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Atmospheric Evolution of Emissions from a Boreal Forest Fire: The Formation of Highly-Functionalized Oxygen-, Nitrogen-, and Sulfur-Containing 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 evolving gas- and particle-phase compounds sampled via aircraft from a boreal forest fire in Saskatchewan, Canada. We observed diverse multifunctional compounds containing oxygen, nitrogen, and sulfur (CHONS), whose structure, formation, and impacts are understudied. The abundance of particle-phase CHONS species increased with plume age, from 19% to 40% of the relative abundance of observed functionalized OA over the first 4 hours of downwind transport. The relative contribution of particle-phase sulfide functional

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groups increased with age from 4% to 40% of observed OA abundance, and were present in up to 75% of CHONS compounds. The increases in sulfides were accompanied by increases in ring-bound nitrogen, and both increased together with CHONS prevalence. A complex mixture of intermediate- and semi-volatile gas-phase organic sulfur species was emitted 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, and highlight chemical pathways that may also be relevant in situations with elevated levels of nitrogen and sulfur emissions 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),

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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 (Ditto et al., 2019; 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 smoke 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 from a boreal forest fire. We examined the molecular-level emissions and evolution of the forest fire plume with an unprecedented analysis of offline aircraft 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 smoke.

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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 plume 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 organic aerosol 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 also identified possible precursors and reaction pathways involved in the formation of these CHONS compounds.

2 Materials and Methods

On June 25th, 2018, two aircraft research flights were conducted by Environment and Climate Change Canada as part of their Air Pollution research program. These flights sampled two boreal forest wildfire smoke plumes originating near Lac LaLoche 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, which when stacked created a virtual screen intercepting the plumes, at each of five downwind locations (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

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mining oil sands facilities (Figure S1). The samples discussed here were collected across both plumes to ensure that enough mass was present to surpass the mass spectrometer's detection limit. 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±0.40 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). While particles were not explicitly filtered out (to reduce losses of lower volatility gases onto upstream surfaces), we assumed that the compounds measured in the adsorbent tubes below C_{22}-C_{23} were primarily in the gas-phase based on (1) significant undersampling for particles at the adsorbent tube 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; (2) partitioning theory and 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, Supporting Information S1, S3, Table S2). 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 predominantly in the gas-phase.

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Dedicated particle-phase samples were collected on 47 mm PTFE filters (2.0 µm pore; Pall Corporation) from a sampling manifold in the 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.

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. The Q-TOF was operated in MS mode (i.e. TOF data collection, hereafter "GC-APCI-MS"). Adsorbent tube data were processed primarily via a targeted approach for C_xH_y, $C_xH_yO_1$, and $C_xH_yS_1$ compounds using custom Igor Pro code (Supporting Information S2-S3).

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 mode, 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 QC/QA were assigned molecular formulas, with candidate formulas limited to 20 oxygen, 3 nitrogen, and/or 1 sulfur atom(s). Note that these compound classes are discussed here without subscripts.

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Additional details on these methods, including an analysis of total mass analyzed from filters and adsorbent tubes, are discussed in Supporting Information S1-S5, with a methods summary in Figure S3.

3 Results and Discussion

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 compounds containing oxygen (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 measured 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 abundance from screens 1-4. These trends were similar in the carbon monoxide-normalized abundance of these compound classes (Figure S5C), where CHO generally decreased from screens 1-4, while CHONS and CHON generally increased, suggesting that CHONS compounds were possibly

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160 formed from CHO, CHN, and/or CHON precursors existing across both gas- and particle-phases
161 in the plume (proposed chemistry discussed in Section 3.5). From MS/MS, these evolving CHO,
162 CHN, CHON, and CHONS compounds were often comprised of variable combinations of
163 hydroxyls, ethers (e.g. primary emissions from forest fires like methoxyphenols and similar
164 structures), amines, imines, cyclic nitrogen features (consistent with past laboratory observations
165 of biomass burning emissions (Laskin et al., 2009; Lin et al., 2018; Liu et al., 2015; Updyke et
166 al., 2012)), and sulfides.
167
168 3.2 Detailed speciation of CHONS compounds in functionalized OA
169 While some individual CHONS functional groups contained grouped oxygen, nitrogen,
170 and sulfur atoms (e.g. sulfonamides), the majority of CHONS compounds had a combination of
171 multiple separate oxygen-, nitrogen-, and/or sulfur-containing functional groups (Figure 2A-2B).
172 Sulfide groups were important contributors to CHONS compounds (Figure 2B) and showed a
173 notable increase in relative contribution to the overall functional group distribution, from 4-40%
174 of measured compound abundance across screens 1-4 (Figure 1C). Their increasing relative
175 contribution to CHONS compounds with plume evolution was even more pronounced—by
176 screen 4, the sulfide functional group was present in 75% of detected CHONS compound
177 abundance (Figure S7A). Here, we focused on the presence of sulfides in CHONS compounds
178 because most of the observed particle-phase sulfides occurred as part of CHONS species (71%),
179 while a smaller fraction occurred as CHOS (21%) or CHNS (8%) (Figure 3A).
180 To explore possible precursors and formation pathways for these particle-phase sulfide-
181 containing CHONS species, we used MS/MS to identify nitrogen-containing functional groups
182 that co-occurred with sulfides. In CHONS compounds, most sulfides co-occurred with cyclic

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nitrogen (36%), 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 amines or imines 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 sulfide-containing CHONS compounds, which increased in prevalence with plume age (precursors discussed in Section 3.3, potential chemical pathways discussed in Section 3.5).

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 lighter gas-phase species. In contrast, with the 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. CO-normalized abundances of functionalized OA in each particle-phase volatility bin (i.e. IVOC, SVOC, LVOC, ELVOC, computed using LC-derived molecular formulas with the Li et al. parameterization (Li et al., 2016)) 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

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are 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 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 possible gas-phase I/SVOC precursors to the observed sulfide-containing CHONS compounds, we performed a targeted search for each adsorbent tube sample 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 sulfide-containing CHONS compounds as they contained sulfur substructures with linear carbon chains or phenyl groups, similar to those observed on CHONS compounds via MS/MS OA 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, in Figure 4A), which could also be involved as precursors.

The observed gas-phase C_{10}-C_{25} $C_xH_yS_1$ compounds were emitted by the fire and likely also evaporated from the particle-phase 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

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with plume age (Figure 4B, Figure S12A). This suggests the emission and/or evaporation of $C_xH_yS_1$ compounds 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). However, to better understand the dynamics of these sulfur-containing compounds, we compared their concentrations to concentrations from a targeted search of adsorbent tube gas-phase compounds that included C_{10}-C_{25} aliphatic and aromatic C_xH_y and $C_xH_yO_1$ species. 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 compounds from the fire (observed at screen 1) and evaporation from the particle-phase as the plume evolved, as well as formation of $C_xH_yO_1$ via oxidation of C_xH_y compounds. 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 concentration of -2.3 $\mu g/m^3$), 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 $\mu g/m^3$, 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

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particle-phase filter sample extracts analyzed via GC-APCI-MS and 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 $C_xH_yS_1$ measurements due to possible solubility limitations in the extraction solvent (Supporting Information S4). Direct thermal desorption of adsorbent tubes or filters with APCI ionization would be better suited for these C_xH_y and $C_xH_yS_1$ measurements (as performed in this study with adsorbent tubes).

Also, as discussed in *Materials and Methods*, the observed semivolatile compounds below ~C_{22}-C_{23} existed primarily in the gas-phase, while larger compounds actively partitioned to and equilibrated with the particle-phase, further corroborating the possibility of contributions from both direct gas-phase emissions and gases from OA evaporation (Supporting Information S3, Table S2). 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/SVOCs in their respective complex mixtures (Figure 4A, Figures S10 and S13). This difference shows that the observed $C_xH_yS_1$ I/SVOCs were removed (possibly by chemical reactivity) relatively more rapidly than C_xH_y, 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 its instrument 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 (Akagi et al., 2011; Andreae, 2019; Hatch et al., 2015; Koss et al., 2018).

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3.4 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 yet been reported; many of the compounds in the complex sulfur-containing mixture measured here were outside the detection range or measurement capability 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- (and oxygen- and nitrogen-) containing compounds (Leustek, 2002). In addition, disulfide bonds contribute to plant protein structure, and these bonds are known to 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

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298 sulfur products from boreal fuels (e.g. DMS, thiophenes (Akagi et al., 2011; Hatch et al., 2015;
299 Koss et al., 2018; Landis et al., 2018)).

300 *Deposition:* While sulfur can be naturally occurring (e.g. Leustek, 2002), it is also
301 associated with anthropogenic activities (e.g. transportation, power generation, industry, etc.).
302 This implies that a portion of the sulfur in the forest fire emissions could have originated from
303 sulfur deposited via such anthropogenic activities. The closest large anthropogenic sulfur source
304 to the fire location was the oil sands mining region north of Fort McMurray, Alberta, which was
305 approximately 150 km away and which contained known SO_2 emitters (Liggio et al., 2017;
306 McLinden et al., 2016). Regional concentrations of SO_2 or other sulfur species from these nearby
307 industrial activities could have led to accumulated deposition of inorganic and/or organic sulfur
308 compounds over time, though it is uncertain how much of this deposited sulfur would have been
309 taken up and transformed by vegetation (vs. accumulated) due to sulfur uptake and assimilation
310 regulatory pathways in plants (Davidian and Kopriva, 2010). This possible accumulated
311 deposition may have acted as a reservoir of sulfur to be emitted during fires via the re-
312 volatilization of deposited compounds, in addition to the evaporation of typical sulfur
313 metabolites or the formation of sulfur-containing combustion by-products. This hypothesis is
314 consistent with recent deposition measurement and modelling results for the region, which
315 indicated that sulfur deposition from the oil sands potentially impacted areas downwind,
316 including the region where this fire occurred (Makar et al., 2018). Interestingly, lichen and
317 spruce trees, which are prominent in the region of the fire discussed here, have been reported to
318 accumulate sulfur from SO_2 in regions near large industrial SO_2 sources (Meng et al., 1995;
319 Nyborg et al., 1991). Also, past studies have reported enhancements in sulfate (as well as nitrate
320 and ammonium) aerosols from biomass burning in areas with urban influence (Fenn et al., 2015;

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321 Hecobian et al., 2011; Hegg et al., 1987). Inorganic aerosol components from both urban (e.g.:
322 Edmonton, Alberta) and industrial (e.g. oil sands) sources could deposit in the area surrounding
323 the emissions source along with an organic phase, which we postulate could contain a range of
324 sulfur-containing species including the $C_xH_yS_1$ compounds shown here. However, further work is
325 needed to disentangle the contribution of natural vs. anthropogenic sulfur to functionalized OA
326 from biomass burning.
327
328 3.5 Potential reaction pathways leading to sulfides in CHONS from sulfur precursors
329 A number of potential reactions involving sulfur-containing precursors, often thiols (R-
330 SH), may have contributed to the formation of the observed sulfide functional groups in particle-
331 phase CHONS compounds (Figure S14). On average, our gas-phase measurements showed a
332 27% contribution of fully saturated sulfur-containing hydrocarbons (i.e. $C_xH_{2x+2}S_1$, Figures S10-
333 11). It is likely that some fraction of the sulfur compounds observed in the gas-phase adsorbent
334 tube measurements (e.g. the compounds identified as $C_xH_{2x+2}S_1$) and in PTR-ToF-MS
335 measurements (e.g. dimethyl sulfide, diethyl sulfide) were thiols, but the distinction between
336 sulfide and thiol isomers was challenging without specific internal standards.
337 In some of the following possible reactions, a thiol interacts with a non-sulfur precursor
338 to yield a sulfide-containing compound. The non-sulfur precursor (in the gas- or particle-phase)
339 may have contained O and N atoms, thus yielding a CHONS compound immediately after
340 participating in one of the proposed reactions. Alternatively, the newly formed sulfide-containing
341 compound may have undergone subsequent, separate reactions with CHO, CHN, and/or CHON
342 compounds (in the gas- or particle-phase) to form the observed sulfide-containing CHONS
343 species. Here, we focused on possible reactions that could have contributed the sulfide group to

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these oxygen- and/or nitrogen-containing compounds (known emissions from forest fires, as discussed above). Earlier, we postulated that because most of the observed CHONS compounds were SVOCs, these compounds were predominantly formed by reactions of more volatile gas-phase I/SVOCs, and thus we examined potential gas-phase precursors in the C_{10}-C_{25} range. However, it is uncertain whether these sulfide-forming and CHONS-forming reactions 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; temperatures that are relevant very close to the fire but unlikely in the rapidly cooling plume (Mashkina, 1991)). (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

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(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 timescales 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 timescales in an ambient smoke 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 smoke plume (e.g. aerosol pH, presence of water).

4 Implications & Conclusions

In this work, we performed the first high resolution tandem mass spectrometry analysis of an evolving smoke 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 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),

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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 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 (including in sulfide functional groups), oxygen, and nitrogen can affect the glass transition temperature and thus the phase state (e.g. solid, semi-solid, liquid), as well as the mixing state (e.g. well-mixed, phase-separated) of particles (DeRieux et al., 2018; Ditto et al., 2019; Van Krevelen and Te Nijenhuis, 2009). These physical properties may influence particles' chemical reactivity and thus persistence in the atmosphere, along with their transport and deposition, 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.

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436 **Competing Interests**

437 The authors declare that they have no conflict of interest.

438

439 **Code and Data Availability**

440 Code and data are available upon request.

441

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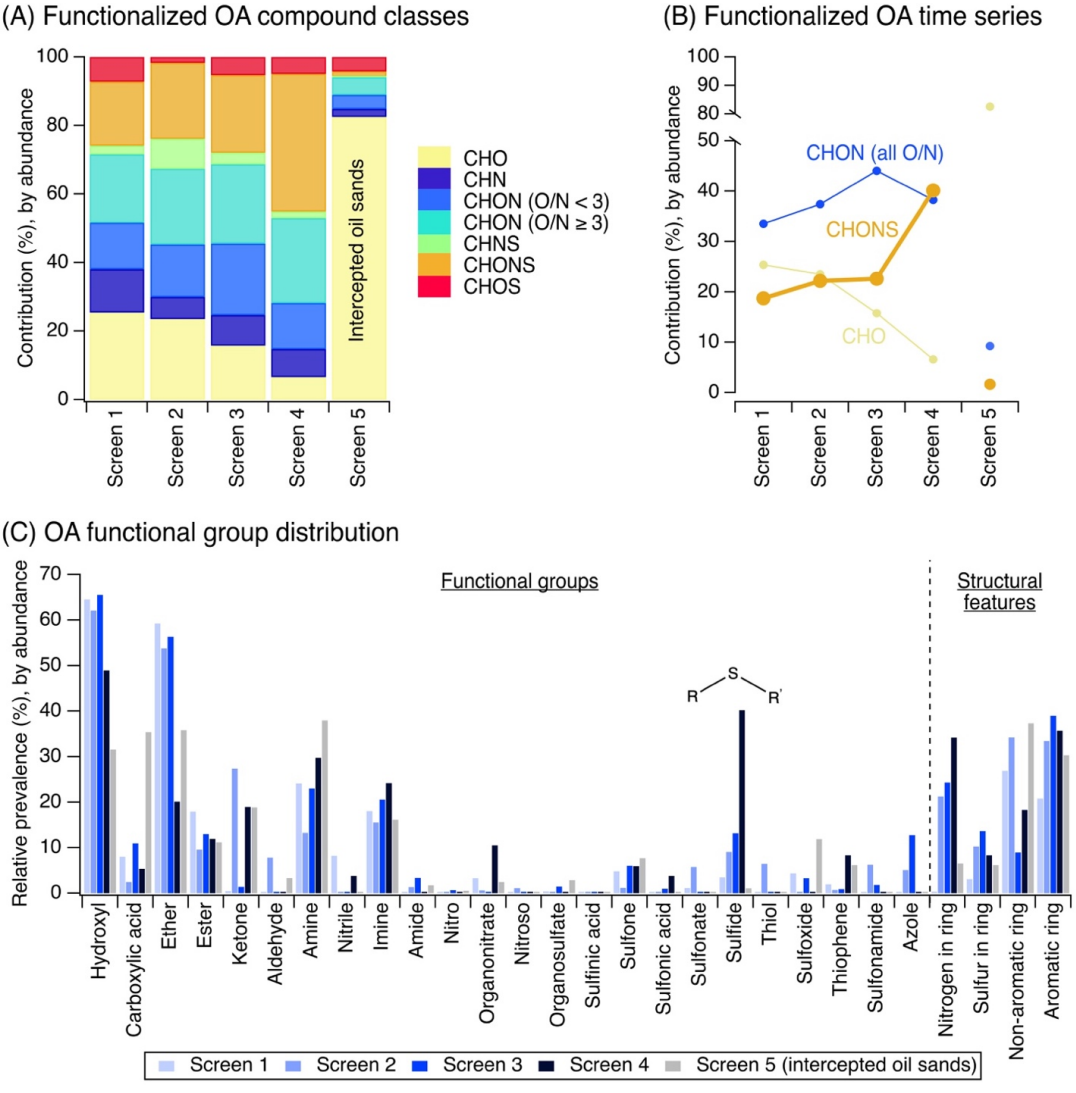

751 **Figure 1.** (A) The compound class distribution of functionalized OA (from non-targeted LC-
752 ESI-MS) weighted by ion abundance, shown as percent contribution of each compound class to
753 the total compound abundance measured by LC-ESI-MS. (B) Percent contribution of CHO,
754 CHON, and CHONS compound classes in functionalized OA as a function of plume age. CHON
755 compounds in panel B are summed across all O/N ratios. (C) Functional groups and structural
756 features present in measured functionalized OA (from non-targeted LC-ESI-MS/MS). The
757 sulfide functional group is shown here for emphasis, and will be the subject of subsequent
758 analyses. For panels A-C, results tabulated by occurrence and absolute ion abundance are shown
759 in Figure S5-S6, and functional group tallying methods are discussed in Supporting Information
760 S3.

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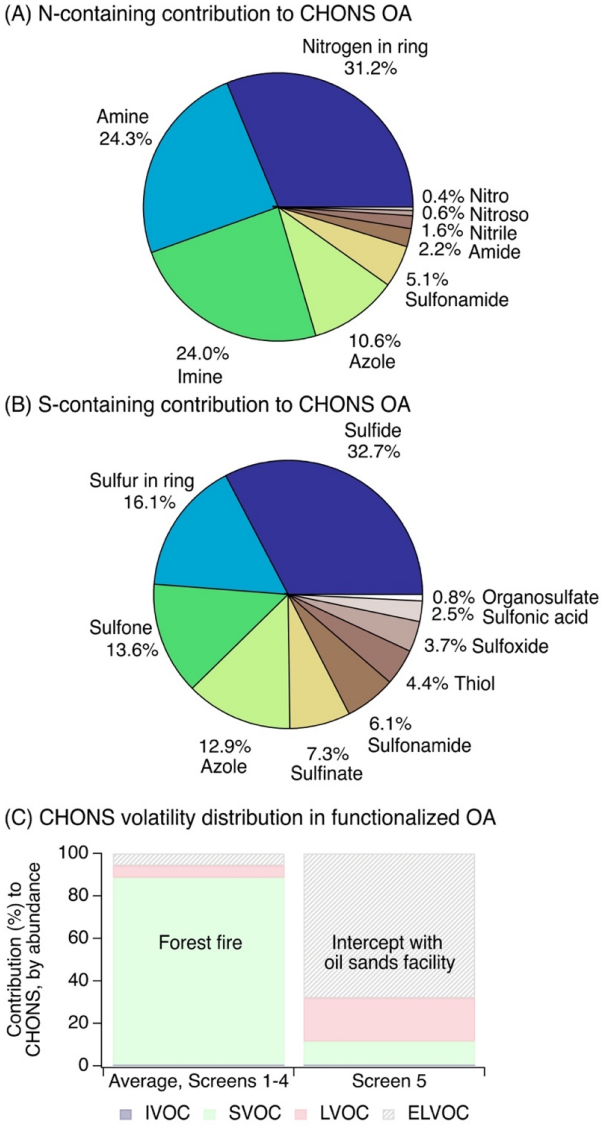

761 **Figure 2.** (A) The observed particle-phase CHONS compounds included cyclic nitrogen and a
762 range of N-containing functional groups (organonitrates are excluded here due to challenges with
763 their identification using SIRIUS with CSI:FingerID, but contributed minimally to CHONS,
764 Supporting Information S3). (B) These CHONS compounds showed a variety of S-containing
765 functional groups with sulfides being the most prominent. For panels A-B, data are averaged
766 across screens 1-4, with individual screens shown in Figure S7A. (C) The particle-phase CHONS
767 compounds formed in the forest fire plume were mostly SVOCs. These volatility data were
768 averaged across screens 1-4, and individual screens are shown in Figure S8. Volatility was
769 estimated with the parameterization in Li et al. (Li et al., 2016) and grouped according to
770 volatility bins in Donahue et al. (Donahue et al., 2011).

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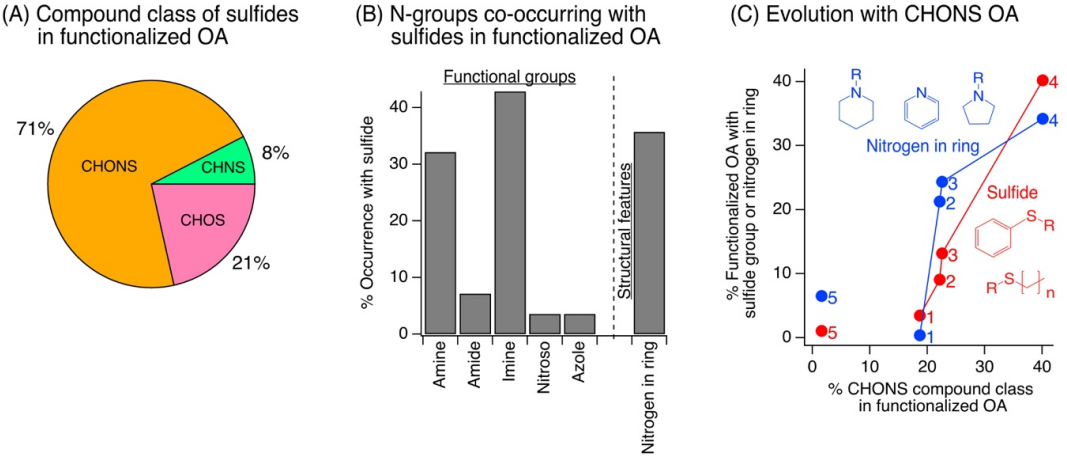

771 **Figure 3.** (A) 71% of sulfide functional groups observed (weighted by ion abundance) were
772 present in CHONS compounds. (B) Sulfides were often paired with amines, imines, and cyclic
773 nitrogen features. Data shown in panels A-B are cumulative across compounds in screens 1-4.
774 (C) The relative contribution of sulfides and cyclic nitrogen groups to all functionalized OA
775 increased together with the increasing contribution of CHONS compounds. The other functional
776 groups shown in panel B showed no relationship with the increase in CHONS (Figure S7B).
777 Structures represent examples of commonly observed sulfide and cyclic nitrogen substructures
778 from SIRIUS and CSI:FingerID (Supporting Information S3), where ring structures associated
779 with nitrogen heteroatoms were free standing, adjacent to other rings, and/or contained additional
780 attached functional groups.

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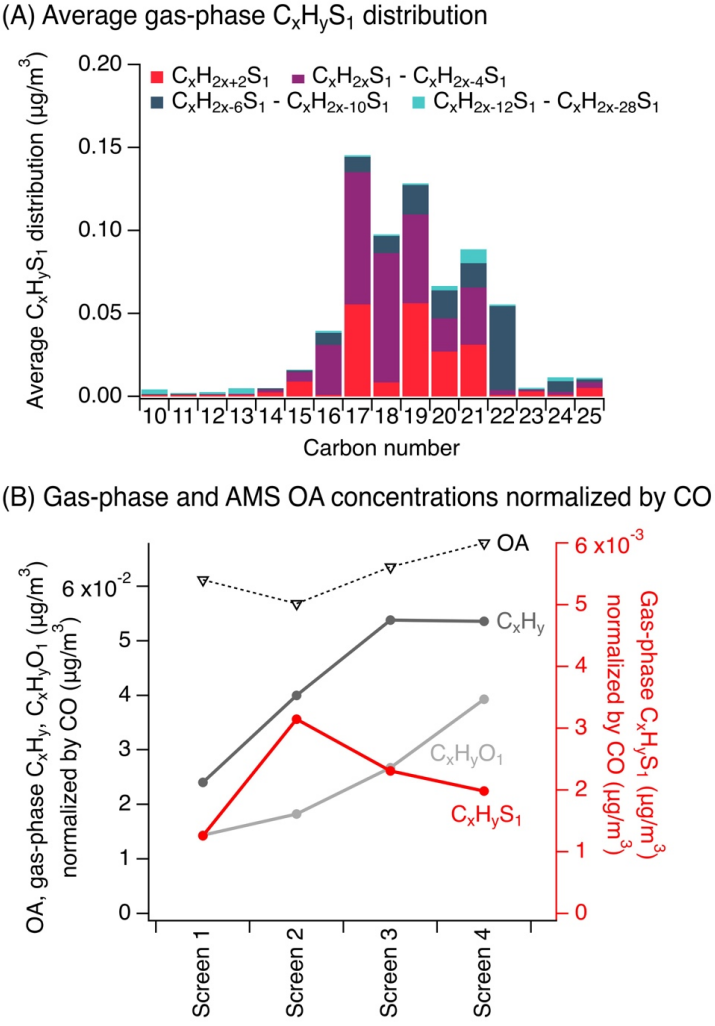

781 **Figure 4.** (A) The average $C_xH_yS_1$ distribution from targeted GC-APCI-MS across all samples
782 from screens 1-4 (see Figure S10 for individual $C_xH_yS_1$ screens, and Figure S13 for C_xH_y). (B)
783 Concentrations of gas-phase C_xH_y, $C_xH_yO_1$, $C_xH_yS_1$ from targeted GC-APCI-MS, and total OA
784 from AMS, all normalized by carbon monoxide concentration across screens 1-4 (see Figure
785 S12A for non-normalized concentrations). Data in panel B are averaged over low and high
786 altitude adsorbent tube samples.