

Supplementary Information

Reconciling the total carbon budget for boreal forest wildfire emissions using airborne observations

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12.0 Methods

12.1 Aircraft measurements

Table S1 provides a summary of the measurements with associated instrumentation, technical details and related references.

12.1.1 Trace gas measurements

All of the trace gas instrumentation except NH₃ and the CIMS were sampled through PTFE tubing from a main aircraft roof hatch that contained multiple inlet ports through which rear-facing tubing was mounted.

The rear-facing inlet minimizes the sampling of particles.

~~NO, NO₂, NO_y, SO₂ and GEM These measurements were made using modified commercial instruments~~

~~(Thermo Scientific Inc. and Tekran Instruments Corp.).~~ NO and SO₂ were directly measured: NO by

chemiluminescence with excess ozone using a 42i TL instrument operated in single mode, while SO₂ was measured by pulsed fluorescence with a 43i TL instrument. A photolytic converter (Air Quality Design Inc.) was used to selectively convert a large fraction of NO₂ to NO. The sum of this NO₂ fraction that was converted to NO plus ambient NO, defined as NO_c, was measured by a second 42i TL chemiluminescent instrument and then NO₂ was calculated based on NO_c, NO and the efficiency of the photolytic converter. NO_y was measured by using an external molybdenum converter heated at 325 °C and placed as close as possible to the sampling point, followed by a third 42i TL instrument. NO and SO₂ calibrations were conducted by generating mixing ratios of 0-100 ppbv using NIST certified cylinders from Scott-Marin (10.3 ppmv accuracy: +/- 2 %), an Environics (Model 6100 Multi-Gas Calibrator), and a Sabio Zero Generator (Model 1001). The efficiencies of the photolytic and NO_y converters were determined using the gas phase titration option of the Environics calibrator. ~~Gas-phase elemental Hg (GEM) was measured with a Tekran 237X instrument (Tekran Instruments Corporation) modified to allow a reduced sampling time of 2 min (McLagan et al., 2021; Cole et al., 2014).~~ Calibrations were conducted periodically throughout the measurement study using NIST-certified standards. Instrument zeros were performed for these instruments 3-5 times per flight for a duration of ~3-5 minutes each time at the beginning, during and after each flight.

NH₃ Ammonia (NH₃) ~~measurements were conducted using Los Gatos Research's (LGR's) NH₃/H₂S Analyzer (Model 911-0039)~~ was sampled through an unfiltered inlet, critical orifice and 4 m of 6.35 mm (1/4") outer diameter Sulfinert-coated tubing heated to 90 °C to minimize NH₃ losses to the tubing walls. The flow rate was 2.5 LPM, controlled through a critical orifice near the unfiltered inlet with the pressure in the fluoropel-coated LGR cell being maintained at 100 Torr. For instrument zeros, ambient air was passed through a Teflon filter coated with citric acid. Calibrations were performed using a certified ammonia standard (Air Liquide; 10.0 ppm NH₃ in N₂, accuracy: +/- 5 %), diluted to near-ambient levels.

CO, CO₂, CH₄, TC and NMOG_f CO, CO₂, CH₄ were measured with a Cavity Ring Down (CRD) spectroscopy instrument (Picarro G2401-m).

TC and NMOG_T A second Picarro G2401-m instrument was used to measure total carbon (TC, in units of ppm_v C) by passing the sample air through a heated (650 °C) platinum catalyst (Shimadzu), adapted from Stockwell et al. (2018) and Veres et al., (2010) which converted all carbon species to CO₂. Approximately 4 g of platinum catalyst (https://www.elementalmicroanalysis.com/product_details.php?product=B1605&description=High%20Sensitivity%20Catalyst%20630-00996) was enclosed in a resistively heated ½” O.D. x 12” long stainless steel tube. As the catalyst assembly was mounted on the roof exterior to the aircraft, with no unheated portion of inlet, TC losses were expected to be negligible. NMOG_T mixing ratios in units of ppm_v C were quantified by subtracting the ambient CH₄, CO and CO₂ measurements (instrument without the upstream-catalyst) from the TC measurements (Fig. S2). Calibrations using two different mixing ratio standards of CO, CO₂ and CH₄, traceable to NOAA GMD standards,- were performed for both Picarro instruments during flight (at the beginning and end) of each flight to assess instrument drift and sensitivity. No significant drift was observed during each flight. NMOG_T was averaged to 10 sec (from the 2 sec native time resolution) to increase the signal to noise ratio. The uncertainty of each instrument was assessed in flight by overflowing the inlet with a constant flow of calibration gas or an ultra pure nitrogen gas stripped of CO₂ via two NaOH pellet traps in series (<https://www.sigmaaldrich.com/CA/en/product/supelco/503215>). In both cases, this resulted in an uncertainty of approximately 60 ppbv C at the 3σ level for each TC channel (dominated by the precision of the CO₂ measurement) (Fig. S2). These uncertainties were added in quadrature resulting in a 3σ uncertainty of ±85 ppb C for NMOG_T. Laboratory experiments indicated that the conversion efficiency of ethane across the catalyst was ~100 %, which is expected to be the most challenging species to combust aside from methane, which is concurrently measured. Additional laboratory experiments using a range of hydrocarbons (>C₂) including aromatics also exhibited ~100 % conversion efficiency (Li et al., 2021; Li et al., 2019). The catalyst material was changed after approximately every 5 flights to further ensure minimal changes in efficiency.

CIMS The CIMS (~~modified Tofwerk/Aerodyne Api-ToF~~) instrument sampled from an insulated rear-facing inlet (PFA, 3/8" OD, 1/4" ID) at 7 LPM (0°C, 1 atm). The instrument was operated using iodide as a reagent ion. The mass resolution at an internal standard peak ($^{13}\text{CC}_2\text{H}_6\text{O}_2\text{I}^-$) was ~5400 Th/Th. The reagent ion was generated by passing 2 sLpm (0°C, 1 atm) of UHP N_2 over a methyl iodide permeation tube held at 40 °C. This flow was then passed through a Polonium-210 ionizer (NRD P-2031) into the ion molecule reactor (IMR). A flow of humidified N_2 (20 sccm through a stainless steel bubbler) was also added to the IMR in order to keep the ratio of $\text{I}(\text{H}_2\text{O})/\text{I}^-$ as constant as possible. The IMR and small segmented quadrupoles (SSQ) were pressure controlled to 70 and 1.5 mBar respectively using Alicat pressure controllers (PC-EXTSEN). Instrument zeros were performed every 15 min by flooding the inlet with 10 sLpm (0°C, 1 atm) of air that had been passed through a Pt/Pd catalyst (CD Nova) heated to 350 °C followed by bicarbonate and charcoal scrubbers (United Filtration). A flow (50 sccm) of isotopically labelled propanoic acid ($^{13}\text{CC}_2\text{H}_6\text{O}_2$) was constantly added to the inlet during the campaign to track instrument sensitivity. Compounds were identified using known/expected sensitivities and available calibration standards (Tables S3).

PTRMS The PTR-ToF-MS (~~Ionicon Analytik GmbH, Austria~~) ~~used chemical ionization with H_3O^+ as the primary reagent ion was operated~~ in a configuration described previously (Table S1). Gases with a proton affinity greater than that of water were protonated in the drift tube. The pressure and temperature of the drift tube region were maintained at a constant 2.15 mbar and 60 °C, respectively for an E/N of 141 Td. The unit contained a catalytic converter heated to 350 °C with a continuous flow of ambient air at a flow rate of one litre per minute. A permeation tube with 1,2,4-trichlorobenzene was placed at the inlet to improve the ~~sensitivity-accuracy~~ of the mass calibration for higher masses. Instrumental backgrounds were performed in flight using a custom-built zero-air generating unit. The data were processed using Tofware software (Tofwerk AG). Calibrations were performed on the ground using gas standard mixtures from Ionicon, Apel-Reimer and Scott-Marrin for 20 compounds (Table S3). ~~For compounds with no available gas standard, a relative response factor was calculated with reaction rate constants using the method described in Sekimoto et al. (2017) and guided by the work of Koss et al. (2018) to define an~~

~~additional 169 ions.~~ Compound identifications for molecular formulas for the PTRMS and CIMS data were assigned based on a limited set of possibilities (particularly for the smaller compounds), known or expected compound sensitivities, and previously published laboratory work by Koss et al. (2018); this is more fully described in the SI Sect. 2.1.3.

AWAS The Advanced Whole Air Sampler (AWAS) was used to ~~take 20-30 sec integrated 'grab' collect~~ **ambient** samples using 1.33-litre electropolished stainless steel canisters in rack-mounted arrays of 12-canister modules (Lerner et al., 2017, and references therein). A metal bellows compressor (Senior Aerospace Metal Bellows, MB-158) was used to pressurize canisters to approximately 30 PSI over a period of approximately ~~15 sec (30 sec maximum)~~ **20 to 30 sec**. Sample lines and manifold tubing were continually flushed with ambient air during the flights. Sampling took place by activating module and pump system valving with custom Labview-based software operating a data logger interface (Labjack Corp., Model T7). The samples were analysed ~~between 5 and 9 days after the flight and cleaned as soon as possible after the flight~~ with an analytical system installed at the Fort McMurray International Airport. The on-site analytical system consisted of a custom fabricated gas chromatograph (GC) system using cryogenic sample pre-concentration, 2-dimensional gas chromatography, Mass Spectrometric Detection (MS) and Flame Ionization Detection (FID). Sample air was cryogenically trapped at -185 °C on a glass bead-filled trap, thus condensing/solidifying the hydrocarbons, and subsequently thermally desorbing them at 135 °C into the multi-column, multi-oven GC/MS/FID instrument. Trapped sample air volumes were calculated by recording pressure differences in a volume-calibrated downstream vacuum vessel before and after sample trapping. Duplicate analysis was carried out on one canister in each AWAS module. The analytical separation of approximately 120 chemical species was carried out by use of a pre-column (SPB-1) where the initial separation of compounds according to boiling point occurred. The low molecular weight compounds (C₂ to C₄) were then directed to two RTX-QS columns connected in series and quantified by a FID. The higher molecular weight compound stream (C₄ to C₁₀) was subsequently split and simultaneously analysed by a second FID connected to an Aluminum Oxide/KCL column (C₄ to C₈) and by a quadrupole Mass Spectrometer (Agilent Technologies, 5977B) connected to an HP-1 column

by means of a fused silica tubing restrictor (C_7 to C_{10}). The precolumn and RTX-QS columns were mounted in the main oven of the gas chromatograph (Agilent Technologies 7890B) and thus were subject to one temperature program. The AlOx/KCL and HP-1 analytical columns were each mounted in a separate temperature-controlled GC oven module (Agilent Technologies, LTM Series II) and operated with a different temperature program. Detector peak areas were calibrated with primary gas standard mixtures in the ppbv concentration range obtained from Apel-Reimer Environmental Inc. (U.S.A.) and the National Physical Laboratory (UK). Compound retention time drift and potential detector sensitivity changes were monitored and compensated for by means of daily analysis of a secondary standard gas. The AWAS modules were cleaned by a custom-fabricated, automated cleaning system similar to that of Lerner et al. (2017). Toluene, benzene and xylenes were not quantified because the method and columns used were not optimized for these compounds. Analytical issues due to incomplete water vapour management in the sample gas stream resulted in retention time shifts and some peak broadening effects resulting in elevated uncertainties. Uncertainties are estimated at $\pm 25\%$ for C_2 to C_5 and C_6 alkanes detected by FID, and $\pm 40\%$ for C_6 alkenes, and the C_7 to C_{10} species detected by MS.

Cartridges Integrated gas phase samples were collected using an automated adsorbent tube sampling assembly (i.e. cartridge) that was mounted in an under-wing pod (see Ditto et al., 2021; ~~SI Sect. 2.1.1~~). Adsorbent tubes were packed with quartz wool, glass beads, Tenax TA, and Carboxen 100 (or “QBTX”), similar to those discussed in Sheu et al. (2018). ~~Samples were collected over the lower set of aircraft transects and higher set of transects, resulting in two integrated cartridge samples for each screen; only the lower altitude samples are used in the analysis as the samples for the higher set of transects included a transect that was above the wildfire plume.~~ Samples were shipped to Yale University where offline analysis was conducted using thermal desorption (GERSTEL TD 3.5+) followed by gas chromatography (Agilent 7890B), atmospheric pressure chemical ionization, and high-resolution mass spectrometry (Agilent 6550) to speciate gas-phase organic compounds (Ditto et al., 2021, Sheu et al., 2018, Khare et al., 2019). ~~The samples provided targeted measurements of gas phase compounds ranging in volatility from C_{10} volatile organic compounds (VOCs) to C_{25} semivolatile organic compounds (SVOCs) including~~

hydrocarbons (CH_n) as well as functionalized compounds containing 1 oxygen atom (CHO_1), and 1 sulfur atom (CHS_1). Ion abundances for CH_n , CHO_1 , and CHS_1 species were converted to mass concentrations assuming average response factors that were calculated based on calibrations using the NIST Reference Gulf of Mexico 2779 Macondo Crude oil reference material following Khare et al. (2019), which accounts for variations in response and fragmentation between components of the complex mixture. CHN_1 species were not quantitatively converted to mass due to the lack of comprehensive and available authentic standards. ~~We acknowledge the limited sample numbers based on flight design, and that the~~ reported emissions are subject to potential variations in sampling efficiency within the under-wing sampling pod across C_{10} - C_{25} and, in the event of losses due to analyte breakthrough, would likely be considered lower limit estimates. Prior breakthrough testing with QBTX adsorbent tubes and similar sampling conditions to those used in this study showed that analyte trapping efficiency in the same carbon number range was generally greater than 85 % (Sheu et al., 2018). ~~CHN_1 was not quantitatively converted to mass due to the lack of available standards.~~ For CH_n , CHO_1 , and CHS_1 , each group of isomers at a given carbon number was categorized by molecular formula, according to their double bond equivalents (DBE) ranging from 0 to 15. Emission ratios (to in-plume CO) were estimated for CH_n , CHO_1 and CHS_1 using observed concentrations for the C_{10} - C_{25} species summed across DBEs. Further discussion of these methods can be found in Ditto et al. (2021), including in the SI (i.e., Section S3).

12.1.2 Particle measurements

Particles were sampled from a forward-facing isokinetic stainless steel diffuser inlet (Droplet Measurement Technologies) that was positioned near the top of the fuselage forward of the engine on the starboard side. Theoretical calculations that take into account the inlet dimensions, volume flow and velocity indicated a 97 % transmission efficiency for particles $< 1 \mu\text{m}$ through the inlet. Air was pulled through the inlet into a main 0.5" O.D. stainless steel sampling line maintained at the isokinetic rate of 70 LPM by two venturis mounted on the fuselage in the aft section of the aircraft. The aerosol instruments subsampled from the main sampling line.

AMS The high resolution aerosol mass spectrometer (AMS) (Aerodyne) measures submicron particles that are sampled through a critical orifice and focussed through an aerodynamic lens into a region of low vacuum. The particles impact a heated surface (600 °C), are vapourized and ionized by 70eV impaction. Ions are then transferred to a time-of-flight mass spectrometer (Tofwerk) where they are accelerated by electric fields and separated by their velocities which are dependent on their mass to charge ratios. Ions are then detected by charged microchannel plates. The AMS was operated only in V mode with 10 sec time resolution. Several ionization efficiency calibrations performed prior to and during the field campaign varied by <10 %. To determine the AMS collection efficiency, number concentrations measured by an Ultra High Sensitivity Aerosol Spectrometer (UHSAS; Droplet Measurement Technologies Inc.) over a size range of 60 nm to 1 µm were converted to volume concentrations using mid-point bin diameters and assuming spherical shapes. ~~Volume concentrations were converted to mass concentrations using densities weighted by the AMS chemical components~~ Total mass was calculated from the UHSAS measurements based on the composition-weighted proportional density determined from the AMS. A collection efficiency of 0.5 was determined. Detailed investigations and discussions around the collection efficiency of the AMS can be found in the literature (Middlebrook et al., 2012; Dunlea et al., 2009; Kleinman et al., 2008; Drewnick et al., 2004; Quinn et al., 2006). PM₁ is the sum of the mass concentrations of AMS components (OA, NO₃, SO₄ and NH₄). ~~The PM₁ from this study is compared with the For comparisons of PM₁ from this study and PM_{2.5} EFs from the Andreae (2019) literature review of boreal forest wildfire studies. While these measurements represent PM over different size ranges (< 1µm vs <2.5µm), the difference is not expected to be significant based on typical size distributions of wildfire emissions (Andreae 2019; Reid and Hobbs, 1998; Reid et al., 2005). This approach has been used previously in literature reviews of EFs for wildfire emissions (Andreae 2019; Akagi et al., 2011). other studies, the mass was estimated between 1 and 2.5 µm to assess the extent of which this might be influencing such comparisons. Using estimated particle mass concentrations from a Fast Cloud Droplet Probe (FCDP) (<2.5 µm) and those from a UHSAS (<1 µm), there is an estimated 10 % of aerosol mass between 1 and 2.5 µm.~~

BC The SP2 (~~Droplet Measurement Technologies~~) measures the mass of rBC contained in individual aerosols through the laser-induced incandescence of heated rBC-containing aerosols (Stephens et al., 2003; Baumgardner et al., 2004; Schwarz et al., 2006). The SP2 was calibrated using fullerene soot (Alpha Aesar lot# F12S011) (Moteki and Kondo, 2010; Kondo et al., 2011; Laborde et al., 2012) nebulized from a water suspension and passed through an aerosol particle mass analyzer (Kanomax APM3600) to select particles with masses ranging from 0.2 fg/particle to 48 fg/particle. Extremely large particles containing more than 520 fg of rBC were excluded from analysis due to saturation of the detector (these accounted for only 2×10^{-3} % of the total number of rBC containing particles measured by the SP2).

UHSAS Particle size distributions were measured using an Ultra-High Sensitivity Aerosol Spectrometer (~~UHSAS; Droplet Measurement Technologies~~). The UHSAS measures the size of individual aerosols passing through a laser beam via Mie scattering (Cai et al., 2008; Kupc et al., 2018). These particles are classified into 99 log-normally spaced bins across the measurement range. Periods where the particle concentration measured by the UHSAS exceeded 3000 particles s^{-1} were excluded from this analysis due to the potential of coincident particles passing through the laser beam. The UHSAS particle sizing was verified using NIST traceable polystyrene latex (PSL) nanospheres of multiple sizes across the measurement range. Total particle mass was calculated from the UHSAS measurements assuming a density of 1.2 g cm^{-3} , based on the ~~composition-weighted~~ proportional density determined from the AMS.

12.1.3 Identification of organic compounds

Three methods were used to provide detailed measurements of gas-phase organic compounds that included the PTRMS, CIMS, and canister samples (AWAS). The PTRMS and CIMS are able to resolve the molecular formula of isobaric species, but cannot distinguish isomers, while the AWAS system can identify and speciate individual compounds. For the PTRMS measurements, compound molecular formulae were assigned based on a limited set of possibilities (particularly for the smaller compounds), known or expected compound sensitivities, and comparing with previously published laboratory work by

Koss et al. (2018) based on typical NMOG structures observed in biomass burning emissions. Koss et al. (2018) used a combination of gas-chromatography (GC) pre-separation, NO^+ CIMS and time series correlations to identify 156 compounds measured in biomass burning laboratory experiments with a PTRMS. Additional comparisons were made with PTRMS ion masses reported in Permar et al. (2021) where they used a PTRMS with two GC methods to speciate isomers for some PTRMS ion masses. For formulas with multiple isomer contributions that were not speciated by the PTRMS, or provided by the AWAS, the fractional contributions in Koss et al. (2018) and Permar et al. (2021) were used to identify the dominant ion and/or contributing compounds. Although the Koss et al. (2018) work was based on laboratory measurements, Permar et al. (2021) found that isomer contributions did not vary much between 24 fires types across the WE-CAN airborne field campaign in western US, which were mainly dominated by fires of pine, fir and spruce trees. For example, in Koss et al. (2018), for the mass spectral ion of $\text{C}_3\text{H}_6\text{O}$ (m/z 58.08), the contribution from acetone was set at 100 % and propanal 0 %, only slightly different from the contribution of 83 ± 6 % for acetone determined by Permar et al., 2021; thus this compound was identified as acetone in this work. Another example is $\text{C}_4\text{H}_8\text{O}$ at m/z 70.091 that has potential contributions from methyl vinyl ketone (MVK), methacrolein and crotonaldehyde, both Koss et al. (2018) and Permar et al. (2021) both reported that MVK is the largest contributor at 48 % and 60 ± 9 % respectively; the compound was labelled here as all three. For C_8H_{10} (m/z 106.168), there are contributions from ethyl-benzene, m- and p-xylenes and o-xylene identified as 10%, 68% and 23%, respectively (Koss et al., 2018), with slightly different isomer contributions as per Permar et al. (2021). In this study, as it was not possible to speciate C_8H_{10} with the AWAS system, it is simply identified as C8 aromatics. Similarly, $\text{C}_{10}\text{H}_{16}$, (m/z 136.238) is identified as total monoterpenes in the present study, with expected contributions from multiple species including alpha and beta pinene, camphene, myrcene, and tricyclene (Permar et al., 2021; Hatch et al., 2017). C_5H_8 at m/z 68.119 was identified as isoprene in the present study, recognizing that there may be a fractional contribution to this mass from methyl-3-buten-2-ol (MBO), although Permar et al. (2021), suggests that MBO may not be significant, based on their analysis of western US wildfires.

For the CIMS, the iodide reagent ion chemistry is most sensitive to polar compounds, particularly carboxylic acids and less sensitive to non-polar compounds (Table S1). Compounds were identified using these known/expected sensitivities and available calibration standards. The AWAS provided speciated measurements of hydrocarbons ($\leq C_{10}$), and no oxygenates.

12.1.4 Overlapping compounds There were a number of compounds (or molecular formulae) that were measured by both the PTRMS and the AWAS, as well as compounds that overlapped between the PTRMS and CIMS. Tables S4 and S5 summarize the decisions of overlapping compounds that were retained for derivation of EFs and Δ ERs, as well as for the carbon/nitrogen budget analyses. For the PTRMS and AWAS, for some molecular formulae, the AWAS provided measurements of individual isomers, while the corresponding PTRMS measurement was expected to reflect ~~the sum of these~~ ~~quantity of the~~ sum of multiple isomers. Comparisons between these two methods are challenging due to the influence of isomers in the PTRMS signal, and the fact that a number of the PTRMS compounds are determined using calculated sensitivities (i.e. not directly calibrated with a standard) with estimated uncertainties of 50 %. These factors limit a comparison between the AWAS and PTRMS for isoprene (C_5H_8) which is shown in Fig. S3a. The comparison for Screens 1 through 3 shows good agreement with an $r^2=0.87$. When including only Screen 1 data, there are two data points (in the SP) where the PTRMS is a factor of 2.5 to 3 higher than the AWAS, resulting in a lower $r^2=0.45$. Although the PTRMS isoprene signal is known to have interferences from cycloalkanes, these compounds are not expected to be emitted from wildfires. 2-methyl-3-buten-2-ol (MBO) produces a fragment at m/z 69.070 that is not separated in the PTRMS, and can also interfere with the isoprene measurement. We do not have measurements to confirm the impact of MBO on the isoprene signal. However, Permar et al. (2021) reported that PTRMS derived isoprene measurements during their study were approximately 2x higher than the AWAS isoprene while sampling smoke, but MBO which was measured during that study was considered too low to account for the higher than expected isoprene. In the present study, it is possible that there were contributions from other unknown isomers to the PTRMS signal in the fresh smoke plumes along Screen

1. Due to these uncertainties, and the comparatively fewer in-plume AWAS samples, EFs and ERs for isoprene are reported from both the PTRMS and AWAS, and isoprene from the PTRMS was used in the carbon budget (Table S4).

In deriving EFs and ~~NERs~~, both the PTRMS and AWAS measurements were included to retain as much information as possible. To avoid double-counting compounds in the carbon and nitrogen budget analyses, only the PTRMS measurement was typically included as it is expected to reflect a sum of ~~all~~ multiple isomers, thus, accounting for more carbon. For example, at the molecular formulas of C₅H₁₀, the PTRMS measurements are expected to reflect the sum of all the isomers, whereas ~~5-7~~ compounds were speciated from the AWAS i.e. c-2-pentene, cyclopentane, 1-pentene, 2-me-1-butene, 3-methyl-1-butene, t-2 pentene, and 2-me-2-butene. In this case, EFs and ~~NERs~~ were derived for both the PTRMS and AWAS measurements, but only the PTRMS measurements were included in the budget analyses.

Between the PTRMS and CIMS, there were 18 overlapping molecular formulae. Although comparisons of exact masses between the PTRMS and CIMS are complicated because of the influence of isomers in the PTRMS signal, four exact masses of which ~~4~~ were identified as the same compound including acetic acid, acrylic acid, formic acid, and isocyanic acid. Figure S3 shows a comparison for the first three compounds, but excludes isocyanic acid as this compound can hydrolyze in the PTRMS drift tube. The CIMS provided measurements of pyruvic acid, but the PTRMS signal at the same mass is likely affected by inlet line losses. Acetic acid and acrylic acid show good agreement with $r^2 > 0.8$ with the PTRMS in-plume measurements ~20 % higher than the CIMS (Fig. S3a, b); this is likely due to additional contributions to the PTRMS signal at these respective exact masses. The comparison for formic acid (Fig. S3c) is poor ($r^2 = 0.3$) likely because the PTRMS measurements are noisy and have a high detection limit of 2 ppbv, whereas the CIMS detection limit is 0.097 ppbv. The CIMS measurements were also directly calibrated (Table S2), whereas the PTRMS formic acid sensitivity (and other compounds) were calculated, and as such, the CIMS measurements for the overlapping compounds were retained for analysis ~~f~~(Table S5). ~~or 3 of these 4 compounds (Table S5) because they were directly calibrated (Table S2), whereas the PTRMS compounds were calculated. For the 4th compound (acetic~~

acid), EFs for both instruments were reported, but only the CIMS data for acetic acid were included in the carbon budget analyses; EFs were very similar (Table A1). The remaining overlapping formulae between the CIMS and PTRMS were calibrated with different analytes, and thus assumed to be different species. While there may in fact be some overlap between isomers contributing to these formulae, their overall contribution to the TC budget is small (<4 %). An attempt was made to quantify as many other peaks that were present in the CIMS mass spectra as possible and apply sensitivity factors. However, the available sensitivity factors were based on laboratory experiments investigating anthropogenic emissions and highly uncertain for biomass burning measurements. Nevertheless, application of these sensitivity factors resulted in average mass from the CIMS spectra totalling < 1.5 % of the TC, so although uncertain, exclusion of these masses is not expected to significantly influence the total carbon budget. It is assumed that all the acids measured by the CIMS are non-aromatic for classifying into chemical structural categories.

1.2 Mass balance method for estimating aircraft-derived emission rates

The Topdown Emission Rate Retrieval Algorithm (TERRA) was designed to estimate emission rates of pollutants measured by aircraft. The algorithm is based on the Divergence Theorem to achieve mass balance and been extensively applied to a range of pollutants measured by aircraft (e.g. Hayden et al., 2021; Baray et al., 2018; Li et al., 2017; Liggio et al., 2017; Gordon et al., 2015). An extension of TERRA previously used for estimating pollutant mass transfer rates across virtual aircraft screens (e.g. Hayden et al., 2021; Baray et al., 2018) was used in the present study to estimate emission rates of NO_x, CO, PM₁ and NH₃ using Screen 1 data. Briefly, pollutant concentrations and horizontal wind speeds were mapped to virtual screens and interpolated using a kriging function, as well as extrapolating the measurements from the lowest aircraft altitude to the surface using applicable extrapolation profiles. Mass transfer rates were derived by integration of the horizontal fluxes across the plume on the screen in

units of t h^{-1} . The main uncertainty in the mass transfer rate is due to extrapolation to the surface as described previously (e.g. Gordon et al., 2015 and Hayden et al., 2021).

2.22.0 Flight and fire description

The 18BN-Larry fire (the Lac LaLoche fires) was detected by the Saskatchewan wildfire management agency on June 23, 2018. Satellite images showed fire hot spots on June 23 and by the evening of June 23 it grew to 1,250 hectares (ha) and to 2,600 ha on June 24th. On the morning of June 25, 2018, there was a very weak nocturnal inversion and moderately strong south to southeast winds at 33 knots above the inversion. The range of fire intensities during the previous night, as well as the observed high humidity (80-90 %) and light to moderate winds observed at the surface also indicates that the fire source at the time of aircraft sampling was in a smoldering combustion state. Flight tracks were flown at Lagrangian distances downwind of the wildfire. Multiple passes (i.e. transects) perpendicular to the plume direction were made at different altitudes. Two plumes were identified: the SP was clearly due to the fire hot spots identified by MODIS (green dots encompassed by a polygon), but the source of the NP is less certain. It is possible that MODIS was unable to detect the fire source because the fire heat signature was below the threshold for satellite instrument detection. However, surface wind measurements at Lac LaLoche (SI Table S1 in McLagan et al., 2021) show that the wind direction was southerly just prior (approx. 30 min) to the start of the aircraft measurements, and then shifted to southeast ($135 \pm 13^\circ$) for the duration of the aircraft flight. Therefore, it is likely that the NP was from the same fire source as the SP that had been transported in a northerly direction just prior to aircraft sampling, and subsequently moved to a northwesterly direction with the wind change. The width of the SP and NP was approximately 14-37 km separated by approximately 8-19 km depending on the sampling altitude, and with an aircraft speed of $\sim 90 \text{ m s}^{-1}$, the plumes were traversed in 3-7 min (Fig. 2).

~~3 Emission ratios, emission factors and combustion efficiency~~

3.01 Combustion state

The combustion efficiency (CE) can be used to characterize and compare the combustion state of the fire, (i.e. the fraction of fuel carbon converted to atmospheric CO₂) (Ward and Radke, 1993). The CE is dependent upon many factors including fire combustion state, fuel chemistry, fuel geometry, growth stage, moisture content and meteorological conditions such as wind speed and temperature. In a flaming fire, high temperature reactions tend to go to completion (>90 %) as rapid reaction of O₂ with the fuel C, H, N and S produces highly oxidized gases including CO₂, NO_x, and SO₂ and BC. As a fire progresses, incomplete combustion characteristics of smoldering fires becomes more dominant resulting in a larger proportion of the emitted carbon in the form of CO, CH₄, NMOC, and OA. Airborne measurements tend to sample a mixture of combustion states; however, there tends to be a dominant phase of combustion at different fire stages (Andreae and Merlet, 2001). If only accounting for CO₂ and CO, the MCE for the SP is 0.90±0.01 and NP is 0.88±0.01, higher than the CE by 7.1 % and 6.6 % for the SP and NP, respectively. These differences are driven mostly by the additional contribution from NMOGs indicating the importance of their inclusion in assessing fire combustion state.

Since the flaming phase was likely more than 14 hrs prior to aircraft sampling, it is possible that the emissions from this fire may also reflect a residual smoldering combustion (RSC) component. RSC produces emissions from combustion of forest floor and woody debris that are not associated with flaming, can be sustained for long periods of time after the passage of a flame front, and are not strongly lofted through fire-induced convection (Bertschi et al., 2003). It is noted though that observations of increased levels of flaming compounds in the plumes including CO₂ and BC (Fig. S42) suggest that to some extent, flaming processes also contributed to the release of these compounds. It is likely that different parts of the fire had varying mixtures of smoldering, flaming and residual combustion processes, but the evidence strongly suggests that the Lac LaLoche fire was predominantly in a smoldering combustion state during the aircraft measurement time period. Smoldering fires can create persistent and poorly ventilated smoke that can be a significant driver in remote community evacuations (McGee, 2020).

383 In addition, boreal fires in this region tend to exhibit a large component of smoldering combustion which
384 can consume large amounts of above and below ground biomass (Akagi et al., 2011).
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386 Table S1. Measurements with associated instrument, principle of operation, sampling time resolution,
 387 **uncertainty, detection limit**, and applicable method references.

Measurement	Instrument	Principle of measurement	Time Resolution (sec)	Uncertainty	Detection Limit	Reference
NO	Thermo 42i	Chemiluminescence with O ₃	1	±5 %	3σ at 1 sec 0.17 ppbv	Clyne et al., 1964 Ridley et al., 1990
NO ₂	Thermo 42i	Photolysis + chemiluminescence with O ₃	1	±7 %	3σ at 1 sec 0.43 ppbv	Penkett et al., 2011
NO _y	Thermo 42i	Heated (350°C) and molybdenum catalyzed conversion + chemiluminescence with O ₃	1	±5 %	3σ at 1 sec 0.18 ppbv	Fehsenfeld et al., 1987; Williams et al., 1998
SO ₂	Thermo 43i	UV pulsed fluorescence	1	±5 %	3σ at 1 sec 1.25 ppbv	Stecher et al., 1997
O ₃	Thermo 42i	Chemiluminescence	1	±5 %	3σ at 1 sec 0.52 ppbv	N/A
NH ₃	LGR model 911-0039	Absorption	1	±5 %	2.1 ppbv at 1 sec 0.3 ppbv at 60 sec	Leifer et al., 2017
Hg (GEM)	Tekran 237X	Fluorescence	120	±0.054 ng m ⁻³	<0.1 ng m ⁻³	Cole et al., 2014; McLagan et al., 2021
CO, CO ₂ , CH ₄	Picarro G-2401-m	Cavity ring down spectrometry	2	CH ₄ ~±3 ppbv	N/A	Baray et al., 2018
Total Carbon (TC)	Picarro G-2401-m	Heated (650°C) platinum catalyzed conversion to CO ₂	2	3σ at 10 sec ±60 ppbv	N/A	Stockwell et al., 2018; Veres et al., 2010.
Total non-methane organic gases (NMOG _T)	Picarro G-2401-m x 2	Difference method, heated (650°C) platinum catalyzed conversion to CO ₂	10	3σ at 10 sec ±85 ppbv	85 ppbv 3σ at 10 sec	Stockwell et al., 2018; Veres et al., 2010
VOCs	CIMS	Chemical ionization/mass spectrometry	1	±10-50% compound dependent	See Table S2	Liggio et al., 2017; Lee et al., 2014
VOCs (≤C ₁₀)	Canister grab samples (AWAS)	Grab samples/GC with MS and FID analysis	Grab 20-30	<C ₆ ±25% ≥C ₆ ±40-%	0.7 to 12.9 pptv for compounds from C ₂ to C ₈ ; 1 to 242 pptv for C ₉ and C ₁₀ compounds	N/A
VOCs	PTRMS	Proton transfer/ionization/mass spectrometry	1	VOCs with available standards: ±15% except CH ₂ O at- ±20%; Calculated	Range of 0.005 to 1 ppbv, CH ₂ O 4.6 ppbv at 1 sec	Li et al., 2017; Sekimoto et al., 2017

				VOCs: ±50%		
VOCs-SVOCs (C10-C25)	Custom packed adsorbent tubes	Offline analysis with TD- GC-APCI-Q-ToF	Variable (245-3140 sec per tube)		1 ppt	Sheu et al., 2018; Khare et al., 2019; Ditto et al., 2021
Particle chemical composition	Aerosol mass spectrometer	Volatilization, ionization and mass spectrometry	10	OA: ±35% SO ₄ : ±25% NO ₃ : ±20% NH ₄ : ±25%	OA: 0.24 µg m ⁻³ SO ₄ : 0.05 µg m ⁻³ NO ₃ : 0.035 µg m ⁻³ NH ₄ : 0.15 µg m ⁻³ at 10 sec	DeCarlo et al., 2008; Jimenez et al., 2003; Allan et al., 2003
Black carbon	SP2	Incandescence	1	15 %	0.01 µg m ⁻³ at 1 sec	Stephens et al., 2003; Baumgardner et al., 2004; Schwarz et al., 2006
Particle size distributions (60 -1000 nm)	Ultra-High Sensitivity Aerosol Spectrometer (UHSAS)	Particle light scattering	1	10 %		Cai et al., 2008; Kupc et al., 2018

Table S2. Standards used to calibrate the CIMS, as well as the compound uncertainty, detection limit and applicable method reference. The iodide chemistry is most sensitive to polar compounds and less sensitive to non-polar compounds. The sensitivity tends to increase for keto-, hydroxy- and acid groups, in order. Most of the keto- groups are attached to a carboxylic acid. For the larger acids (>C4) where there can be several isomers, they are generally identified as saturated C4 carboxylic acids and unsaturated C5 acids.

Molecular weight	Molecular formula	Compound Name	Calibration standard	Calibration Source	Uncertainty (%)	Detection Limit (pptv)	Reference
27.026	HCN	hydrogen cyanide	Hydrogen Cyanide	High Pressure Cylinder (Air Liquide)	20	17	Stockwell et al 2018
32.06	SO ₂	sulphur dioxide	Sulfur Dioxide	High Pressure Cylinder (Air Liquide)	N/A	N/A	Lee et al 2018
43.025	HNCO	isocyanic acid	Isocyanic Acid	Thermal Decomposition/ Diffusion	30	10	Roberts et al 2010
46.025	CH ₂ O ₂	formic acid	Formic Acid	Liquid Standard supplied by Liquid Calibration Unit (LCU)	20	156	Mungall et al 2017
47.013	HONO	nitrous acid	Nitrous Acid	Acid Displacement (output quantified by ion chromatography)	30	12	Roberts et al 2010
57.052	C ₂ H ₃ NO	hydroxy acetonitrile	Glycolic Acid Nitrile	Liquid Standard supplied by Liquid Calibration Unit (LCU)	20	0.12	Mungall et al 2017
60.052	C ₂ H ₄ O ₂	acetic acid	Acetic Acid	Liquid Standard supplied by Liquid Calibration Unit (LCU)	20	576	Mungall et al 2017
63.012	HNO ₃	nitric acid	Nitric Acid	Permeation Tube (output quantified by ion chromatography)	N/A	58	Neuman et al 1999
72.063	C ₃ H ₄ O ₂	acrylic acid	Acrylic Acid	Liquid Standard supplied by Liquid Calibration Unit (LCU)	20	17	Mungall et al 2017
74.079	C ₃ H ₆ O ₂	propionic acid	Propionic Acid	Liquid Standard supplied by Liquid	20	55	Mungall et al 2017

				Calibration Unit (LCU)			
79.011	HNO ₄	pernitric acid	Pernitric Acid	Reaction of HO ₂ with NO ₂ (quantified by thermal decomposition Cavity Ringdown Spectroscopy of NO ₂)	50	2	Veres et al 2015
84.074	C ₄ H ₄ O ₂	C₄H₄O₂	2(5H)-Furanone	Liquid Standard supplied by Liquid Calibration Unit (LCU)	20	51	Mungall et al 2017
85.062	C₃H₃NO₂	cyanoacetic acid	Cyanoacetic Acid	Liquid Standard supplied by Liquid Calibration Unit (LCU)	20	0.17	Mungall et al 2017
86.09	C₄H₆O₂	methacrylic acid	Methacrylic Acid	Liquid Standard supplied by Liquid Calibration Unit (LCU)	N/A	N/A	Mungall et al 2017
88.062	C ₃ H ₄ O ₃	pyruvic acid	Pyruvic Acid	Liquid Standard supplied by Liquid Calibration Unit (LCU)	20	253	Mungall et al 2017
88.106	C₄H₈O₂	C4 saturated carboxylic acids	Butyric Acid	Liquid Standard supplied by Liquid Calibration Unit (LCU)	20	63	Mungall et al 2017
91.066	C₂H₅NO₃	C2 Nitro alcohol	2-Nitroethanol	Liquid Standard supplied by Liquid Calibration Unit (LCU)	20	0.80	Mungall et al 2017
100.117	C ₅ H ₈ O ₂	unsaturated C5 carboxylic acids	4-Pentenoic Acid	Liquid Standard supplied by Liquid Calibration Unit (LCU)	20	19	Mungall et al 2017
102.089	C ₄ H ₆ O ₃	C4 oxo-carboxylic acids	2-Ketobutyric Acid	Liquid Standard supplied by Liquid Calibration Unit (LCU)	20	354	Mungall et al 2017
102.133	C₅H₁₀O₂	C5 saturated carboxylic acids	Valeric Acid + Isovaleric Acid (equal parts)	Liquid Standard supplied by Liquid	20	46	Mungall et al 2017

				Calibration Unit (LCU)			
104.105	C ₄ H ₈ O ₃	C4-hydroxy-carboxylic acids	3-Hydroxybutyric Acid	Liquid Standard supplied by Liquid Calibration Unit (LCU)	20	4	Mungall et al 2017
108.009	N ₂ O ₅	dinitrogen pentoxide	Dinitrogen Pentaoxide	Titration of NO ₂ with O ₃ (quantified by thermal decomposition Cavity Ringdown Spectroscopy of NO ₂)	50	0.14	Lee et al 2018
114.144	C ₆ H ₁₀ O ₂	sum of cyclic saturated and n-unsaturated C5 carboxylic acids	Cyclopentanecarboxylic Acid	Liquid Standard supplied by Liquid Calibration Unit (LCU)	20	28	Mungall et al 2017
116.116	C ₅ H ₈ O ₃	C5 oxo-carboxylic acids	Levulinic Acid	Liquid Standard supplied by Liquid Calibration Unit (LCU)	20	11	Mungall et al 2017
116.16	C ₆ H ₁₂ O ₂	C6-saturated carboxylic acids	Hexanoic Acid + 4-Methyl-Valeric Acid (equal parts)	Liquid Standard supplied by Liquid Calibration Unit (LCU)	20	13	Mungall et al 2017
118.132	C ₅ H ₁₀ O ₃	C5-hydroxy-carboxylic acids	2-Hydroxy-2-methylbutyric Acid	Liquid Standard supplied by Liquid Calibration Unit (LCU)	20	59	
126.155	C ₇ H ₁₀ O ₂	unsaturated C6 cyclic carboxylic acid	3-Cyclohexene-1-carboxylic Acid	Liquid Standard supplied by Liquid Calibration Unit (LCU)	20	6	
128.171	C ₇ H ₁₂ O ₂	C6 unsaturated carboxylic acids	6-Heptenoic Acid	Liquid Standard supplied by Liquid Calibration Unit (LCU)	20	11	
130.187	C ₇ H ₁₄ O ₂	C7-saturated carboxylic acids	Heptanoic Acid	Liquid Standard supplied by Liquid Calibration Unit (LCU)	20	23	
132.159	C ₆ H ₁₂ O ₃	C6 hydroxy-carboxylic acids	2-Hydroxyisocaproic Acid	Liquid Standard supplied by Liquid	20	1.6	

				Calibration Unit (LCU)			
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Table S3. Standards used to calibrate the PTRMS. ^aC8 aromatics - expected contributions from ethyl benzene, m- and p-xylenes and o-xylene. ^bMonoterpenes - expected contributions from camphene, α -pinene, β -pinene, myrcene, and tricyclene.

Molecular weight	Molecular formula	Compound Name	Calibration standard
30.026	CH ₂ O	formaldehyde	formaldehyde
32.042	CH ₄ O	methanol	methanol
34.076	H ₂ S	hydrogen sulfide	hydrogen sulfide
41.053	C ₂ H ₃ N	acetonitrile	acetonitrile
44.053	C ₂ H ₄ O	acetaldehyde	acetaldehyde
56.064	C ₃ H ₄ O	acrolein	acrolein
58.08	C ₃ H ₆ O	acetone	acetone
62.13	C ₂ H ₆ S	dimethyl sulfide	dimethyl sulfide
68.119	C ₅ H ₈	isoprene	isoprene
70.091	C ₄ H ₆ O	MVK, methacrolein, crotonaldehyde	crotonaldehyde
72.107	C ₄ H ₈ O	MEK, 2-methyl acetate, ethyl formate	methylethyl ketone
76.157	C ₃ H ₈ S	2-propanethiol, ethyl methyl sulfide	ethylmethyl sulfide
78.114	C ₆ H ₆	benzene	benzene
84.136	C ₄ H ₄ S	thiophene	thiophene
90.184	C ₄ H ₁₀ S	diethyl sulfide, butanethiol	diethyl sulfide
92.141	C ₇ H ₈	toluene	toluene
98.163	C ₅ H ₆ S	methyl thiophene	2-methylthiophene
106.168	C ₈ H ₁₀	C8 aromatics ^a	o-xylene
112.19	C ₆ H ₈ S	dimethylthiophene	2,3-dimethylthiophene
136.238	C ₁₀ H ₁₆	monoterpenes ^b	camphene

418 Table S4. Overlapping compounds measured between the PTRMS and AWAS.

Molecular Weight	Formula	Compound Name	Instrument	Decision for budget	Decision for EFs
42.081	C ₃ H ₆	propene	AWAS and PTRMS	AWAS	AWAS
54.092	C ₄ H ₆	butadiene/fragments	PTRMS	PTRMS	PTRMS and AWAS
		1,3-butadiene	AWAS		
56.108	C ₄ H ₈	butenes	PTRMS	AWAS	AWAS
		cis-2-butene	AWAS		
		isobutene	AWAS		
		trans-2-butene	AWAS		
		1-butene	AWAS		
58.124	C ₄ H ₁₀	butanes	PTRMS	AWAS	AWAS
		isobutane	AWAS		
		n-butane	AWAS		
68.119	C ₅ H ₈	isoprene	PTRMS and AWAS	PTRMS	PTRMS and AWAS
70.135	C ₅ H ₁₀	pentene/fragments	PTRMS	PTRMS	PTRMS and AWAS
		cis-2-pentene	AWAS		
		cyclopentane	AWAS		
		1-pentene	AWAS		
		2-methyl-1-butene	AWAS		
		2-methyl-2-butene	AWAS		
		3-methyl-1-butene	AWAS		
		t-2 pentene	AWAS		
78.114	C ₆ H ₆	benzene	PTRMS and AWAS	PTRMS	PTRMS
82.146	C ₆ H ₁₀	cyclohexene	PTRMS and AWAS	PTRMS	PTRMS
84.162	C ₆ H ₁₂	hexene	PTRMS and AWAS	PTRMS (hexane) AWAS (cyclohexane)	PTRMS and (hexane) AWAS (cyclohexane) AWAS
		cyclohexane	AWAS		
		cis-2-hexene	AWAS		
86.178	C ₆ H ₁₄	hexanes	PTRMS and AWAS	AWAS	AWAS
		n-hexane	AWAS		
		2,3-dimethyl butane	AWAS		
		2,3-dimethylpentane	AWAS		

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Table S5. Overlapping compounds measured between the PTRMS and CIMS. ^aThe PTRMS signal at molecular weight 60.052 is reported as acetic acid fragment; the signal can also be due to glycoaldehyde (Koss et al., 2018), but the PTRMS and CIMS acetic acid mixing ratios and EFs match each other closely suggesting that the PTRMS fragment is mostly due to acetic acid.

Molecular weight	Formula	CIMS compound name	PTRMS compound name	Decision
43.025	HNCO	Isocyanic acid	Isocyanic acid	CIMS and PTRMS for reporting EF and ER; CIMS for carbon budget
46.025	CH ₂ O ₂	Formic acid	Formic acid	CIMS
57.052	C ₂ H ₃ NO	Hydroxy acetonitrile	Methyl isocyanate	CIMS and PTRMS
60.052	C ₂ H ₄ O ₂	Acetic acid	Acetic acid fragment ^a	CIMS and PTRMS for reporting EF and ER; CIMS for carbon budget
72.063	C ₃ H ₄ O ₂	Acrylic acid	Methyl glyoxal/acrylic acid	CIMS
74.079	C ₃ H ₆ O ₂	Propionic acid	Hydroxy acetone/ethyl formate	CIMS and PTRMS
84.074	C ₄ H ₄ O ₂	Unidentified	Furanone	CIMS and PTRMS
85.062	C ₃ H ₃ NO ₂	Cyanoacetic acid	Methyl cyanofomate	CIMS and PTRMS
86.09	C ₄ H ₆ O ₂	Methacrylic acid	Butanedione/isomers	CIMS and PTRMS
88.062	C₃H₄O₃	Pyruvic acid	Pyruvic acid	CIMS
88.106	C ₄ H ₈ O ₂	C4 saturated carboxylic acids	Methyl propanoate	CIMS and PTRMS
100.117	C ₅ H ₈ O ₂	Unsaturated C5 carboxylic acids	Methyl methacrylate/isomers	CIMS and PTRMS
102.089	C ₄ H ₆ O ₃	C4 oxo-carboxylic acids	Acetic anhydride	CIMS and PTRMS
102.133	C ₅ H ₁₀ O ₂	C5 saturated carboxylic acids	Valeric acid	CIMS and PTRMS
114.144	C ₆ H ₁₀ O ₂	Sum of cyclic saturated and n-saturated C5 carboxylic acids	Caprolactone/c6 esters/c6diketone isomers	CIMS and PTRMS
116.16	C ₆ H ₁₂ O ₂	C6 carboxylic acids	Butyl acetate/c6 esters	CIMS and PTRMS
118.132	C ₇ H ₁₀ O ₂	Unsaturated C6 cyclic carboxylic acids	Cyclohexene carboxylic acid	CIMS and PTRMS
128.171	C ₇ H ₁₂ O ₂	C6 unsaturated carboxylic acids	Cyclohexanoic acid	CIMS and PTRMS
130.187	C ₇ H ₁₄ O ₂	C7 saturated carboxylic acids	Amyl acetate	CIMS and PTRMS

427 Table S6. Compounds with no significant observed emissions

Molecular Weight	Formula	Compound Name	Instrument
34.08	H ₂ S	hydrogen sulfide	PTRMS
70.05	C ₂ H ₃ O ₂	Propiolic acid	PTRMS
72.17	C ₅ H ₁₂	2,2-dimethylpropane	AWAS
82.06	C ₄ H ₂ O ₂	cyclobutenedione	PTRMS
85.06	C ₃ H ₃ NO ₂	cyanoacetic acid	CIMS
86.2	C ₆ H ₁₄	2,2-dimethylbutane	AWAS
91.07	C ₂ H ₅ NO ₃	C2 nitro alcohol	CIMS
100.07	C ₄ H ₄ O ₃	dihydro furandione	PTRMS
102.195	C ₅ H ₁₀ S	cyclopentanethiol	PTRMS
104.105	C ₄ H ₈ O ₃	C4 hydroxy-carboxylic acids	CIMS
112.24	C ₈ H ₁₆	cis-1,2-dimethylcyclohexane	AWAS
112.56	C ₆ H ₅ Cl	chlorobenzene	PTRMS
118.13	C ₅ H ₁₀ O ₃	C5 hydroxy-carboxylic acids	CIMS
128.29	C ₉ H ₂₀	2,5-dimethylheptane	AWAS
134.24	C ₁₀ H ₁₄	1-methyl-2-n-propylbenzene	AWAS
140.25	C ₈ H ₁₂ S	butylthiophene	PTRMS
142.32	C ₁₀ H ₂₂	2,2-dimethyloctane	AWAS
147.00	C ₆ H ₄ Cl ₂	dichlorobenzene	PTRMS
154.12	C ₇ H ₆ O ₄	dihydroxybenzoic acid	PTRMS
n/a	Cl ⁻	p-chloride	AMS

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Table S7. Emission ratios (relative to CO, as $\mu\text{g m}^{-3}$ of I/SVOC per $\mu\text{g m}^{-3}$ CO) for complex mixtures of gas-phase CH, CHO₁, and CHS₁ compounds grouped by carbon number for all targeted molecular formulas, derived from the integrated cartridge samples, using the sample taken across the lowest transects of Screen 1. ~~Note: based on flight design, it was not possible to directly derive emission factors due to the lack of background cartridge samples in the upwind region of the fire so ratios to CO in the concentrated lower (Screen 1) transects are used in the analysis to approximate emission factors from the wildfire.~~ The ERs are reported as a range with the lower limit reflecting the subtraction of a slightly contaminated background, and the upper limit having no background subtracted.

Carbon Number	CH ($\mu\text{g m}^{-3}$)/ CO ($\mu\text{g m}^{-3}$)	CHO ₁ ($\mu\text{g m}^{-3}$)/ CO ($\mu\text{g m}^{-3}$)	CHS ₁ ($\mu\text{g m}^{-3}$)/ CO ($\mu\text{g m}^{-3}$)
10	1.1E-02 - 1.1E-02	3.2E-03 - 3.2E-03	7.2E-06 - 7.9E-06
11	0.0E+00 - 0.0E+00	6.6E-04 - 6.6E-04	1.6E-05 - 1.6E-05
12	5.4E-05 - 5.4E-05	4.6E-04 - 7.4E-04	0.0E+00 - 2.4E-06
13	3.3E-06 - 2.4E-04	4.4E-05 - 5.4E-04	9.2E-06 - 1.4E-05
14	5.3E-05 - 1.6E-04	3.7E-04 - 1.1E-03	4.4E-06 - 5.8E-06
15	6.0E-05 - 3.7E-04	3.3E-04 - 1.0E-03	2.2E-05 - 2.4E-05
16	3.4E-04 - 1.1E-03	3.6E-04 - 7.0E-04	5.4E-05 - 6.8E-05
17	7.6E-04 - 1.2E-03	1.2E-03 - 1.9E-03	3.3E-04 - 3.4E-04
18	1.0E-03 - 1.7E-03	2.1E-04 - 1.3E-03	1.2E-04 - 1.2E-04
19	1.6E-03 - 1.9E-03	5.7E-04 - 1.2E-03	3.9E-04 - 4.3E-04
20	1.9E-03 - 2.8E-03	3.1E-04 - 9.1E-04	1.1E-04 - 1.4E-04
21	2.5E-03 - 2.5E-03	2.6E-04 - 5.2E-04	2.3E-04 - 2.9E-04
22	3.8E-03 - 4.0E-03	1.7E-04 - 3.3E-04	1.9E-05 - 8.9E-05
23	2.1E-03 - 2.2E-03	6.7E-05 - 1.5E-04	2.9E-05 - 2.9E-05
24	7.6E-04 - 1.0E-03	3.3E-05 - 1.2E-04	4.4E-05 - 6.0E-05
25	4.0E-04 - 4.3E-04	9.0E-06 - 5.5E-05	1.3E-05 - 6.1E-05

461 Table S8. Compounds shown in Fig. 9 where the identifications/naming are not exact matches with
462 the current study. 1 Individually identified compounds were summed for comparison to the present study;
463 2 Each compound was compared with the value from the present study.

Molecular Weight	Compound	Instrument	Compound Name	Andreae Names	Koss Names	Permar Names	Urbanski Names
54.092	C ₄ H ₆	PTRMS	butadiene/fr agments	butadiene	1,3-butadiene + 1,2- butadiene	1,3-butadiene, 1,2-butadiene	n/a
54.092	C ₄ H ₆	AWAS	1,3- butadiene	butadiene	1,3-butadiene + 1,2- butadiene	1,3-butadiene, 1,2-butadiene	n/a
57.052	C ₂ H ₃ NO	CIMS	hydroxy acetonitrile	n/a	methyl isocyanate + hydroxyaceto nitrile	methyl isocyanate, hydroxyacetonitril e	n/a
58.124	C ₄ H ₁₀	AWAS	isobutane	n/a	n/a	n-Butane	n/a
60.052	C ₂ H ₄ O ₂	CIMS	acetic acid	Acetic acid	acetic acid + glycolaldehyd e	acetic acid, glycolaldehyde (=hydroxylacetalde hyde)	n/a
60.096	C ₃ H ₈ O	PTRMS	propanol	n/a	n/a	Isopropanol	n/a
66.103	C ₅ H ₆	PTRMS	cyclopentan diene	n/a	n/a	1,3- cyclopentadiene	1,3- Cyclopentadie nePIT
70.091	C ₄ H ₆ O	PTRMS	MVK, methacrolein , crotonaldeh yde	Methacrolei n	MVK + methacrolein + crotonaldeh yde	Methyl vinyl ketone, Methacrolein, 2- Butenal (=crotonaldehyde)	¹ Crotonaldehy de + Methacrolein + Methyl Vinyl Ketone MVK
70.135	C ₅ H ₁₀	PTRMS	pentene/met hyl butene/frag ments	1-Pentene + 2-pentene	pentene+met hyl butene	pentenes, methylbutenes	n/a
70.135	C ₅ H ₁₀	AWAS	c-2-pentene	2 pentene cis&tran	pentene+met hyl butene	pentenes, methylbutenes	n/a
70.135	C ₅ H ₁₀	AWAS	cyclopentan e			cyclopentane	n/a
70.135	C ₅ H ₁₀	AWAS	1-pentene	1-Pentene	pentene+met hyl butene	pentenes, methylbutenes	n/a
70.135	C ₅ H ₁₀	AWAS	methyl-1- butene	1-Pentene	pentene+met hyl butene	pentenes, methylbutenes	n/a
70.135	C ₅ H ₁₀	AWAS	methyl-2- butene	1-Pentene	pentene+met hyl butene	pentenes, methylbutenes	n/a
72.063	C ₃ H ₄ O ₂	CIMS	acrylic acid	n/a	n/a	pyruvaldehyde (=methyl glyoxal), acrylic acid	n/a
72.107	C ₄ H ₈ O	PTRMS	methy ethyl ketone + butanal + 2- methylpropa nal	2-butanone (methyl ethyl ketone)	methyl ethyl ketone + butanal + 2- methylpropan al	methyl ethyl ketone, 2- methylpropanal, butanal	¹ Methyl Ethyl Ketone MEK + n-Butanal + 2-

							Methylpropanal
72.151	C ₅ H ₁₂	AWAS	methylbutane	n/a	n/a	n-pentane	n/a
74.079	C ₃ H ₆ O ₂	PTRMS	hydroxyacetone/ethyl formate	n/a	methyl acetate + ethyl formate + hydroxyacetone	Hydroxyacetone, Methyl acetate, Ethyl formate	Ethyl Formate
81.118	C ₅ H ₇ N	PTRMS	pentene nitriles/methyl pyrrole	n/a	n/a	n/a	1-Methylpyrrole
82.102	C ₅ H ₆ O	PTRMS	methyl furan	n/a	2-methylfuran + 3-methylfuran + general HCO	2-Methylfuran, 3-Methylfuran	² 2-Methylfuran, 3-Methylfuran
84.118	C ₅ H ₈ O	PTRMS	cyclopentanone/ isomers	n/a	3-methyl-3-buten-2-one + cyclopentanone + HCO1 isomers	3-Methyl-3-buten-2-one, Cyclopentanone	Cyclopentanone
84.162	C ₆ H ₁₂	PTRMS	hexene/fragments	1-hexene	n/a	n/a	² 1-Hexene, cis-2-Hexene
86.09	C ₄ H ₆ O ₂	PTRMS	butanedione/ isomers	2,3-butanedione	2,3-butanedione + methyl acrylate + other HCO2	2,3-butanedione, methyl acrylate	2,3-Butadione
86.134	C ₅ H ₁₀ O	PTRMS	pentanone	n/a	n/a	n/a	² 2-Pentanone, 3-Pentanone
86.178	C ₆ H ₁₄	AWAS	2+3-methylpentane	n/a	n/a	3-methylpentane	3-Methylpentane
96.085	C ₅ H ₄ O ₂	PTRMS	furfural	furfural (2-furaldehyde)	2-furfural + 3-furfural + other HCO2	2-furfural (=furaldehyde), 3-furfural	2-Furaldehyde
98.189	C ₇ H ₁₄	PTRMS	heptene	n/a	n/a	n/a	1-Heptene
100.117	C ₅ H ₈ O ₂	PTRMS	methyl methacrylate / isomers	n/a	Methyl methacrylate + other HCO2	Methyl methacrylate	Methyl Methacrylate
100.161	C ₆ H ₁₂ O	PTRMS	hexanal/hexanones	n/a	hexanal + hexanones	Hexanones, Hexanal	¹ n-Hexanal + Hexanones
103.124	C ₇ H ₅ N	PTRMS	benzonitrile	n/a	Benzonitrile	Benzonitrile	Benzenenitrile
106.168	C ₈ H ₁₀	PTRMS	C8 aromatics	n/a	Ethyl benzene + m-xylene + p-	C8 Aromatics	¹ Ethylbenzene + m,p-Xylenes + o-Xylene

					xylene + o-xylene		
112.216	C ₈ H ₁₆	PTRMS	octene	n/a	n/a	n/a	1-Octene
118.135	C ₈ H ₆ O	PTRMS	benzofuran	n/a	Benzofuran	Benzofuran	BenzofuranPI T
118.179	C ₉ H ₁₀	PTRMS	methylstyrenes/ propenyl benzenes	n/a	Indane + methyl styrenes + propenyl benzenes	Methylstyrenes, Indane, Propenylbenzenes	¹ 1-Propenylbenzene, 2-Methylstyrene, 2-Propenylbenzene, 3-Methylstyrene, 4-Methylstyrene, alpha-Methylstyrene
120.195	C ₉ H	PTRMS	C9 aromatics	1,2,3-trimethylbenzen, 1,2,4-trimethylbenzen, 1,3,5-trimethylbenzene (Simpson et al., 2011)	C9 aromatics	C9 aromatics	¹ 1,2,3-Trimethylbenzene, 1,2,4-Trimethylbenzene, 1,3,5-Trimethylbenzene, 1-Ethyl-2-Methylbenzene, 1-Ethyl-3,4-Methylbenzene, Isopropylbenzene, n-Propylbenzene
132.162	C ₉ H ₈ O	PTRMS	methyl benzo furans	n/a	Methyl benzofuran	Methylbenzofurans	¹ Methylbenzofuran isomer 1, Methylbenzofuran isomer 2, Methylbenzofuran isomer 3
132.206	C ₁₀ H ₁₂	PTRMS	ethyl styrene/ methyl propenyl benzene	n/a	Methyl propenyl benzene + ethyl styrene	Ethyl styrenes, Methylpropenylbenzenes, Butenylbenzenes	¹ 1-Methyl-1-Propenylbenzene, Ethylstyrene
134.222	C ₁₀ H ₁₄	PTRMS	C10 Aromatics	n/a	C10 Aromatics	C10 Aromatics	¹ 1,4-Diethylbenzene,

							1-Butenylbenzene, Ethyl Xylene isomer 1, Ethyl Xylene isomer 2, Isobutylbenzene, Methyl-n-Propylbenzene isomer 1, Methyl-n-Propylbenzene isomer 2, n-Butylbenzene, p-Cymene
136.238	C ₁₀ H ₁₆	PTRMS	monoterpenes	sum of alpha + beta-pinene (Simpson et al., 2011)	monoterpenes	monoterpenes	n/a
148.249	C ₁₁ H ₁₆	PTRMS	C11 aromatics/pentamethylbenzene	n/a	n/a	n/a	C11 Aromatics

464

465

466 Table S9. Emission speciation profile for SAPRC11 chemical mechanism derived from normalized EFs
 467 from the present study and compared with wildfire smoldering emission speciation profile from the EPA
 468 SPECIATEv4.5 #95428 dataset. Note that SESQ (sesquiterpene), WSOC (water soluble organic carbon)
 469 and IVOC are non-standard SAPRC11 mechanism species. Please refer to Carter and Heo (2013) for
 470 mechanism species definition.

SAPRC11 Lumped Species Name	Molecular Weight (g/mol)	Normalized Mass Fraction (Hayden et al.)	Normalized Mass Fraction (SPECIATEv4.5 #95428)
CCOOH	60.05	0.038	0.031
ACET	58.08	0.024	0.0072
ACYL	26.04	0.0080	0.00059
ALK1	30.07	0.039	0.011
ALK2	36.73	0.013	0.0043
ALK3	58.61	0.0063	0.0077
ALK4	77.6	0.0055	0.030
ALK5	118.89	0.0053	0.28
ARO1	95.16	0.031	0.034
ARO2	118.72	0.042	0.067
BACL	86.09	0.021	0.0050
BALD	106.13	0.0020	0.0034
BENZ	78.11	0.013	0.0035
CATL	110.1	0.0032	0.014
CCHO	44.05	0.032	0.023
CH4	16.043	0.24	0.044
CRES	108.14	0.0026	0.0027
ETHE	28.05	0.044	0.0065
HCOOH	46.03	0.0050	0.0038
GLY			0.000046
HCHO	30.03	0.030	0.0084
IPRD	100.12	0.00020	0.0037
ISOP	68.12	0.021	0.00041
MACR	70.09	0.010	0.0044
MEK	72.11	0.0066	0.0028
MEOH	32.04	0.057	0.016
MGLY			0.000037
MVK	70.09	0.0057	0.019
NROG	1	0.11	0.13
NVOL	1	1.18E-05	
OLE1	72.34	0.079	0.049
OLE2	75.78	0.019	0.025
PACD	74.08	0.055	0.00047
PHEN	94.11	0.0055	0.0054
PROD2	116.16	0.0044	0.027

RCHO	58.08	0.038	0.0035
TERP	136.24	0.024	0.032
XYNL	122.16	0.0080	
SESQ	204.35	0.039	
WSOC	227	0.013	
IVOC	227.3	0.0063	

471

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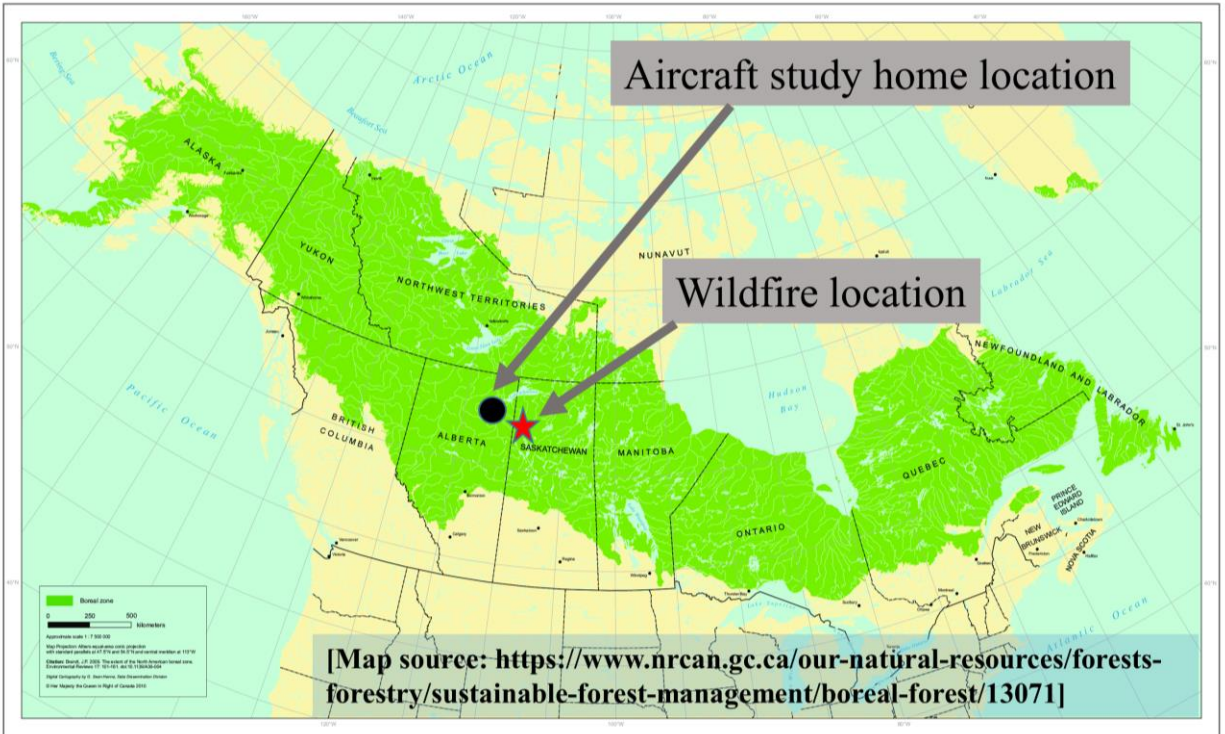


Figure S1. Map showing the home location of the airborne study at Fort McMurray, Alberta and the location of the wildfire in Saskatchewan. The green shaded region shows the extent of the boreal forest coverage across Canada and Alaska.

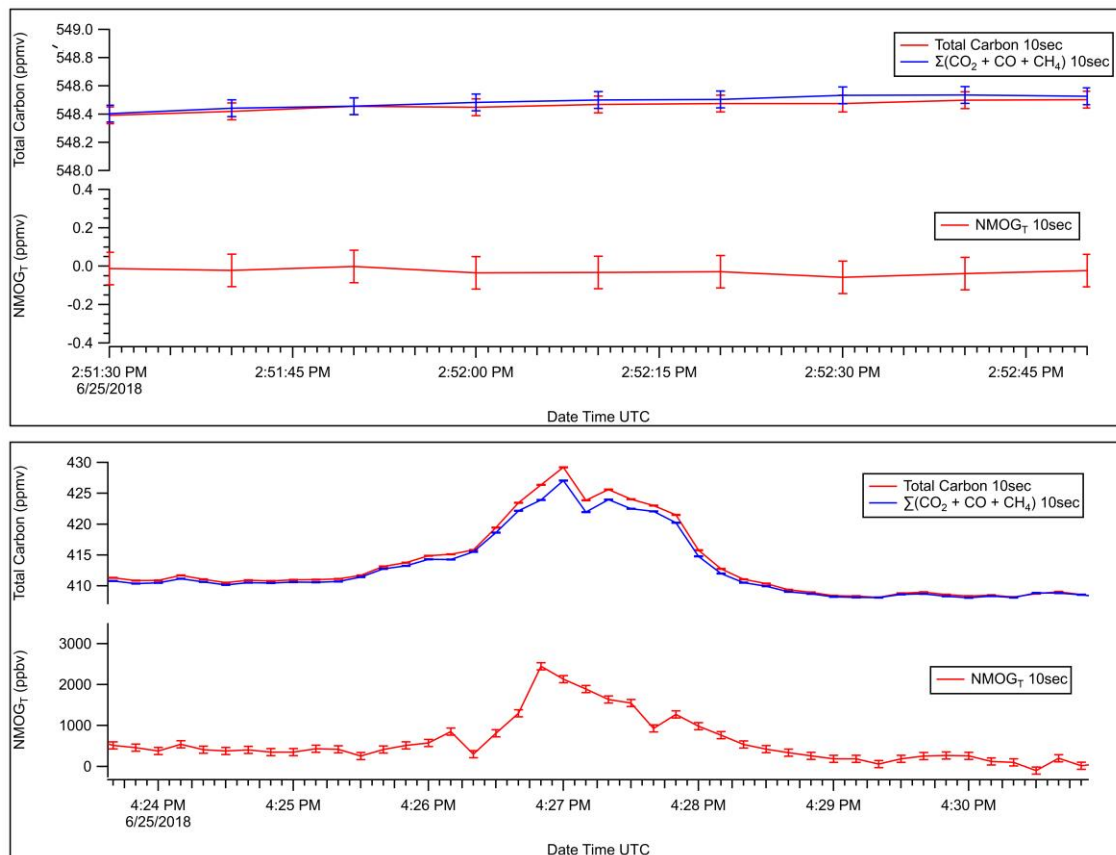


Figure S2. Total carbon (TC), $\Sigma(\text{CO}_2+\text{CO}+\text{CH}_4)$ (ppmv C), and NMOG_T (ppmv C or ppbv C) averaged to 10 sec for a) a portion of the in-flight calibration time period, and b) a selected plume along Screen 1. NMOG_T , the difference between the TC and $\Sigma(\text{CO}_2+\text{CO}+\text{CH}_4)$, has an uncertainty of ± 85 ppbv C.

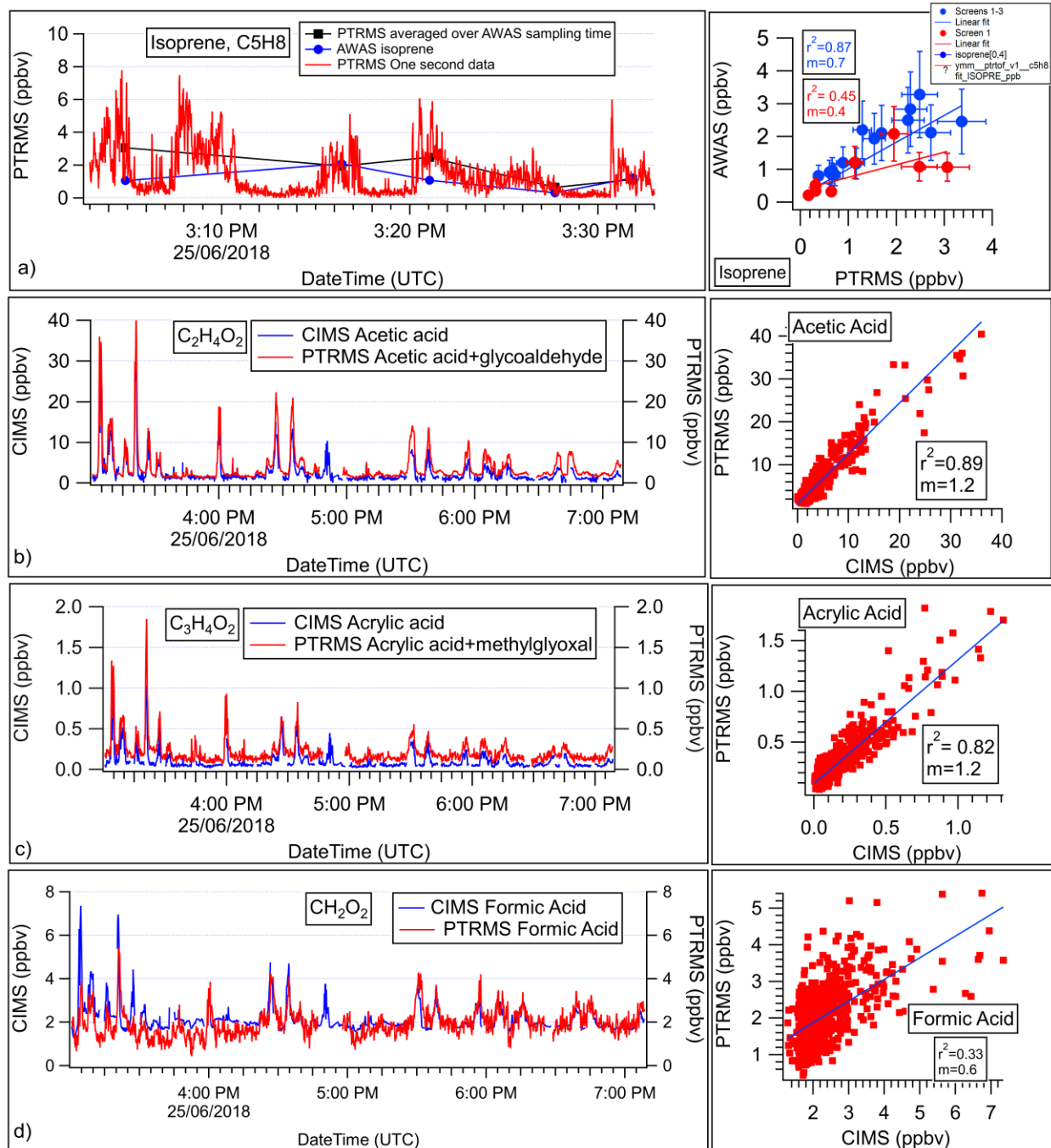


Figure S3. Intercomparisons of overlapping compounds between the PTRMS and AWAS, and between the PTRMS and CIMS for a) isoprene, b) acetic acid, c) acrylic acid, and d) formic acid.

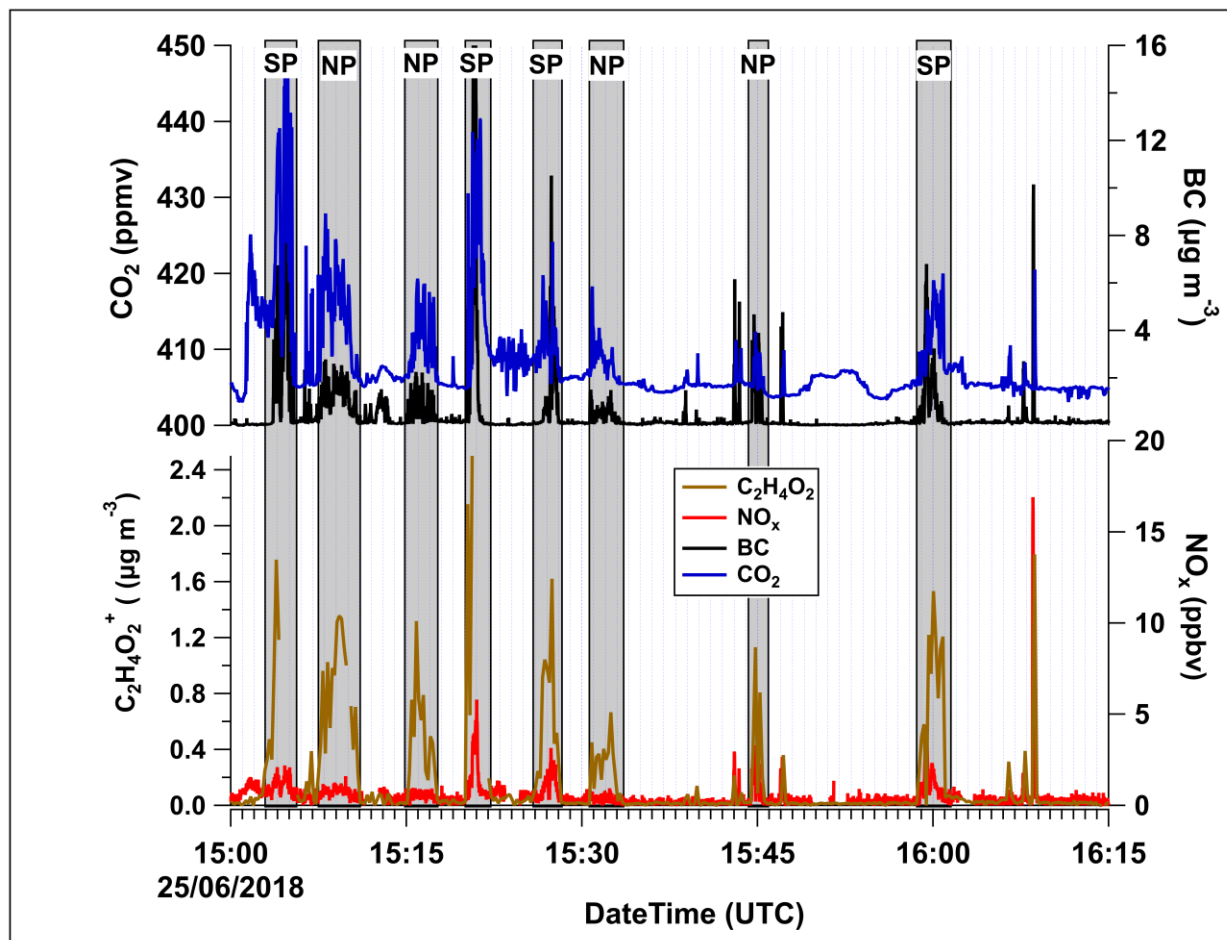


Figure S42. Time series of CO₂, BC and NO_x mixing ratios, and C₂H₄O₂⁺ (levoglucosan fragment derived from the AMS) concentrations for Screen 1. The in-plume portions are indicated by the vertical grey bars. The aircraft flew back and forth across the plumes at increasing altitudes to complete five transects; a transect represents one pass across the SP and NP at the same altitude.

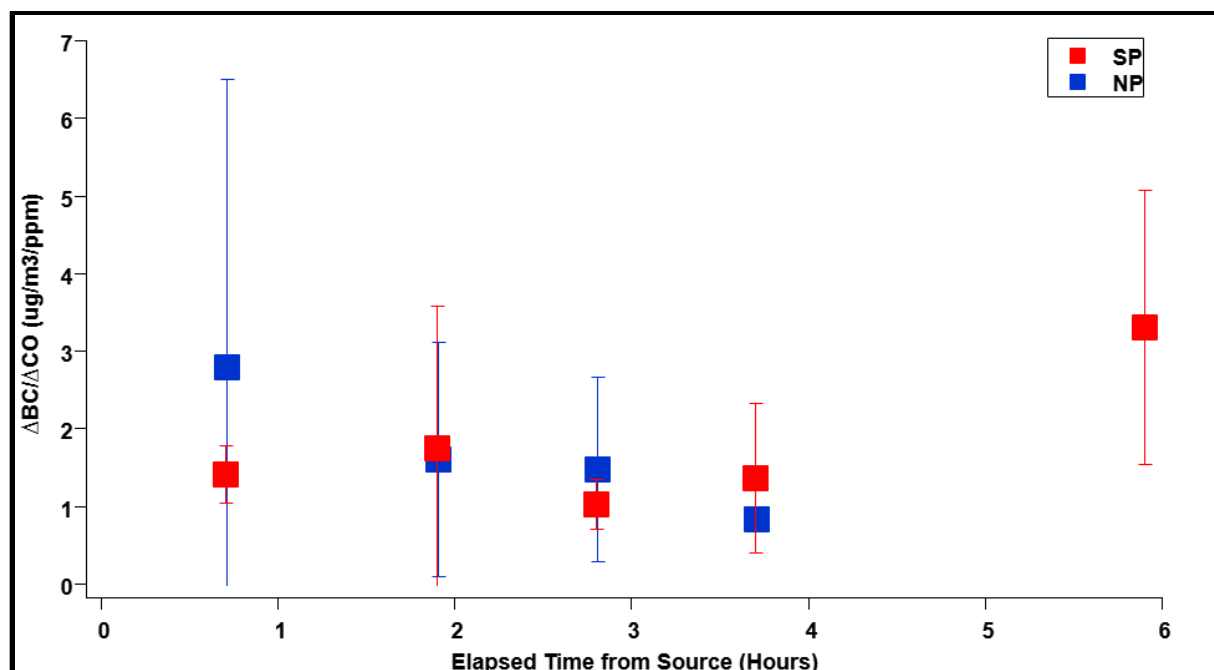
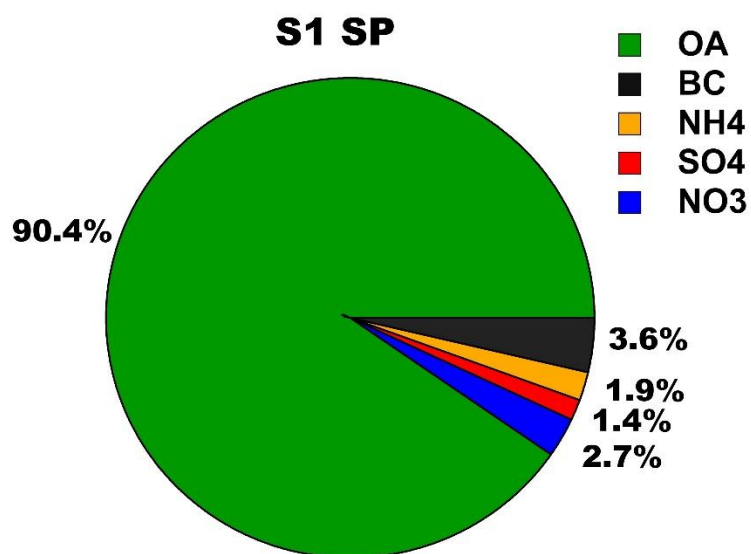
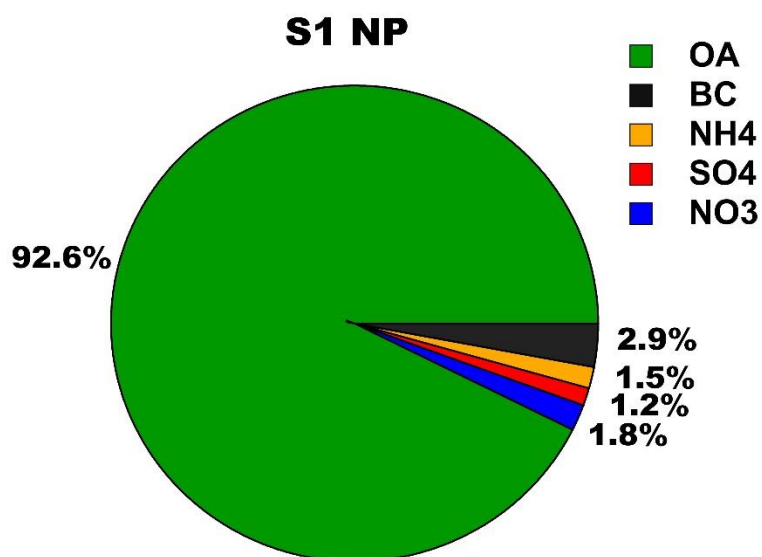


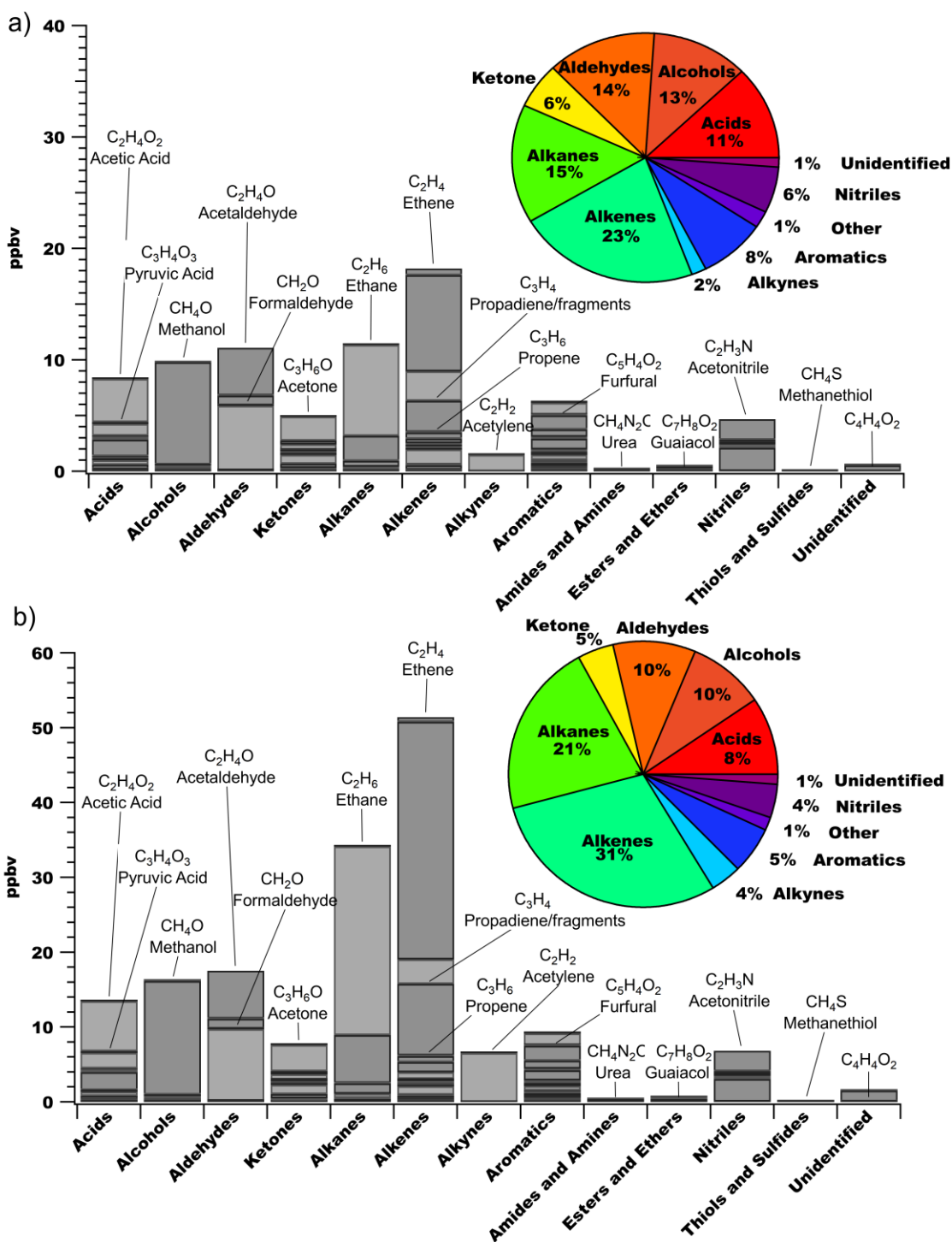
Figure S53. Using $\Delta BC/\Delta CO$ (Selimovic et al., 2019) as an indicator of plume mixing downwind of the Lac LaLoche fire. The squares show the average and the vertical lines the standard deviation for the transects within the mixed layer for each screen.



521
 522 Figure S64. Percent contribution from individually measured particle-phase species for the NP and SP
 523 including p-organics (OA), black carbon (BC), ammonium (NH₄), sulphate (SO₄) and nitrate (NO₃), based
 524 on mass concentrations.

525

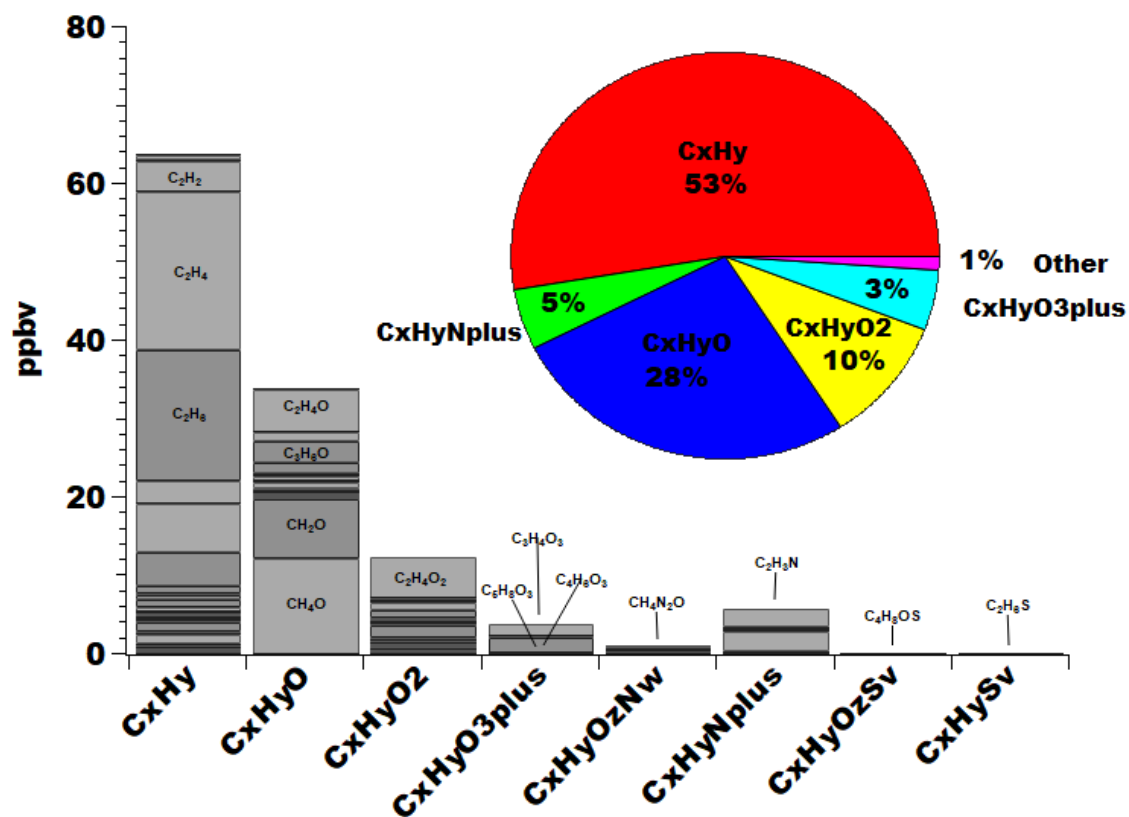
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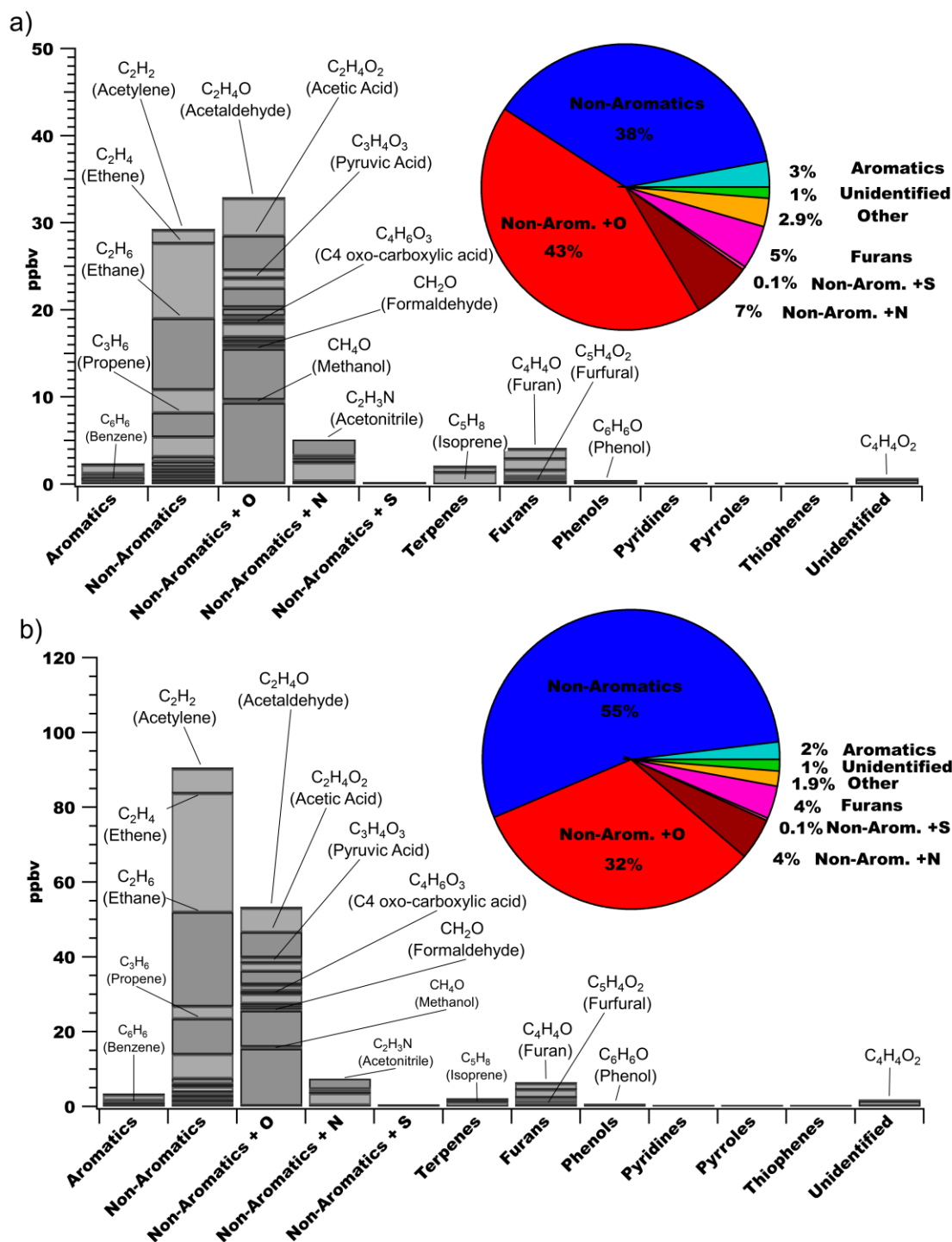


527

528 Figure S75. Background-subtracted mixing ratios of individually measured NMOGs from the PTRMS,
 529 CIMS and AWAS are shown for thirteen chemical classes for the a) NP and b) SP. In some cases,
 530 compounds are double- (or triple-) counted if they can be identified in more than one category. For
 531 example, phenol is an alcohol + an aromatic; guaiacol is an alcohol + an ether + an aromatic. In the pie

532 chart, the *Other* category includes amides, amines, ethers, thiols and sulfides. The *Unidentified* category
 533 contains molecular formulas detected but the compound(s) could not be identified.





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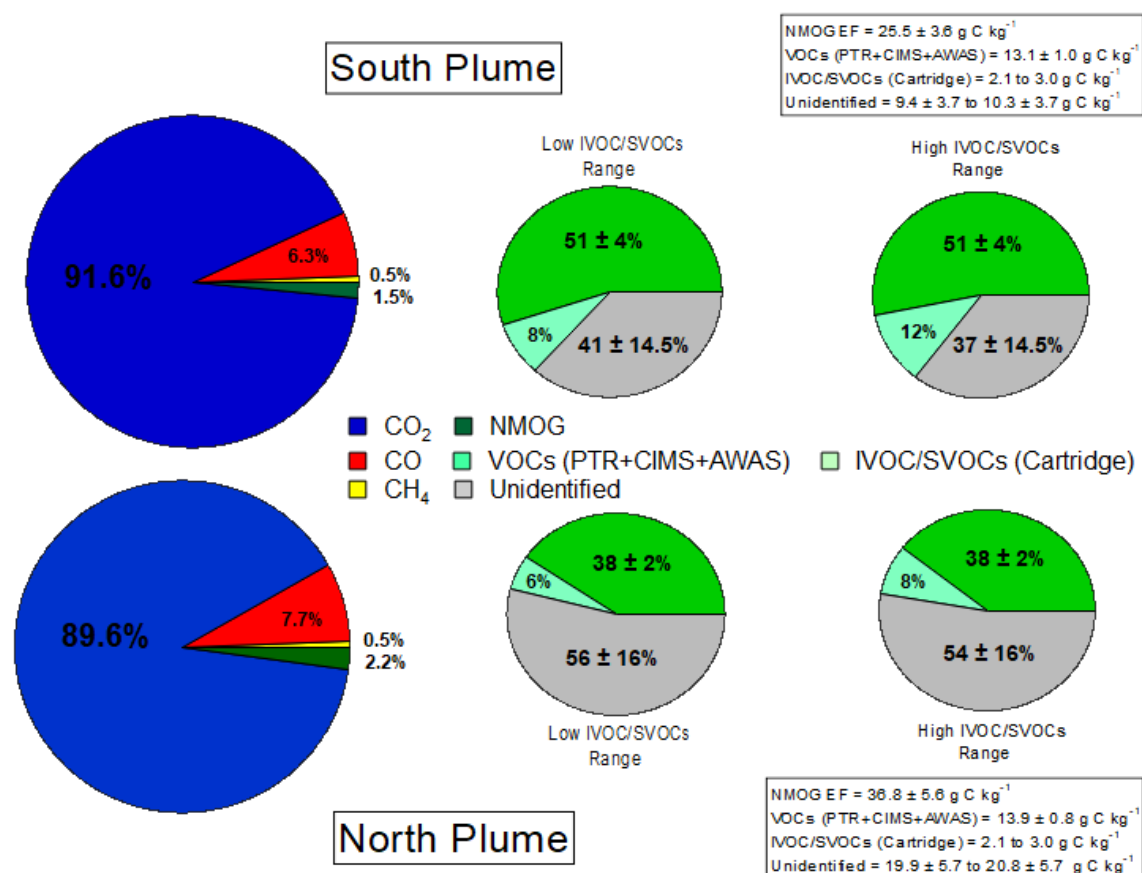
540 Figure S97. Average mixing ratios of individually measured NMOGs from the PTRMS, CIMS and

541 AWAS by structural group for the a) NP and b) SP. The *Other* category is the sum of terpenes, phenols,

542 pyridines, pyrroles and thiophenes.

543

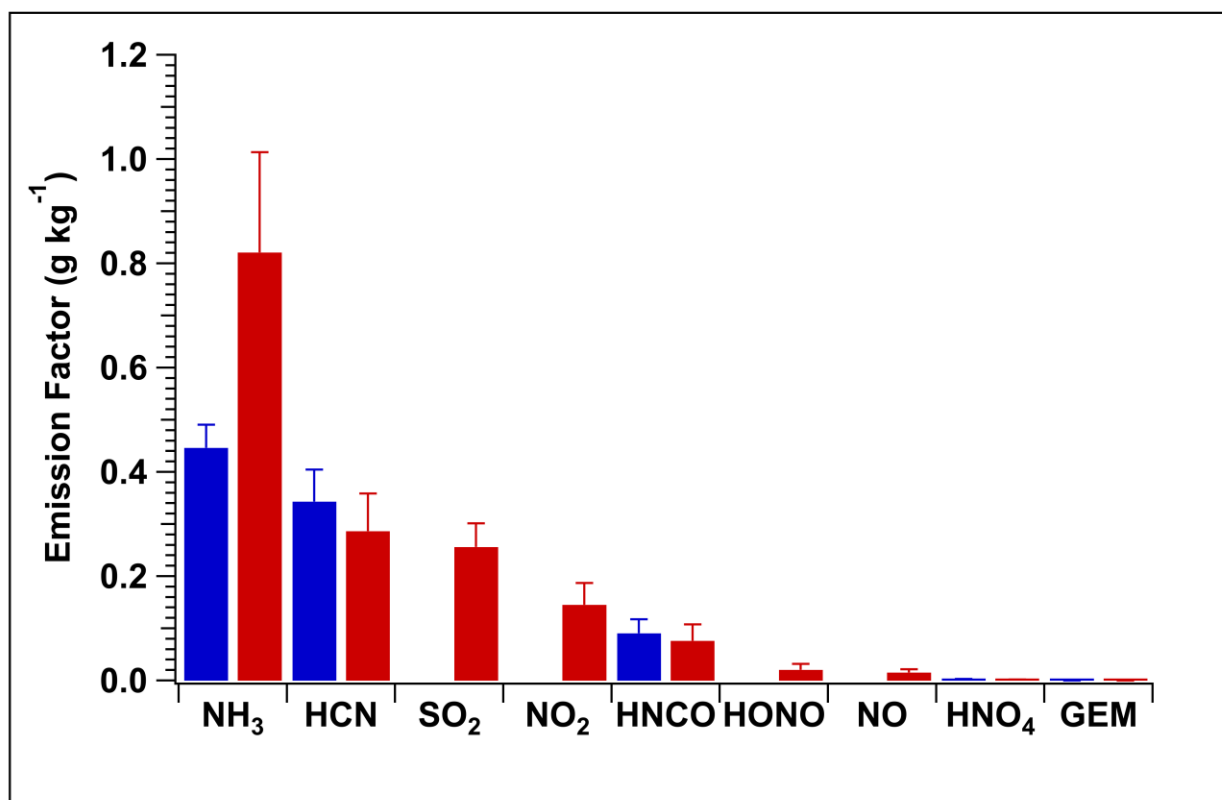
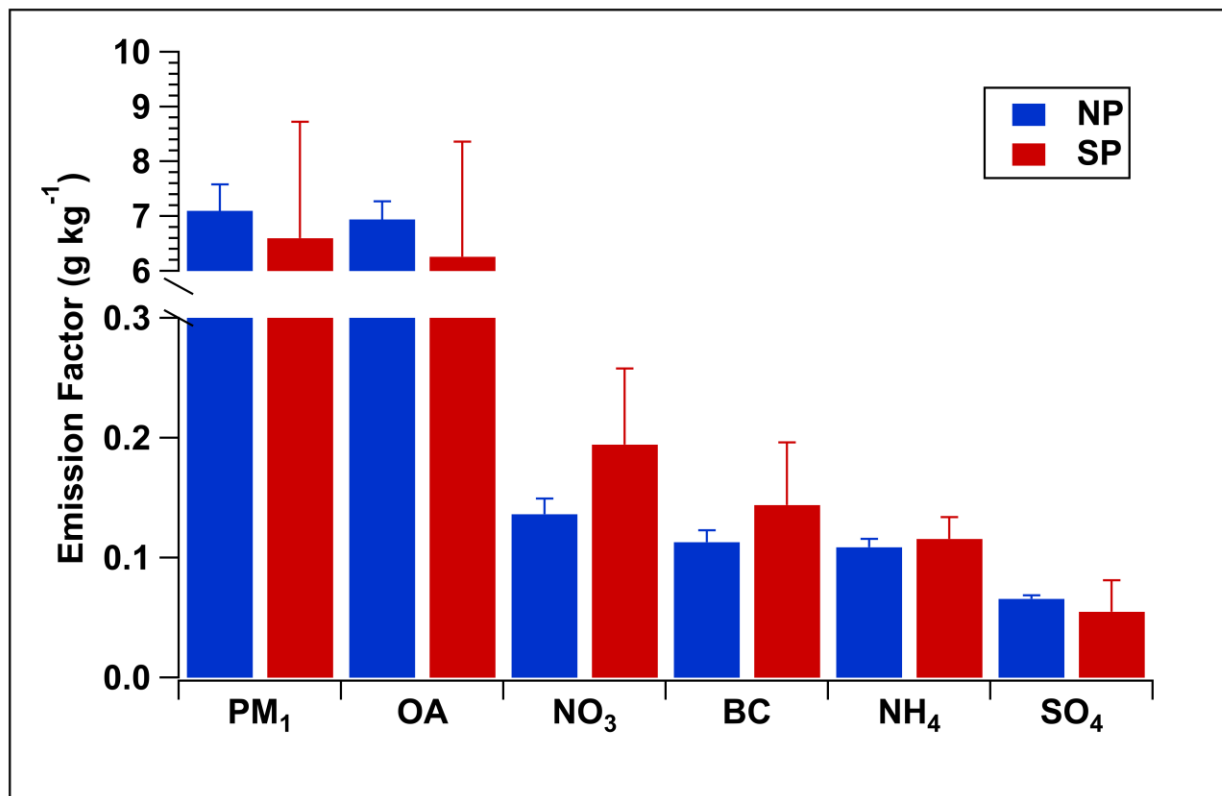
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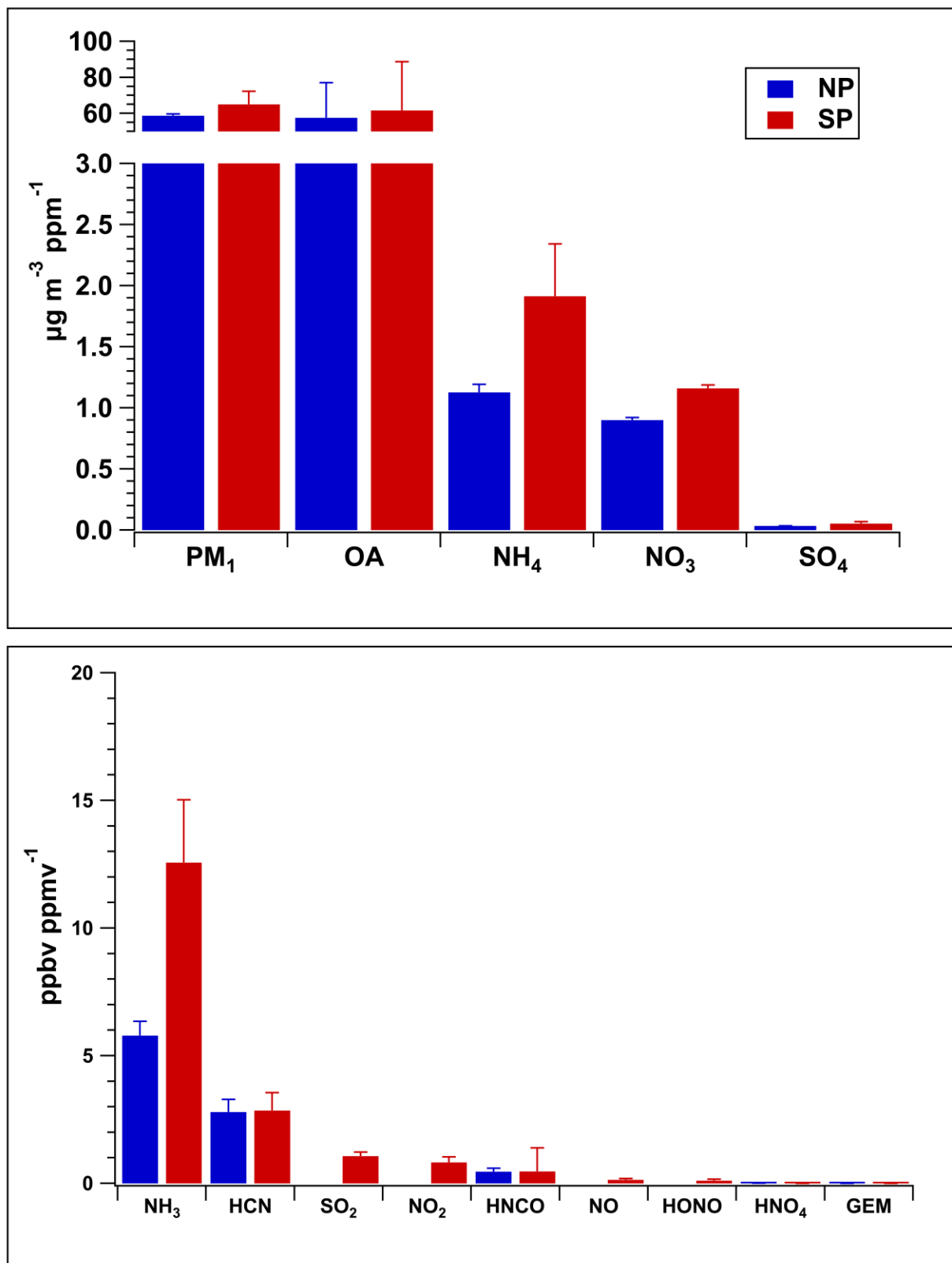
545

546 Figure S108. Percent contributions of carbon-containing compounds to the TC based on EFs (in terms of
 547 carbon fraction) for the SP and NP. The two pie charts on the right, representing the low and high
 548 I/SVOC EF estimates, show the percent breakdown of the measured NMOGs and the remaining
 549 unidentified portion. The EF values (g C kg⁻¹) are identified in the boxes. Note, the I/SVOC
 550 measurements represent the integrated average encompassing both plumes.

551



552
 553 Figure S119. Emission factors (EF) (g kg⁻¹) for the SP and NP determined from measurements of a)
 554 particle species; and b) inorganic gas-phase species.



555
 556 Figure S120. Emission ratios (ER) for the SP and NP determined from measurements of a) particle
 557 species ($\mu\text{g m}^{-3} \text{ ppm}^{-1}$); and b) inorganic gas-phase species (ppbv ppm^{-1}).

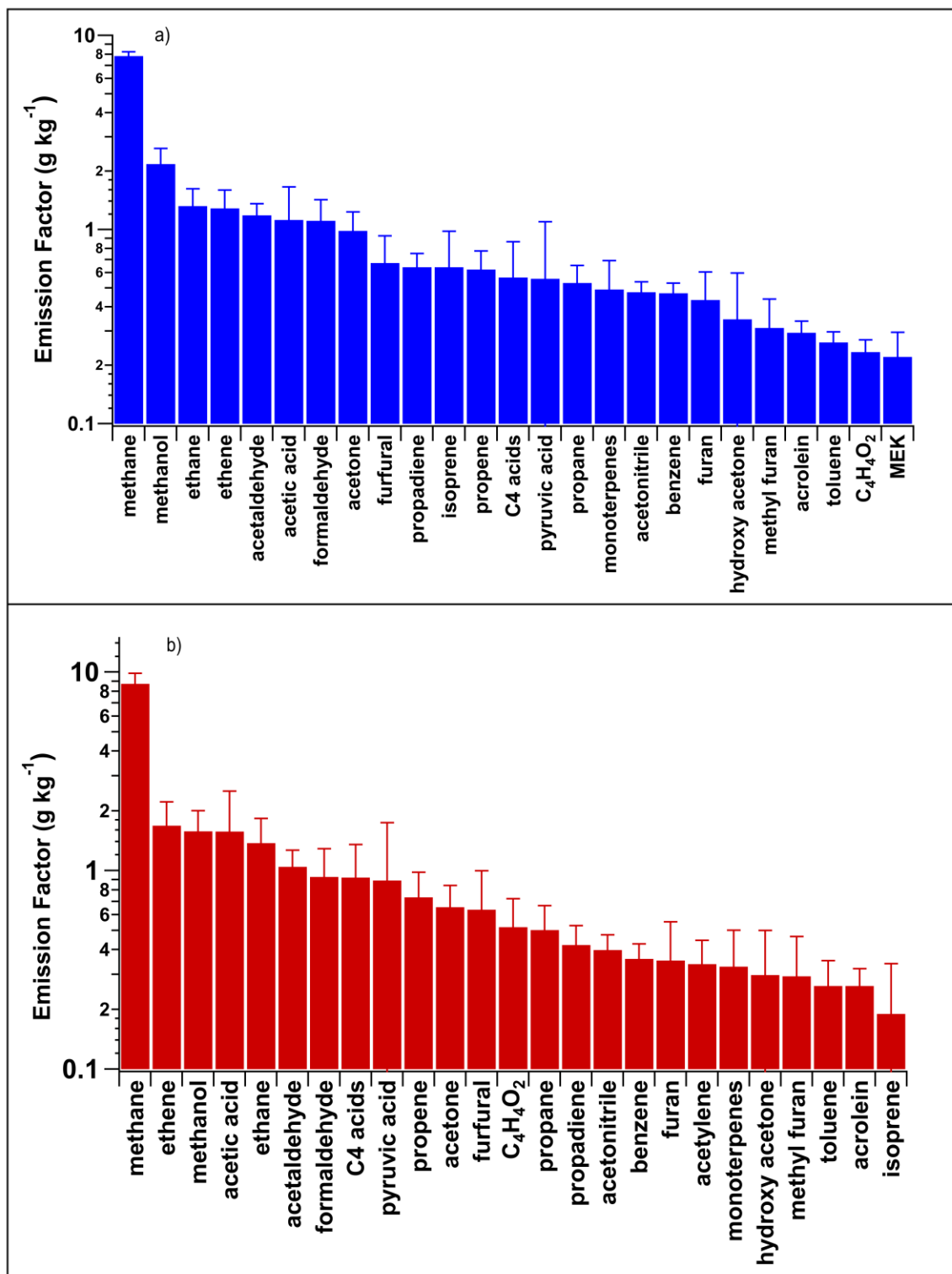


Figure S134. Emission factors (EF) (g kg⁻¹) for the a) NP and b) SP for the top 25 measured gas-phase organic species. ~~C5 acids = C5 oxo-carboxylic acids~~, C4 acids = C4 oxo-carboxylic acids, propadiene = fragments/propadiene, hydroxy acetone = hydroxy acetone/ ethyl formate; MEK = MEK, butanal and 2-methylpropanal .

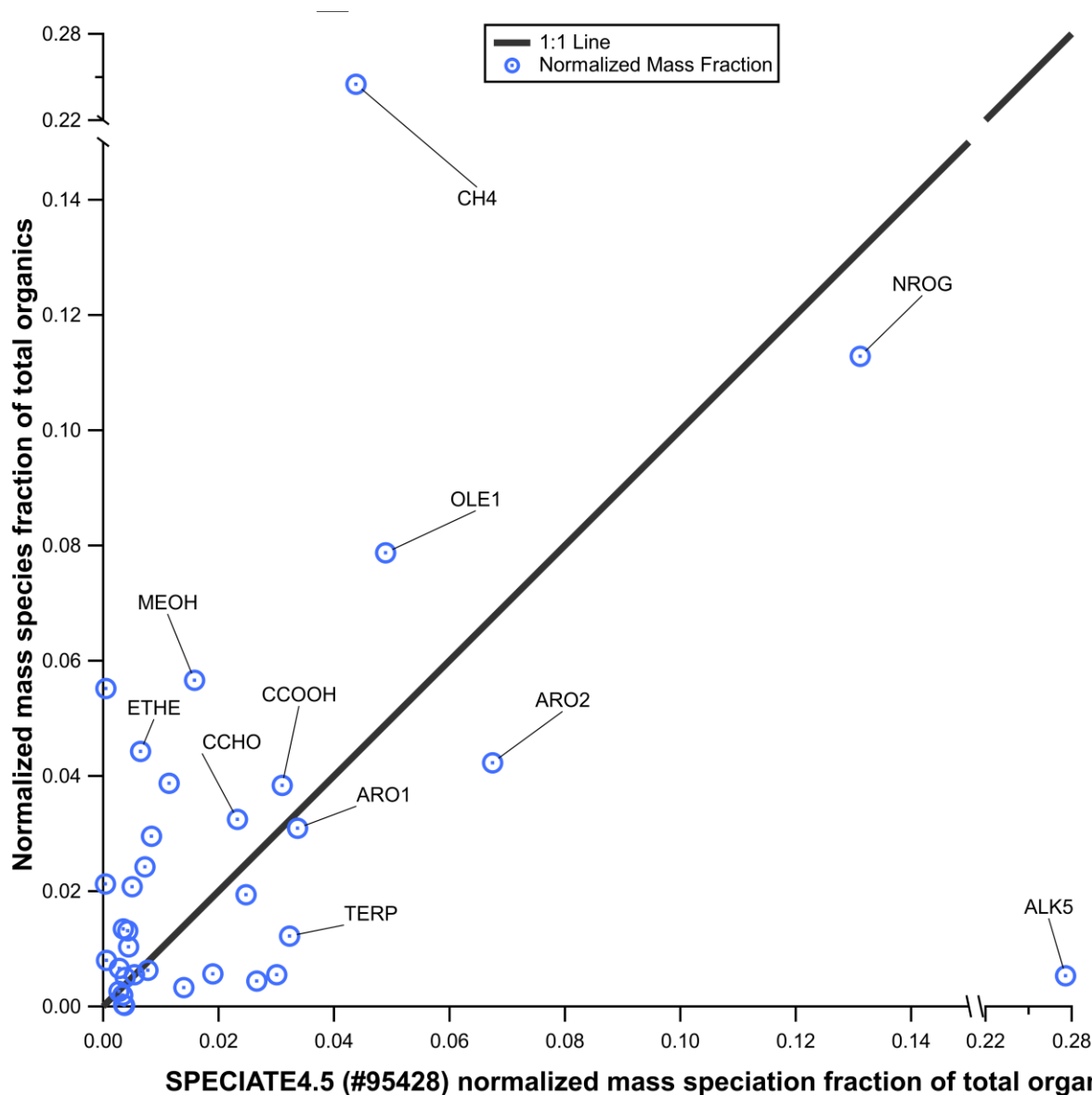


Figure S142. Comparison of the normalized organic gas speciation profile derived from this study (Hayden et al.) with that from the EPA's SPECIATE4.5 (#95428) profile. used by the SAPRC-11 mechanism (SPECIATE4.5#95428). EFs in the present study were mapped to the SAPRC-11 model mechanism species and normalized to the NMOG_{total organic gas} (which does not includes the unidentified mass fraction), to create the a total organic gas mass speciation profile. The normalized model-species-fraction-total organic mass speciation profile is plotted against the similarly treated mass speciation profile from the EPA SPECIATEv4.5 #95428 for wildfire smoldering emissions. Note that for comparison purposes the non-standard SAPRC-11 species in the present study are lumped, such that SESQ is summed with TERP, and IVOC, WSOC and NVOL are summed with NROG.

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