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.

Atmospheric Evolution of Emissions from a Boreal Forest Fire: The Formation of Highly-Functionalized Oxygen-, Nitrogen-, and Sulfur-Containing Organic Compounds

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Abstract

Forest fires are major contributors of reactive gas- and particle-phase organic compounds to the atmosphere. We used offline high resolution tandem mass spectrometry to perform a molecular-level speciation of gas- and particle-phase compounds sampled via aircraft from an evolving boreal forest fire smoke plume in Saskatchewan, Canada. We observed diverse multifunctional compounds containing oxygen, nitrogen, and sulfur (CHONS), whose structures, formation, and impacts are understudied. The dilution-corrected absolute ion abundance of particle-phase CHONS compounds increased with plume age by a factor of 6.4 over the first 4 hours of downwind transport, and their relative contribution to the observed functionalized

organic aerosol (OA) mixture increased from 19% to 40%. The dilution-corrected absolute ion abundance of particle-phase compounds with sulfide functional groups increased by a factor of 13 with plume age, and their relative contribution to observed OA increased from 4% to 40%. Sulfides were present in up to 75% of CHONS compounds and the increases in sulfides were accompanied by increases in ring-bound nitrogen; both increased together with CHONS prevalence. A complex mixture of intermediate- and semi-volatile gas-phase organic sulfur species was observed in emissions from the fire and depleted downwind, representing potential precursors to particle-phase CHONS compounds. These results demonstrate CHONS formation from nitrogen/oxygen-containing biomass burning emissions in the presence of reduced sulfur species. In addition, they highlight chemical pathways that may also be relevant in situations with elevated emissions of nitrogen- and sulfur-containing organic compounds from residential biomass burning and fossil fuel use (e.g. coal), respectively.

1 Introduction

Forest fires are predicted to become increasingly prevalent and severe with climate change (Abatzoglou and Williams, 2016; Barbero et al., 2015; Jolly et al., 2015). These fires are an important and uncontrolled source of gas- and particle-phase compounds to the atmosphere, including a complex mixture of gas-phase reactive organic carbon, primary organic aerosol (POA), carbon monoxide, carbon dioxide, methane, ammonia, nitrogen oxides, and black carbon (Akagi et al., 2011; Gilman et al., 2015; Hatch et al., 2015, 2018; Koss et al., 2018; Vicente et al., 2013; Yokelson et al., 2013). Many of these emitted compounds are precursors to downwind ozone and secondary organic aerosol (SOA) production (Ahern et al., 2019; Buysse et al., 2019; Gilman et al., 2015; Hennigan et al., 2011; Lim et al., 2019).

Primary and secondary pollutants from biomass burning have important effects on air quality locally, regionally, and continentally (Burgos et al., 2018; Colarco et al., 2004; Cottle et al., 2014; Dreessen et al., 2016; Forster et al., 2001; Rogers et al., 2020; Val Martín et al., 2006), and their impacts on human health and climate (e.g. via light absorbing brown and black carbon) have been well documented (Forrister et al., 2015; Jiang et al., 2019; Liu et al., 2017; Di Lorenzo et al., 2018; Reid et al., 2016; Sengupta et al., 2018; Wong et al., 2019). These health and climate effects are sensitive to the elemental and structural composition of gas- and particle-phase emissions and transformation products (Hallquist et al., 2009; Nozière et al., 2015). As a result, past studies have used online and offline mass spectrometry techniques to characterize the chemical composition of fresh and aged biomass burning emissions and have revealed a wide array of emitted hydrocarbons and oxygen-, nitrogen-, or sulfur-containing functionalized species (Ahern et al., 2019; Bertrand et al., 2018; Gilman et al., 2015; Hatch et al., 2015, 2018, 2019; Iinuma et al., 2010; Koss et al., 2018; Laskin et al., 2009; Yokelson et al., 2013). However, the emissions and chemical transformations occurring in ambient biomass burning plumes are extremely complex and despite previous measurements remain poorly understood at the molecular-level.

In this study, we used an aircraft sampling system developed to collect offline gas- and particle-phase organic compounds above a boreal forest fire. We examined the molecular-level emissions and evolution of the forest fire plume via an analysis of these offline samples using gas and liquid chromatography (GC/LC) with high resolution mass spectrometry (MS), including tandem mass spectrometry (MS/MS). This degree of detailed chemical speciation is important to advance knowledge of in-plume chemical pathways and reaction products, long-distance

transport, and fate of biomass burning products—all of which will improve modeling capabilities and our understanding of the health and environmental impacts of biomass burning.

Specifically, the goals of this study were: (1) to perform a detailed speciation of gas- and particle-phase organic compounds derived from the boreal forest fire in terms of elemental and functional group composition, to assess changes in composition at the molecular-level as the plume aged; and (2) to examine the evolution of oxygen-, nitrogen-, and sulfur-containing (CHONS) compounds. These CHONS compounds made up 19-40% of functionalized OA here and have been observed at other ambient sites (e.g. 9-11% (Ditto et al., 2018)), though little is known about their structures or formation mechanisms. Using our observations of gas-phase sulfur species, we identified possible precursors and reaction pathways involved in the formation of these CHONS compounds.

2 Materials and Methods

On June 25th, 2018, two research flights were conducted by Environment and Climate Change Canada as part of their Air Pollution research program. These flights sampled two boreal wildfire smoke plumes originating near Lac La Loche in northern Saskatchewan, Canada (Figure S1). The region is dominated by pine and spruce trees (Canada's National Forest Inventory, 2020). Gas- and particle-phase samples were collected from the National Research Council of Canada's Convair-580 research aircraft for analysis with offline high resolution mass spectrometry, alongside many other measurements (Supporting Information S1-S2). The aircraft flew the same straight-line tracks at multiple altitudes through the smoke plumes (average altitudes shown in Table S1), which when stacked created a virtual screen intercepting the plumes at each of five downwind locations (with flight design similar to those previously

reported (Li et al., 2017; Liggio et al., 2016)). Screen 1 was ~10 km from the fire with screens 2-4 following the plumes downwind, and screen 5 intercepting the plumes after they had passed over several major surface and in-situ mining oil sands facilities (Figure S1). The samples discussed here were collected across both plumes to ensure that enough mass was present to well surpass the mass spectrometer's detection limits. Based on satellite information and aircraft measurements at the start of sampling (i.e. screen 1), the fire was a low-intensity surface fire with smoldering conditions; aircraft measurements indicated a modified combustion efficiency of 0.90±0.01 for both plumes.

Combined gas- and particle-phase samples were collected onto custom adsorbent tubes packed with high-purity quartz wool, glass beads, Tenax TA, and Carbopack X (Sheu et al., 2018). Samples were collected along screens 1-4 in Figure S1 (no adsorbent tubes collected at screen 5) via an external pod mounted under the wing of the aircraft, which included remote switching between adsorbent tubes at various transect altitudes and online measurements of temperature, pressure, and flow (Supporting Information S1, Figure S2).

All adsorbent tubes were analyzed using a GERSTEL Thermal Desorber TD 3.5+ with gas chromatography (Agilent 7890B GC), atmospheric pressure chemical ionization (APCI), and quadrupole time-of-flight mass spectrometry (Agilent 6550 Q-TOF), similar to past work (Khare et al., 2019). For adsorbent tubes, the APCI was operated in positive ionization mode and the Q-TOF was operated in MS mode (i.e. TOF data collection only, hereafter "GC-APCI-MS"). Adsorbent tube data were processed primarily via a targeted approach for C_xH_y, $C_xH_yO_1$, $C_xH_yS_1$, and $C_xH_yN_1$ compounds using custom Igor Pro code (Supporting Information S2-S3).

In order to reduce losses of lower volatility gases onto upstream surfaces, particles were not explicitly filtered out at the inlet of the wing-pod sampler used for adsorbent tube collection.

For several reasons, it was concluded that the C_xH_y hydrocarbons smaller than C_{22-23} (and $C_xH_yS_1$/$C_xH_yO_1$/$C_xH_yN_1$ compounds of similar volatility) measured in the adsorbent tubes were predominantly in the gas-phase. This was based on (1) significant undersampling for particles at the wing pod inlet since the adsorbent tube sampling flow rate was a factor of ~4 lower than its corresponding isokinetic flow rate, resulting in a significant divergence of particles away from the inlet during sampling; and (2) partitioning theory, using average in-plume organic aerosol (OA) concentrations of 18-22 μg/m^3 across adsorbent tube sampling periods for screens 1-4, concurrently measured by an aerosol mass spectrometer (AMS) onboard the aircraft (see Supporting Information S1, S3, Table S2). Thus, the C_{22} and smaller C_xH_y compounds (and other compound classes of similar volatility) should have primarily been in the gas phase at equilibrium. As such, we limited the following adsorbent tube data analysis to compounds in the C_{10}-C_{25} range to focus on intermediate-volatility and semivolatile (I/SVOCs) compounds present in the gas phase. In our analyses and interpretation, the compounds included in each of these volatility ranges are defined based on fixed values of saturation mass concentrations (e.g. Donahue et al., 2011; Murphy et al., 2014) at the observed 18-22 ug/m^3 OA loadings present during adsorbent tube sampling times.

Dedicated particle-phase samples were collected on 47 mm PTFE filters (2.0 μm pore; Pall Corporation) from a sampling manifold in the aircraft cabin containing six independent anodized aluminum filter holders. The filters were sampled behind an isokinetic inlet with a size cutoff of approximately 2.5 μm. One filter sample was collected per screen for screens 1-5 shown in Figure S1.

Filter samples were extracted in methanol (Ditto et al., 2018). Samples were analyzed via liquid chromatography (Agilent 1260 LC) with electrospray ionization (ESI) and the same Q-

TOF. For filters, the ESI source was operated in both positive and negative ionization modes, and the Q-TOF was operated in both MS mode (i.e. TOF data collection, "LC-ESI-MS") and MS/MS mode (i.e. tandem mass spectral data collection, "LC-ESI-MS/MS") (Ditto et al., 2018, 2020). Filter extracts were also analyzed using GC-APCI-MS in positive ionization mode. Filter data from LC-ESI-MS, LC-ESI-MS/MS, and GC-APCI-MS were analyzed with a non-targeted approach, using Agilent Mass Hunter, SIRIUS with CSI:FingerID, and custom R code (Supporting Information S2-S3) (Ditto et al., 2018, 2020). All peaks that passed strict QA/QC (Section S3) were assigned molecular formulas, with candidate formulas limited to 20 oxygen, 3 nitrogen, and/or 1 sulfur atom(s). Hereafter, LC-ESI compound classes are discussed here without subscripts.

The particle-phase compounds observed via LC-ESI vs. GC-APCI techniques varied significantly in their oxygen, nitrogen, and sulfur content since these two chromatographic and ionization approaches are sensitive towards different types of compounds (see Section S5). As the forest fire plume aged, the complex mixture of emissions and secondary products became increasingly functionalized and thus less GC-amenable without derivatization. Therefore, we focused on LC-ESI-MS data to study these functionalized particle-phase compounds. We acknowledge that this method excludes fully-reduced hydrocarbons and fully-reduced sulfur-containing particle-phase compounds (i.e. CH and CHS (Ditto et al., 2018)) and thus these compound classes are not accounted for in the relative particle-phase distributions shown here.

For particle-phase analyses, we estimated saturation mass concentration based on the Li et al. parameterization (Li et al., 2016), then grouped compounds based on fixed volatility bins (Donahue et al., 2011; Murphy et al., 2014). Particle-phase compounds were observed across the IVOC, SVOC, LVOC, and ELVOC ranges. Particle-phase IVOCs have been observed in the

past, and despite their higher volatility, may exist in the particle-phase due to their polarity and water solubility. Additional details on these methods, including a discussion of total mass analyzed from filters/adsorbent tubes and QA/QC, are discussed in Supporting Information S1-S5, with a methods summary shown in Figure S3.

3 Results

3.1 Evolution of organic aerosol elemental composition and functionality with plume age

Our analysis of functionalized OA showed several compositional trends in the evolving boreal forest fire smoke plume (screens 1-4) and exhibited marked changes after emissions from the oil sands facilities were mixed with the forest fire plume (screen 5). Here, we focused on the forest fire plume in screens 1-4. We observed a diverse elemental composition in functionalized OA across oxygen-, nitrogen-, and/or sulfur-containing compound classes (Figure 1A-1B, Figure S5). This included oxygenates (CHO), such as common biomass burning tracers and their isomers (e.g. levoglucosan, Supporting Information S2); as well as oxygen- and nitrogen-containing compounds (CHON); oxygen- and sulfur-containing compounds (CHOS); reduced nitrogen-containing compounds (CHN); reduced nitrogen- and sulfur-containing compounds (CHNS); as well as compounds containing oxygen, nitrogen, and sulfur (CHONS).

There was a continual decrease in the relative abundance of particle-phase CHO compounds in the observed functionalized OA across screens 1-4, accompanied by a consistent relative increase in CHON and CHONS compounds (Figure 1B). Notably, the relative abundance of CHONS compounds increased from 19% to 40% of measured functionalized OA from screens 1 to 4. Trends in absolute ion abundances were also similar (note: carbon monoxide mixing ratio was used to account for dilution). This is shown in Figure 1C (inset) and Figure S5C; CHO

generally decreased from screens 1 to 4, while CHONS and CHON generally increased, suggesting that CHONS compounds were possibly formed from CHO, CHN, and/or CHON precursors in the gas- and/or particle-phases. Specifically, the dilution-corrected abundance of CHONS species increased by a factor of 6.4 from screen 1 to 4 (Figure 1C, inset). In Figure 1, we primarily presented data as relative contributions to functionalized OA to examine changes in the evolution of the complex mixture as a whole and the relationships between different compound classes and functional groups with plume age. However, dilution-corrected abundances are also important for understanding absolute formation (or depletion), and are shown for all species in Figures S5-S6.

Based on MS/MS analyses, these evolving CHO, CHN, CHON, and CHONS compounds were often comprised of variable combinations of hydroxyl and ether functional groups (e.g. primary emissions from forest fires like methoxyphenols and similar structures), as well as amine, imine, and sulfide groups, along with cyclic nitrogen structural features (consistent with past laboratory observations of biomass burning emissions (Laskin et al., 2009; Lin et al., 2018; Liu et al., 2015; Updyke et al., 2012)).

3.2 Detailed speciation of CHONS compounds in functionalized OA

While some individual CHONS species contained grouped oxygen, nitrogen, and sulfur atom moieties (e.g. sulfonamides), the majority of CHONS compounds had a combination of multiple separate oxygen-, nitrogen-, and/or sulfur-containing functional groups (Figure 2A-2B). Sulfide groups were important contributors to CHONS compounds (Figure 2B) and showed a notable increase in relative contribution to the overall functional group distribution with plume age (Figure 1C). They increased from 4% to 40% of measured compound abundance across

screens 1 to 4 (Figure 1C), which corresponded to an increase by a factor of 13 in terms of their dilution-corrected abundance (Figure 1C, inset). Their increasing relative contribution to CHONS compounds with plume evolution was even more pronounced—by screen 4, the sulfide functional group was present in 75% of detected CHONS compound abundance (Figure S7A). Here, we focused on the presence of sulfides in CHONS compounds because most of the observed particle-phase sulfides occurred as part of CHONS species (71%), while a smaller fraction occurred in CHOS (21%) or CHNS (8%) compounds (Figure 3A).

To explore possible precursors and formation pathways for these particle-phase sulfide-containing CHONS species, we used MS/MS to identify nitrogen-containing functional groups that co-occurred with sulfides. In CHONS compounds, most sulfides co-occurred with cyclic nitrogen (36% of sulfide-containing species), amine (32%), or imine features (43%) (Figure 3B). The prevalence of sulfide and cyclic nitrogen features in the measured functionalized OA increased together screen-to-screen, and increased together with the rising proportion of CHONS compounds (Figure 3C). While sulfides often co-occurred with amines or imines and while amines and imines were prevalent in all 4 screens (Figure 1C), there was no relationship between these functional groups and the increasing contribution of CHONS compounds to measured functionalized OA (Figure S7B).

The sulfide substructures observed via MS/MS often contained linear carbon chains or phenyl groups bonded to the sulfur atom (Figure 3C inset). Thus, we hypothesize that precursors with similar reduced sulfur-containing structures reacted with cyclic nitrogen-containing species to form the observed particle-phase sulfide-containing CHONS compounds (see further discussion of possible precursors in Section 3.3, and potential chemical pathways in Section 4.2).

CHONS compounds were predominantly SVOCs in screens 1-4 (i.e. 89% of CHONS ion abundance, Figure 2C, Figure S8), suggesting that these compounds were formed from higher volatility gas-phase species. In contrast, with the added influence of the oil sands facilities in screen 5, 68% of CHONS compounds were extremely low volatility organic compounds (ELVOCs), though CHONS made up only 2% of functionalized OA at screen 5.

Overall, dilution-corrected abundances of functionalized OA in each particle-phase volatility bin increased with plume age, but the relative contribution of SVOCs increased from 37% to 58% while the relative contribution of IVOCs dropped from 38% to 20%, potentially due to oxidation reactions that formed SVOCs and/or due to evaporation (Figure S9). These particle-phase IVOCs consisted predominantly of CHO, CHN, and CHON (O/N < 3) compounds, which could include possible non-sulfur containing precursors to the observed CHONS species. Fragmentation of particle-phase L/ELVOC compounds also could have contributed to some of the observed SVOC mass, but the overall increasing total abundance across all volatility bins with plume age supports the idea that these compounds were predominantly formed from more volatile precursors (e.g. I/SVOCs).

3.3 Targeted search for CHONS precursors in the gas-phase

To investigate the precursors and chemistry that could have formed the sulfide-containing CHONS species observed in the particle-phase samples, we performed a targeted search for possible gas-phase I/SVOC species in each adsorbent tube, across all C_{10}-C_{25} $C_xH_yS_1$ species with the equivalent of 0-15 double bonds and/or rings (i.e. $C_xH_{2x+2}S_1$- $C_xH_{2x-28}S_1$, Figure 4A, Figure S10). We observed a distribution of $C_xH_yS_1$ compounds and their isomers; based on the high mass resolution and high mass accuracy molecular formulas from targeted GC-APCI-MS

analysis, 27% of $C_xH_yS_1$ compounds were fully saturated (i.e. $C_xH_{2x+2}S_1$) and 25% contained the equivalent of 4-6 double bonds and/or rings (i.e. $C_xH_{2x-6}S_1$- $C_xH_{2x-10}S_1$), which included single ring aromatics. We focused on these sulfur-containing gases as candidate precursors to the observed particle-phase sulfide-containing CHONS compounds as they contained sulfur substructures with linear carbon chains or phenyl groups, similar to those observed on particle-phase CHONS compounds via MS/MS analysis (Figure 3C inset, Figures S10-S11). However, we also observed contributions from other sulfur-containing structures (e.g. with the equivalent of 1-3 double bonds and/or rings, Figure 4A), which could also have been precursor species.

The observed gas-phase C_{10}-C_{25} $C_xH_yS_1$ compounds were present in gas-phase emissions from the fire and likely also evaporated from primary OA during early plume dilution. Gas-phase C_{10}-C_{25} $C_xH_yS_1$ concentrations increased relative to carbon monoxide from screen 1 to 2, then steadily decreased with plume age (Figure 4B, Figure S12A). This suggests the gas-phase emission and/or evaporation of $C_xH_yS_1$ compounds from OA between screens 1 and 2, and subsequent participation in plume chemistry from screens 2 to 4.

Similar OA evaporation with plume dilution has been observed in many past studies (Ahern et al., 2019; Garofalo et al., 2019; Hennigan et al., 2011; Lim et al., 2019). To better understand the dynamics of these sulfur-containing compounds and their possible particle-phase origin, we compared their concentrations to those of C_{10}-C_{25} aliphatic and aromatic C_xH_y and $C_xH_yO_1$ species from a similar targeted search of adsorbent tube gas-phase compounds. Overall, C_xH_y and $C_xH_yO_1$ compound classes dominated the observed C_{10}-C_{25} compounds (Figure 4B, Figure S12B), with 61% C_xH_y, 36% $C_xH_yO_1$, and just 3% $C_xH_yS_1$ on average. C_xH_y and $C_xH_yO_1$ concentrations generally increased with plume age (Figure 4B) and included many known compound types (e.g. monoterpenes, aromatics, hydroxyls, carbonyls (Akagi et al., 2011;

Andreae, 2019; Gilman et al., 2015; Hatch et al., 2015, 2019; Koss et al., 2018)). This suggests the direct emission of these gas-phase compound classes from the fire (observed at screen 1) along with the evaporation of semivolatile particle-phase emissions as the plume evolved, and formation of $C_xH_yO_1$ via C_xH_y oxidation. AMS measurements of total OA concentrations provided supporting evidence of OA evaporation; the ratio of AMS OA concentration to CO decreased by 7% from screen 1 to 2 (corresponding to an AMS OA/CO ratio of -0.0044 or a decrease in OA concentrations of -2.3 μg/m^3), while the ratio of total gas-phase C_xH_y, $C_xH_yO_1$, and $C_xH_yS_1$ concentration to CO increased by 55% (corresponding to a total gas-phase concentration/CO ratio of 0.022 or an increase in gas-phase concentration of 7.0 μg/m^3, with changes summarized in Table S3). While not the focus of the analytical approaches applied in this study, to further substantiate the observation of OA evaporation, we performed the same targeted analysis of C_{10}-C_{25} C_xH_y, $C_xH_yO_1$, and $C_xH_yS_1$ compounds in the particle-phase filter sample extracts analyzed via GC-APCI-MS. We observed a similar decrease in concentration from screen 1 to 2. However, these filter measurements (even with APCI ionization) were not geared towards C_xH_y and $C_xH_yS_1$ speciation due to possible solubility limitations in the extraction solvent (Supporting Information S4). Direct thermal desorption of quartz filters with GC-APCI analysis would be better suited for these C_xH_y and $C_xH_yS_1$ measurements (as performed in this study with adsorbent tubes).

As discussed in *Materials and Methods*, the observed compounds with volatilities below that of ~C_{22}-C_{23} hydrocarbons existed primarily in the gas-phase (Table S2), while larger compounds favored the particle-phase (with a smaller fraction in the gas-phase at equilibrium). The presence of gas-phase compounds across this I/SVOC range (e.g. Figures S10, S13) further corroborates the possibility of contributions from both direct gas-phase emissions and from

evaporation of particle-phase emissions (Supporting Information S3). In contrast to C_xH_y concentrations, $C_xH_yS_1$ concentrations dropped markedly after screen 2 despite similarities in the volatility distribution of C_xH_y and $C_xH_yS_1$ I/SVOC mixtures (Figure 4A, Figures S10 and S13). This difference across screens shows that the observed $C_xH_yS_1$ I/SVOCs were removed (e.g. via chemical reactions) more quickly than C_xH_y (Figure 4B), thus supporting their potential contribution to CHONS formation.

In addition to the C_{10}-C_{25} $C_xH_yS_1$ compounds measured in the adsorbent tubes, smaller sulfur-containing compounds could have also acted as CHONS precursors, like those identified by the onboard proton transfer reaction-mass spectrometer (PTR-ToF-MS). While dimethyl sulfide (DMS, previously observed in biomass burning smoke (Andreae, 2019)) was often below the instrument's limit of detection, both dimethyl and diethyl sulfide showed good correlation with acetonitrile (a well-known biomass burning product (Andreae, 2019)) in the smoke plume during screen 1 ($r \sim 0.95$, Figure S12C). This suggests that these compounds were co-emitted by the fire.

4 Discussion

4.1 Investigating possible origins of gas-phase sulfur compounds

The gas-phase sulfur-containing compounds observed in the plume were emitted from the smoldering fire. However, their origins are uncertain, since the broader range of sulfur species found here (Figure 4A, Figures S10-11) has not been previously reported; many of the compounds in the complex mixture of sulfur-containing compounds discussed in this work were outside the detection range of previously employed methods (Hatch et al., 2015; Khare et al., 2019; Koss et al., 2018; Sekimoto et al., 2018). Here, we explore two potential origins of these

gas-phase sulfur-containing precursors to the observed particle-phase CHONS compounds: the biomass fuel itself and the deposition of sulfur species from anthropogenic/industrial operations.

Fuel: In past studies, emissions of sulfur-containing organic compounds were typically minor compared to oxygen- or nitrogen-containing compounds, and the relative balance of oxygen-, nitrogen-, or sulfur-containing compound emissions was typically proportional to fuel content (Hatch et al., 2015; Ward, 1990). The estimated N:S ratio for boreal forest fuel near the fire was ~10:1 (Huang and Schoenau, 1996), which was similar to the average N:S ratio from a non-targeted search for nitrogen- and sulfur-containing I/SVOCs from the adsorbent tube samples in this study of (8.1 ± 4.8):1. Sulfur is an essential nutrient in plants, and can be taken up from soil (as sulfate) or from the atmosphere via deposition (as SO_2 and sulfate) (Aas et al., 2019; Gahan and Schmalenberger, 2014; Leustek, 2002). Both SO_2 and sulfate are metabolized in plants to yield a variety of compounds critical to plant functions including cysteine and a range of other sulfur- (as well as oxygen- and nitrogen-) containing compounds (Leustek, 2002). In addition, disulfide bonds contribute to plant protein structure, and these bonds can cleave and form thiols (Gahan and Schmalenberger, 2014; Leustek, 2002; Onda, 2013). Sulfur-containing compounds like these may have been emitted during the fire, along with other known sulfur products from boreal fuels (e.g. DMS, thiophenes (Akagi et al., 2011; Hatch et al., 2015; Koss et al., 2018; Landis et al., 2018)).

Deposition: While sulfur can be naturally occurring, it is also associated with anthropogenic activities (e.g. transportation, power generation, industry, etc.). A portion of the sulfur in the forest fire emissions could have originated from sulfur deposited via such anthropogenic activities. The closest large anthropogenic sulfur source to the fire location was the oil sands mining region north of Fort McMurray, Alberta, which was approximately 150 km

away and which contains known SO_2 emitters (Liggio et al., 2017; McLinden et al., 2016). Regional concentrations of SO_2 or other sulfur species from these nearby industrial activities could have led to accumulated deposition of inorganic and/or organic sulfur compounds over time, though it is uncertain how much of this deposited sulfur would have been taken up and transformed by vegetation due to sulfur uptake and assimilation regulatory pathways in plants (Davidian and Kopriva, 2010). This possible accumulated deposition may have acted as a reservoir of sulfur to be emitted during fires via the re-volatilization of deposited compounds, in addition to the evaporation of typical sulfur metabolites or the formation of sulfur-containing combustion by-products. This hypothesis is consistent with recent deposition measurement and modeling results for the region, which indicated that sulfur deposition from the oil sands operations potentially impacted areas downwind, including the region where this fire occurred (Makar et al., 2018).

Interestingly, lichen and spruce trees, which are prominent in the region of the fire discussed here, have been reported to accumulate sulfur from SO_2 in regions near large industrial SO_2 sources (Meng et al., 1995; Nyborg et al., 1991). Also, past studies have reported enhancements in sulfate (as well as nitrate/ammonium) aerosols coming from biomass burning in areas with urban influence (Fenn et al., 2015; Hecobian et al., 2011; Hegg et al., 1987). Inorganic aerosol components from both urban (e.g. Edmonton, Alberta) and industrial (e.g. oil sands) sources could deposit in the area surrounding the emissions source along with an organic phase, which we postulate could contain a range of sulfur-containing species including the $C_xH_yS_1$ compounds shown here. These deposited inorganic and organic species may have re-volatilized during the fire. However, further work is needed to disentangle the contribution of natural vs. anthropogenic sulfur to biomass burning emissions in the region. Also, we note that

the fire was ~1 hour old at the time of sampling, so the recent application of fire suppressants was unlikely to contribute to the species observed.

4.2 Potential reaction pathways leading to sulfides in CHONS from sulfur precursors

A number of potential reactions involving sulfur-containing precursors, often thiols (R-SH), may have contributed to the formation of the observed sulfide functional groups in particle-phase CHONS compounds (Figure S14). On average, our gas-phase measurements were comprised of 27% fully saturated sulfur-containing hydrocarbons (i.e. $C_xH_{2x+2}S_1$, Figures S10-11). It is likely that some fraction of the sulfur compounds observed in the gas-phase adsorbent tube measurements (e.g. the compounds identified as $C_xH_{2x+2}S_1$) and in PTR-ToF-MS measurements (e.g. dimethyl sulfide, diethyl sulfide) were thiols, but the distinction between sulfide vs. thiol isomers was challenging with these methods without specific internal standards.

In some of the following possible reactions, a thiol interacts with a non-sulfur precursor to yield a sulfide-containing compound. The non-sulfur precursor (in the gas- or particle-phase) may have contained O and N atoms, thus yielding a CHONS compound immediately after participating in one of the proposed reactions. Alternatively, the newly formed sulfide-containing compound may have undergone subsequent, separate reactions with oxygen- and/or nitrogen-containing species (in the gas- or particle-phase) to form the observed sulfide-containing CHONS species. Here, we focused on possible reactions that could have contributed the sulfide group to these oxygen- and/or nitrogen-containing compounds (known emissions from forest fires, as discussed above). Earlier, we postulated that because most of the observed particle-phase CHONS compounds were SVOCs, these compounds were predominantly formed by reactions with more volatile gas-phase compounds. However, it is uncertain whether these

sulfide-forming and CHONS-forming reactions all occurred in the gas-phase with subsequent partitioning to the particle-phase, heterogeneously, or in a combination of separate gas- and particle-phase chemistry. We suggest some possible sulfide-forming reactions here, yet we note that these proposed reactions are likely not comprehensive. Further work to elucidate the chemistry driving this sulfide and CHONS formation is needed.

Some possible reactions include: (1) thiol-ene reactions, where a thiol reacts with an alkene (or alkyne), which can form carbon-sulfur bonds (Lowe, 2010). Alkenes are known to be prominent in emissions from boreal fires (Gilman et al., 2015; Hatch et al., 2015), and we observed similar structures in our gas-phase samples that likely included alkenes, cyclic alkanes, and/or monoterpenes (Figure S13). (2) Thiol reactions with carbonyls, which can form hemithioacetals that subsequently dehydrate in the atmosphere to yield sulfides (Jencks and Lienhard, 1966). This reaction is similar to the formation of enamines from carbonyls and dimethyl amine via the formation and subsequent dehydration of a carbinolamine, which has been shown to occur in ambient conditions (Duporté et al., 2016, 2017). (3) Thiol reactions with alcohols, which can form sulfides; these reaction rates are low in the absence of catalysts and require relatively high temperature to occur (i.e. 200-450°C (Mashkina, 1991), temperatures that are relevant very close to the fire but unlikely in the cooled plume). (4) Another possibility is that a radical intermediate product formed during atmospheric oxidation of DMS (e.g. the methylthiomethyl radical ($CH_3SCH_2^{\bullet}$) from $OH^{\bullet}$-driven hydrogen abstraction of DMS (Barnes et al., 2006)) interacted with CHN and CHON precursors to yield the observed sulfide-containing CHONS products. However, the concentrations of the methylthiomethyl radical and similar radicals from other small sulfide precursors would likely be lower than those of other major

drivers of in-plume radical chemistry (e.g. O_2, NO_x, etc.), thus making this reaction pathway less likely to contribute.

Based on our observations of these sulfide-containing products across flight screens, the overall timescale for these sulfide-forming reactions was likely approximately 1 hour (or less). For the literature reactions referenced above, reaction timescales ranged from minutes to hours in laboratory experiments, but extrapolation to rates in an ambient wildfire plume is uncertain. Specifically, it is challenging to compare to predicted timescales for the proposed reactions without knowing the exact structure/identities of the reactants or the possible role of other key modifying factors in the plume (e.g. aerosol pH, presence of water).

5 Implications and Conclusions

In this work, we performed the first high resolution tandem mass spectrometry analysis of an evolving plume from a smoldering boreal forest fire. The results show clear evidence of gas-phase sulfur-containing emissions from the fire, and an increasing contribution from particle-phase CHONS compounds with sulfide functional groups as the plume evolved. Together, these results suggest the emission of gas-phase sulfur-containing compounds from the fire and subsequent gas- and/or particle-phase chemistry that produced multifunctional sulfide-containing CHONS compounds.

Sulfide functional groups in ambient air have been reported at a range of U.S. locations from urban inland (1-7% sulfides), urban coastal (5-12% sulfides), and remote forested (7% sulfides), and on average, sulfides comprised 28% of sulfur-containing functional groups at these sites (Ditto et al., 2020). However, in past work, 53% of these sulfides were present in CHOS compounds, while 34% were CHONS, and 13% were CHNS (in contrast to 21%, 71%, and 8%

in this study, respectively). Notably, at a Northeastern U.S. coastal site where there were several pollution events linked to long distance transport of biomass burning smoke during field sampling (Rogers et al., 2020), 70-90% of sulfides were present in CHONS compounds (Ditto et al., 2020), similar to the compound class distribution of sulfides discussed here (Figure 3A).

These results, along with past observations, highlight that this type of chemistry and these types of reaction products may be relevant to other regions where concentrations of nitrogen and sulfur-containing precursors are high, such as in developing regions, emerging economies, or megacities where residential biomass burning is common and coincident with extensive use of sulfur-containing fossil fuels (e.g. coal). CHONS compounds have been reported in similar regions in past studies (Lin et al., 2012; Pan et al., 2013; Song et al., 2019; Wang et al., 2017a, 2016, 2017b). Their formation is potentially important since the presence of sulfur, oxygen, and nitrogen atoms in organic compounds can affect particle phase state (e.g. solid, semi-solid, liquid), and mixing state (e.g. well-mixed, phase-separated) (DeRieux et al., 2018; Ditto et al., 2019; Van Krevelen and Te Nijenhuis, 2009). These physical properties may influence particles' chemical reactivity and overall persistence in the atmosphere, all of which contribute to the health and environmental impacts that communities and ecosystems experience from OA exposure. Future work to identify prominent functional groups in CHONS species in regions with high CHONS concentrations will help elucidate the formation chemistry of these functionalized compounds and understand and mitigate their associated impacts.

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Author Contributions

J.C.D. ran samples, processed filter data, compiled and interpreted results. M.H. processed adsorbent tube data. T.H-M. contributed to MS/MS analysis. S.G.M., K.H., J.L., and D.R.G. collaborated on data interpretation. K.H. collected and processed AMS data. A.L. collected and processed PTR-ToF-MS data. S.-M.L. designed the aircraft adsorbent tube collection system. P.L. and J.J.B.W. implemented the wing pod design. P.L. prepared the wing pods for collection and J.J.B.W. and J.L. collected the adsorbent tube samples. M.J.W. and J.L. designed the filter collection system. M.J.W. and K.H collected filter samples. S.-M.L., K.H., and J.L. designed the aircraft sampling study. J.C.D. and D.R.G. wrote the manuscript, with input from all co-authors.

Competing Interests

The authors declare that they have no conflicts of interest.

Code and Data Availability

Code and data are available upon request.

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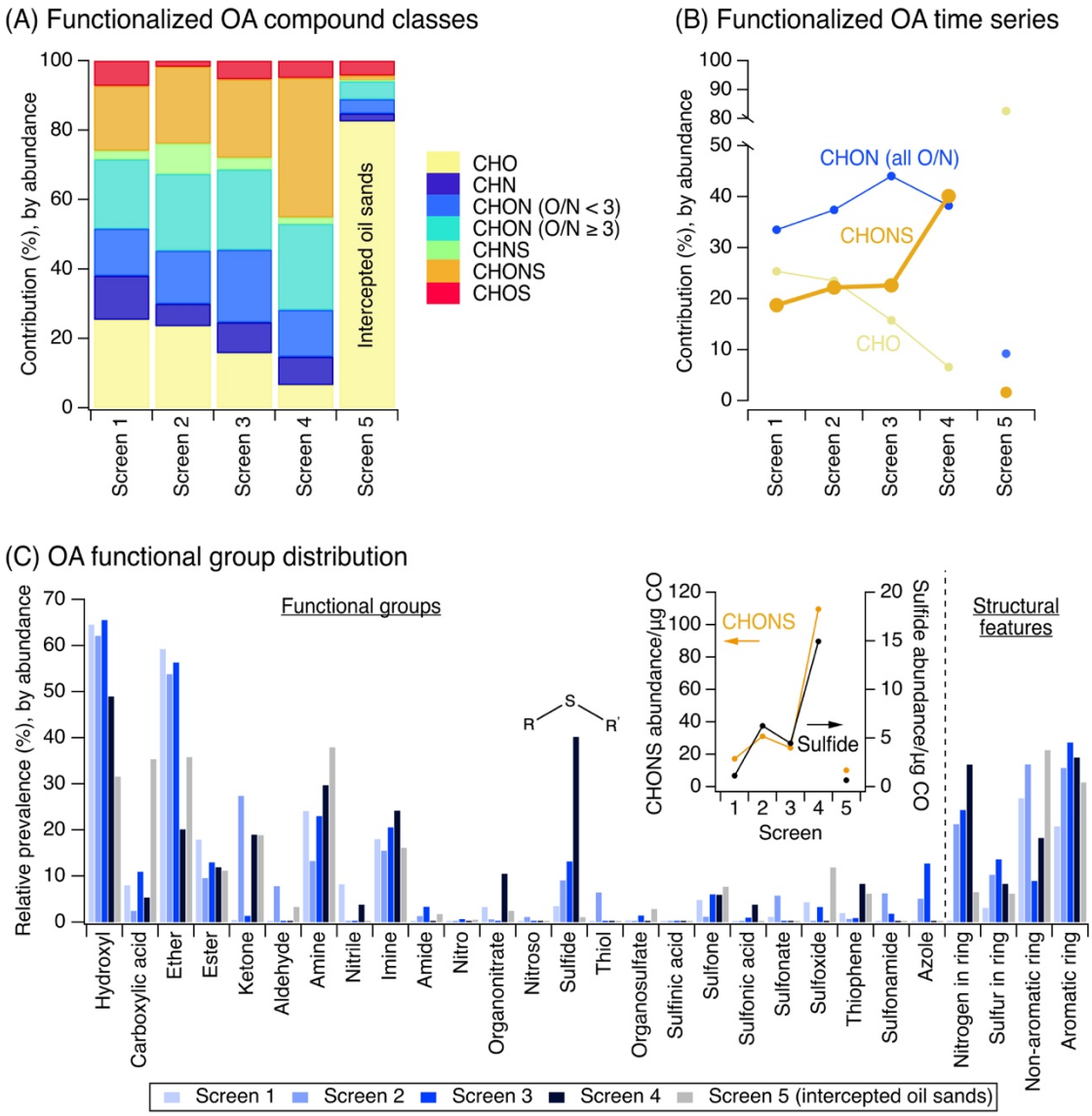

Figure 1. (A) The compound class distribution of functionalized OA (from non-targeted LC-ESI-MS) weighted by ion abundance, shown as percent contribution of each compound class to the total compound abundance measured by LC-ESI-MS. (B) Percent contribution of CHO, CHON, and CHONS compound classes in functionalized OA as a function of plume age. CHON compounds in panel B are summed across all O/N ratios. (C) Functional groups and structural features present in measured functionalized OA (from non-targeted LC-ESI-MS/MS). The sulfide functional group is shown here for emphasis, and will be the subject of subsequent analyses. The inset in panel C shows the absolute CHONS ion abundance normalized by CO mass (orange trace, left y-axis) and the absolute sulfide ion abundance normalized by CO mass (black trace, right y-axis). Full CO-adjusted compound class and functional group abundance data are shown in Figures S5-S6. For panels A-C, results tabulated by occurrence are also shown in Figure S5-S6.

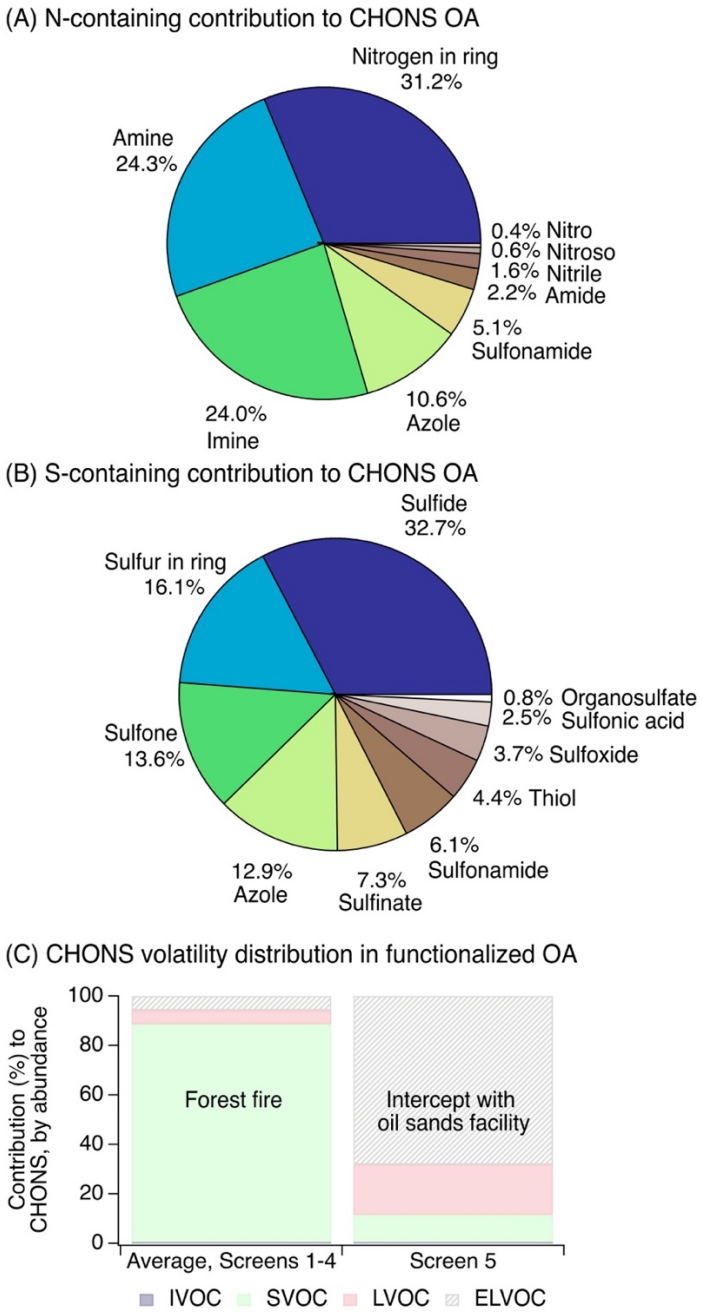

Figure 2. (A) The distribution of nitrogen-containing functional groups to particle-phase CHONS compounds (organonitrates are excluded here due to challenges with their identification using SIRIUS with CSI:FingerID, but contributed minimally to CHONS, Supporting Information S3). (B) The distribution of sulfur-containing groups to particle-phase CHONS compounds. For panels A-B, data are averaged across screens 1-4, with individual screens shown in Figure S7A. (C) Volatility distribution of particle-phase CHONS species. These volatility data were averaged across screens 1-4, and individual screens are shown in Figure S8. Volatility was estimated with the parameterization in Li et al. (Li et al., 2016) and grouped according to volatility bins in Donahue et al. (Donahue et al., 2011).

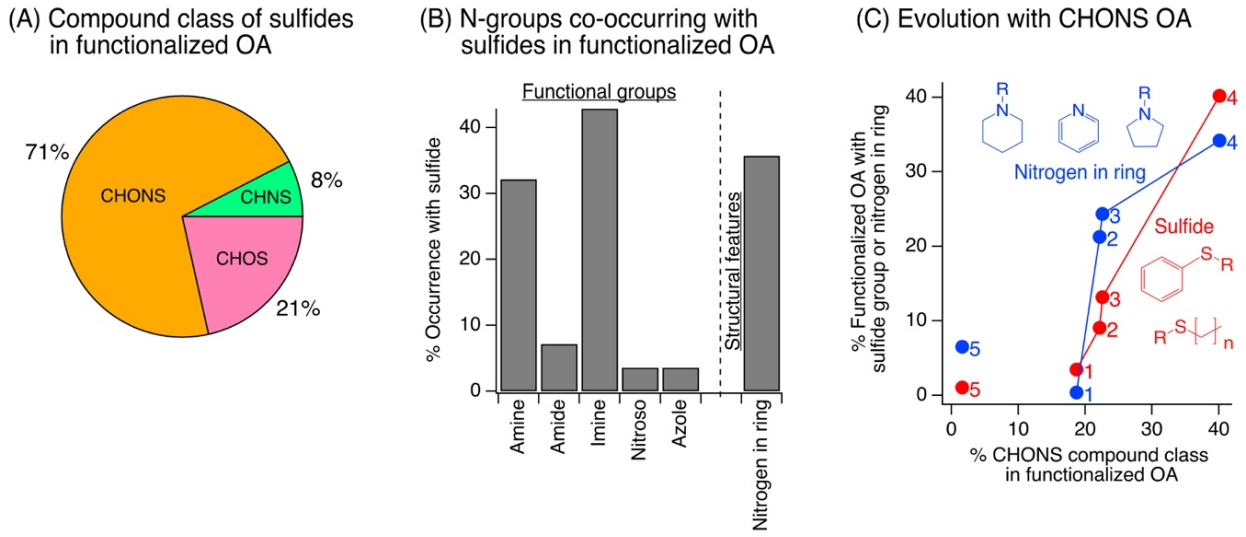

Figure 3. (A) Compound class distribution of sulfide groups: 71% of sulfide functional groups observed (weighted by ion abundance) were present in CHONS compounds. (B) Co-occurrence of sulfides and nitrogen-containing groups. Data shown in panels A-B are cumulative across compounds in screens 1-4. (C) The relative contribution of sulfides and cyclic nitrogen groups to all functionalized OA increased together with the increasing contribution of CHONS compounds. The other functional groups in panel B showed no relationship with the increase in CHONS (Figure S7B). Structures represent examples of commonly observed sulfide and cyclic nitrogen substructures from SIRIUS and CSI:FingerID (Supporting Information S3), where ring structures associated with nitrogen heteroatoms were free standing, adjacent to other rings, and/or contained additional attached functional groups.

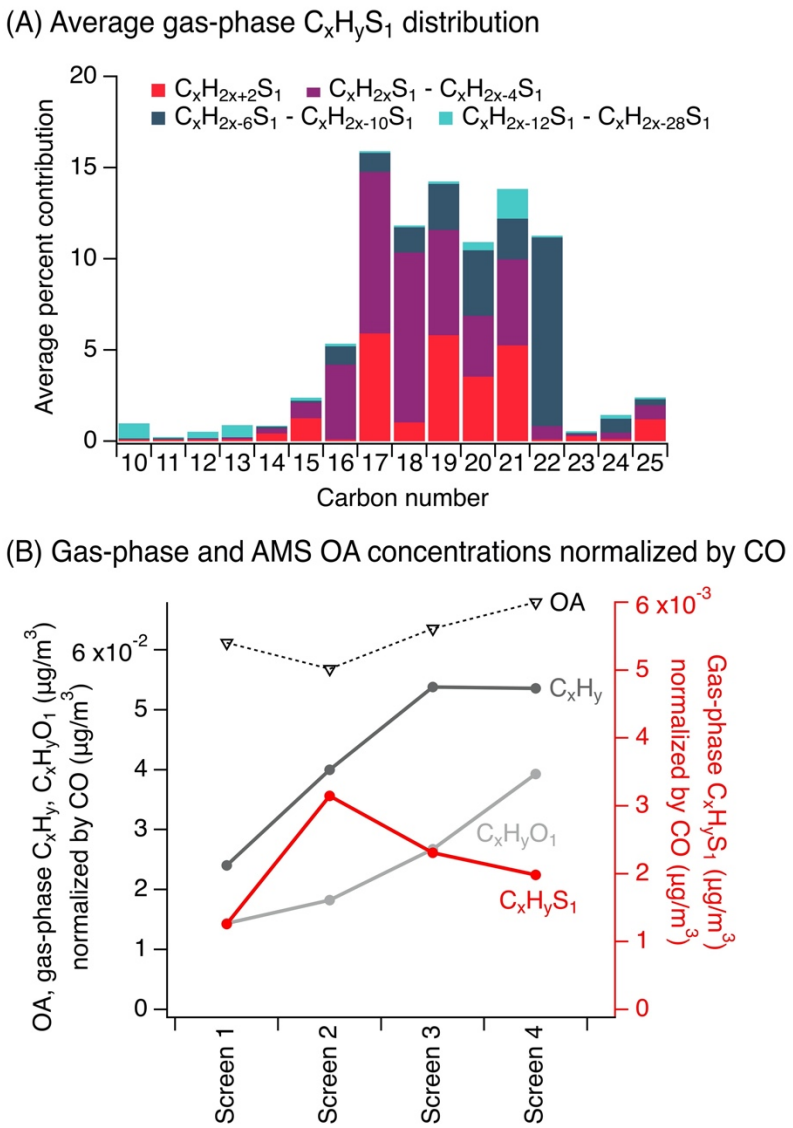

Figure 4. (A) The average $C_xH_yS_1$ distribution from targeted GC-APCI-MS across all gas-phase adsorbent tube samples from screens 1-4 (see Figure S10 for individual $C_xH_yS_1$ screens, and Figure S13 for C_xH_y). (B) Concentrations of gas-phase C_xH_y, $C_xH_yO_1$, $C_xH_yS_1$ from targeted GC-APCI-MS analysis of adsorbent tubes, shown with total OA from AMS, all corrected for dilution using carbon monoxide measurements (see Figure S12A for non-normalized concentrations). Data in panel B are averaged over low and high altitude adsorbent tube samples.