observed complex mixture of emissions and transformation products. We agree that changes in relative contributions could be driven by a number of factors, such as chemical formation and different relative rates of evaporation that could vary between compound classes and functional groups. For this study, we were interested in looking at both the absolute formation of CHONS and sulfide species *and* the evolution of the overall complex mixture of compound classes/functional groups. As a result, we chose to include relative contributions of compound classes and functional groups in the main text, and in the interest of space, absolute contributions corrected for dilution (using carbon monoxide measurements) in the SI. We recognize that both ways of presenting results (i.e. as relative or absolute contributions) are valuable for different purposes. In both cases, the observed trends in CHONS and sulfide contributions were similar. Both approaches showed an overall growing contribution of CHONS and sulfides from screen 1 to 4, peaking at screen 4.

To address the reviewer's concern and provide more information the reader in the main text, we added an inset to Figure 1 that shows the absolute contributions of CHONS and sulfides with plume age (using dilution-corrected abundances). We added an inset rather than replacing the full figure because we did not want to lose the information presented in the current Figure 1A-C on the evolution of the complex mixture as a whole. In Figure 1's caption, we added an additional reference to the SI figures that show all compound classes and functional groups by absolute dilution-corrected abundance. We also note that we already show dilution corrected values for the gas-phase data in Figure 4. Also, in the abstract (lines 21-22 and 24-26) and in other instances where we reported the change in relative contribution of CHONS and sulfide species, we added a mention of their increase in dilution-corrected abundance. Finally, we included a note to the results section that draws attention to both methods of tabulation (lines 187-192).

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.

This concern is addressed above. At line 186-187, we added a sentence to show increases in absolute abundance (corrected for dilution using CO) to more strongly support the conclusion of CHONS formation. Similar additions were made when sulfides were discussed (lines 207-208).

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.

> The results shown in select SI figures tabulated by both abundance and occurrence are for comparison purposes only. The results tabulated by abundance are the ones discussed throughout the manuscript. However, due to uncertainty in ionization efficiency of individual multifunctional compounds within the complex mixture, we provide the reader with supporting data on the detailed distribution of compound classes, volatility ranges, and functional groups by occurrence as well (i.e. by number of compounds in each category). Trends in most cases were similar, suggesting that the interpretation of the abundance-weighted results was not substantially skewed by differences in ionization efficiency. This was originally discussed briefly at the end of SI Section S4. To address the reviewer's comment, we added a mention of the specific figures in the SI for which we showed both abundance-weighted and occurrence-based results for emphasis (SI lines 287-289). We also added a reference to Section S4 in the captions of the relevant figures, to draw attention to the discussion (Figures S5, S6, S8, S9).

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.

> Thank you for the suggestion. We added a few sentences to the Materials and Methods section to discuss this for adsorbent tubes and filters (clarified lines 113-124, added lines 127-130 and lines 157-162).

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.

> Based on analyses of satellite imagery and ground meteorological measurements, the NP was likely from the same source as the South Plume (SP). The NP likely occurred due to a switch in wind direction just prior to sampling. This means that the NP may be slightly older than the SP—we estimate this age difference to be <30 minutes, so they are roughly the same age. We added a brief mention of the ages of the plumes to the caption of Figure S1. Because the source of the NP was not identified via satellite imagery, it is not included explicitly in Figure S1 (this is mentioned in the caption).

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

> The average altitude of samples varied ~650-1650 m for adsorbent tubes (collected on distinct low and high altitude passes through the plume), and ~900-1600 m for filters (one filter per screen). Average altitudes were originally shown in Table S1, and we

added a reference to this table at line 90 to ensure that this information is readily found by readers.

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 sampled via adsorbent tubes.

We edited this sentence to make the transition clearer to readers (line 246-248).

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?

Smoke from this fire was sampled when the fire was less than 1 hour old and there had been no prior active fire suppression activities. Fire suppressant from past applications could have deposited on forest surfaces and re-volatilized, though historically, fire suppressants are not heavily used this region due to the abundance of lakes in the area. Also, this region uses water almost exclusively as a fire retardant. While it is possible that non-water fire suppressants were applied historically, the exact type and quantity are uncertain. It appears that one of the most commonly used fire suppressants in Canada today contains ammonium phosphate salts, sometimes with sulfate-containing salts mixed in. The exact composition of a few example fire suppressants that we searched for were proprietary, so the contribution of sulfate salts is unknown, but likely minor compared to that of phosphate salts. The contribution of any sulfur-containing compounds from fire suppressants to the observed gas/particle-phase species is therefore expected to be minor or negligible (if 100% water was used). We added a sentence to briefly mention fire suppressants at lines 366-368.

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).

Thank you for the suggestion. We turned section 3 into "Results", moved 3.4-3.5 to "Discussion" (now 4.1-4.2), and adjusted the "Conclusions" to become section 5.

SI line 75: extra s in VOCs

This has been corrected.

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

> We added a legend to panel A.

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.

> We thank the reviewer for the supportive comment. We felt that the comprehensive discussion of the differences between LC-ESI and GC-APCI methods was better suited to the SI, so that we could include several numerical details that described the types of compounds accessible with each technique without bogging down the reader with too many supplemental details in the main text. However, we have taken the reviewer's recommendation and added a short paragraph to the end of the Materials and Methods section that introduces the longer discussion in the SI (lines 148-156).

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.

> The LC-ESI methods used in this work are better suited for detecting more functionalized and polar compounds present in the OA sampled on PTFE filters (IVOCs-SVOCs included). LC-ESI (using both positive and negative mode) is known to be effective for a wide range of species that contain at least one oxygen atom or one nitrogen atom (in addition to combinations of sulfur with oxygen and/or nitrogen, and combinations of all three heteroatoms), making it conducive for measurements of biomass burning emissions and transformation products. While these methods exclude CH and CHS species (i.e. fully reduced hydrocarbons and compounds containing reduced sulfur only), this was acknowledged in the text and filter samples were run on the GC-APCI to explore the contribution of CH and CHS species to the particle-phase. From the GC-APCI analysis of particle-phase samples, we observed a greater contribution from CHO species and relatively lower fractions of the other heteroatom-containing groups, including CHS. This is likely because these other heteroatom-containing species were less GC-amenable, and thus were lost during solvent extraction, lost to the GC inlet, or lost to the GC column during analysis.
>
> Both LC-ESI and GC-APCI methods have column transmission and ionization strengths and weaknesses for different classes of compounds. The focus of this manuscript was on the formation of functionalized products from biomass burning emissions, so the LC-ESI approach and results were more extensively used because they were better suited for highly-functionalized species. The compositional percentages shown in Figure 1A are shifted in an absolute sense by the exclusion of CH and CHS compounds, but particle-phase CH and CHS species were outside the scope of this study. We did not up including

the full Section S5 in the main text, but to address the reviewer's concerns we added a shorter paragraph summarizing Section S5 (lines 148-156) and included an acknowledgement in that section that LC-ESI methods excluded CH and CHS species.

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.

Agreed, we have edited our title accordingly.

Reviewer 2

ACP manuscript 2020-619 reports on the detailed chemical composition of gas- and particle-phase samples collected from a boreal forest fire under ambient conditions. Samples were analyzed using gas and liquid chromatography (GC, LC) with detection by high-resolution and tandem mass spectrometry (MS, MS/MS). The focus of the analysis was on organic compounds, particularly those containing carbon, hydrogen, oxygen, nitrogen, and/or sulfate functionalities ("CHONS"); including as a function of plume age. Targeted and non-targeted approaches were used. Using both GC and LC allowed analysis of less polar (GC) and more polar/more functionalized compounds (LC) than could be achieved using a single method. Results are largely discussed in the context of elemental composition, with less focus on compound identification. It was observed that during aging particle-phase CHO compounds became less abundant, while particle-phase CHON(S) became significantly more abundant. The paper also presents precursors and pathways leading to the formation of observed sulfides included among the CHONS compounds. The paper is well written and presents interesting analysis and results that have not been presented before. The results, implications, and approach should be of interest to ACP readers. The methods are generally well described and could be reproduced based on the information provided in the SI. A few comments are provided below, both technical and editorial in content. The most significant comment on the technical side is that there are places in the manuscript where it is not clear if the compound volatility classes are being appropriately defined (i.e., based on published saturation vapor concentration ranges) based on the observed gas- and particle- phase distributions.

We thank the reviewer for their supportive comments. We have addressed each of their comments below, including a discussion of volatility.

Technical Comments:

line 96: Is the uncertainty on the MCE values really +/- 0.4? That seems very large, given the typical range of ambient MCE values.

We thank the reviewer for pointing this out. This was originally a typo. This has been revised in the main text to say +/- 0.01.

Starting on line 104, the description of the volatility range of compounds sampled is a little unclear. It seems that compounds that are largely in the gas phase at OA mass loadings of 10-30 ug/m3 would be classified as I/VOCs and not SVOCs. On the other end of the spectrum, C10-20 *compounds that are largely in the gas phase may be in the VOC range (and not necessarily in the I/SVOC range).*

> We thank the reviewer for pointing out this possible point of confusion for readers. We would like to clarify that all volatility bins (VOC, IVOC, SVOC, LVOC, ELVOC) were based on fixed values of saturation mass concentration, C* (as discussed in e.g. Donahue et al., 2009, and Murphy et al., 2014) at typical OA mass loadings (e.g. 18-22 ug/m^3 of OA during the adsorbent tube sampling times). In these conditions, VOCs extend up through hydrocarbons (i.e. CH compounds) with 11 carbon atoms (specifically compounds with an n-alkane-equivalent volatility of C_{11}). IVOCs include hydrocarbons with 12-18 carbon atoms, which are shown to equilibrate primarily to the gas-phase in outdoor conditions at the observed particle loadings. SVOCs, which begin with hydrocarbons with 19 carbon atoms, are present in both the gas- and particle-phase, with hydrocarbons less than C_{22}-C_{23} existing predominantly in the gas-phase in the observed conditions. To estimate gas-particle partitioning of these C_{22}-C_{23} compounds, we used the partitioning coefficient calculation described in Donahue et al., 2009 (Equation 1 in the SI), which relates the effective saturation mass concentration of mixture components to the overall OA mass loading. This is discussed in the SI (lines 230-243) and in Table S2.
>
> To ensure that our volatility calculations and definitions were clear, we edited the Materials and Methods discussion of volatility for adsorbent tube samples (lines 113-130), and added more discussion of the volatility calculations for filter samples (lines 157-162). We also added a note at line 123 to direct readers to Section S3 and Table S2 in the SI, which discuss volatility further.
>
> References:
>
> - Donahue et al., “Atmospheric organic particulate matter: From smoke to secondary organic aerosol.” *Atmospheric Environment,* 2009
> - Murphy et al., “A naming convention for atmospheric organic aerosol.” *Atmospheric Chemistry and Physics,* 2014

This continues in 204-205, with discussion of “particle-phase” IVOCs; it isn’t clear why at mass loadings of 10-30 ug/m3 of OA, particle-phase IVCOs would be above detection limits. By definition, such compounds are largely in the gas phase except at high OA loadings.

> The IVOCs discussed here refer specifically to functionalized particle-phase compounds, where polarity can affect partitioning behavior. We have observed particle-phase IVOCs in several past studies by our group (e.g. Ditto et al., 2018, Ditto et al., 2020) and others (e.g. studies of isoprene oxidation products that show species like 2-methyltetrols and methylglyceric acid in the particle phase, e.g. Carlton et al., *Atmos. Chem. Phys.,* 2009), which could be attributed to the presence of more polar and water-soluble compounds that are commonly observed in organic aerosol.

References:

- Ditto et al., "An omnipresent diversity and variability in the chemical composition of atmospheric functionalized organic aerosol." *Communications Chemistry*, 2018
- Ditto et al., "Nontargeted Tandem Mass Spectrometry Analysis Reveals Diversity and Variability in Aerosol Functional Groups across Multiple Sites, Seasons, and Times of Day." *Environmental Science and Technology Letters*, 2020
- Carlton et al., "A review of Secondary Organic Aerosol (SOA) formation from isoprene." *Atmospheric Chemistry and Physics,* 2009

In lines 241-243, it is suggested that compound types that have widely been observed in gas-phase smoke samples, evaporated with dilution. While a fraction of the directly emitted gas-phase compounds may partition to the particles, many of the compounds in the classes listed are not expected to contribute directly to the particle phase. Such compounds first undergo chemical transformation to create lower volatility products and then condense to the particle phase. It is not clear whether the parent compounds and their products would be observed as the same mass fragments using the techniques described.

We thank the reviewer for pointing out this potentially confusing phrasing. In our original text, we intended to discuss the possibility of evaporation of these compound classes from particle-phase emissions, in addition to direct gas-phase emissions of these compound classes. Evaporation of particle-phase species to the gas-phase has been observed in many past studies of IVOCs and SVOCs (e.g. those referenced at line 267, in addition to other studies on the semivolatile nature of primary organic aerosol such as Robinson et al., *Science,* 2007). We have edited this section in the text to ensure that our intended meaning is clear (line 276-278).

References:

- Robinson et al., "Rethinking Organic Aerosols: Semivolatile Emissions and Photochemical Aging." *Science*, 2007

The discussion of volatility and partitioning needs to be carefully reviewed throughout the manuscript, and revised for accuracy, consistency, and clarity.

We have carefully gone through the text to ensure that our discussion of volatility and partitioning was clear, and have edited language to improve clarity where needed.

line 134: What were the "strict" QC/QA guidelines for peak retention? These are not defined in the manuscript or SI.

A brief discussion of QA/QC was originally included in the SI in section S3.1. We added a note in the main text so readers know to consult this section for QA/QC information (line 145). We also added "QA/QC" to the section titles for S3.1 and S3.2 to emphasize this discussion. The QA/QC methods are discussed more thoroughly in the following publications referenced in the manuscript:

- Ditto et al., "An omnipresent diversity and variability in the chemical composition of atmospheric functionalized organic aerosol." *Communications Chemistry*, 2018
- Ditto et al., "Nontargeted Tandem Mass Spectrometry Analysis Reveals Diversity and Variability in Aerosol Functional Groups across Multiple Sites, Seasons, and Times of Day." *Environmental Science and Technology Letters*, 2020

line 198: Is quantification of filter species affected at all by compound volatility? Or is the extraction process sufficient to extract the presumed ELVOCs with reasonable recovery?

We expect that the filter extraction process across the reported volatility ranges should be fairly uniform. It is possible that the solvent extraction is slightly more or less effective for different chemical functionalities (i.e. compound classes), though upon testing, we did not observe any distinct trends with compound class, and the selected solvent (methanol) has been used extensively in past work (e.g. Riva et al., 2016, Surratt et al., 2008, Ng et al., 2008) that studied similarly functionalized organic aerosol species. We added a mention of this to the Supporting Information (SI line 250-252).

References:

- Riva et al., "Characterization of organosulfates in secondary organic aerosol derived from the photooxidation of long-chain alkanes." *Atmospheric Chemistry and Physics,* 2016
- Surratt et al., "Organosulfate Formation in Biogenic Secondary Organic Aerosol." *Journal of Physical Chemistry A,* 2008
- Ng et al., "Secondary organic aerosol (SOA) formation from reaction of isoprene with nitrate radicals (NO3)." *Atmospheric Chemistry and Physics,* 2008

SI line 48: How was the collection efficiency of the AMS determined? Lim et al. 2019 ACP demonstrated the significant impact of CE on

The collection efficiency of the AMS was determined using the method of Middlebrook et al. (Aerosol Science and Technology, 2012). The collection efficiency was also estimated by comparing the total mass concentrations with those derived from the UHSAS (Ultra-high sensitivity aerosol spectrometer). UHSAS volume concentrations were converted to mass concentrations using densities weighted by the AMS components. Both methods yielded similar results. In addition, there was no evidence to suggest that the AMS collection efficiency changed in and out of the fire plumes, which is consistent with previous AMS wildfire deployments (e.g. in the published data sets associated with ARCTAS – Hecobian et al., 2011; Cubison et al., 2011; SEAC4Rs – Liu et al., 2016; SCREAM – May et al., 2015). We have added a mention of these methods to the Supporting Information (SI line 47-52).

References:

- Middlebrook et al., "Evaluation of Composition-Dependent Collection Efficiencies for the Aerodyne Aerosol Mass Spectrometer using Field Data." *Aerosol Science and Technology*, 2012
- Hecobian et al., "Comparison of chemical characteristics of 495 biomass burning plumes intercepted by the NASA DC-8 aircraft during the ARCTAS/CARB-2008 field campaign." *Atmospheric Chemistry and Physics*, 2011
- Cubision et al., "Effects of aging on organic aerosol from open biomass burning smoke in aircraft and laboratory studies." *Atmospheric Chemistry and Physics*, 2011
- Liu et al., "Agricultural fires in the southeastern U.S. during SEAC^{4}RS: Emissions of trace gases and particles and evolution of ozone, reactive nitrogen, and organic aerosol." *Journal of Geophysical Research: Atmopheres*, 2016
- May et al., "Observations and analysis of organic aerosol evolution in some prescribed fire smoke plumes." *Atmospheric Chemistry and Physics*, 2015

SI line 83: I'm assuming that the field blanks were used to correct for background, and not to reduce background as stated here.

Yes, blanks were used to account and correct for any contamination in the sampling and analytical systems. We have changed the word "reduce" to "correct for", now at SI line 87.

Editorial Comments: line 62: In this context, what is meant by "unprecedented"? Is it in reference to the analytical techniques used? Or the extent of chemical composition data obtained? Other?

In this context, we used "unprecedented" to mean that the analytical methods and degree of chemical speciation were novel. We removed the term to reduce possible confusion.

line 113: No hyphen is needed between "gas" and "phase" (also in line 224 in the SI).

These have been corrected.

SI line 75: remove one of the "s" on "VOCss"

Corrected.

line 129: "mode" should be plural

Corrected.

SI line 295: suggest to move the Kroll et al reference as it suggests the values themselves (rather than the approach) are from Kroll et al.

We moved the reference so that it appears earlier in the sentence.