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Supporting Information For:

Chemical Characterization of Prescribed Burn Emissions from a Mixed Forest in Northern Michigan

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Organic Carbon-Nitrate-Sulfate Particle Type

6.5 ± 0.3%, by number, of the 5,894 total individual particles measured during the smoke plume periods did not correspond to biomass burning particles and were instead classified as organic carbon-nitrate-sulfate (**Figure S5**). The organic carbon-nitrate-sulfate individual particles measured with the ATOFMS had prominent organic carbon positive ion markers (*m/z* 27 ($C_2H_3^+$ and/or CHN^+), 37 (C_3H^+), and 43 ($C_2H_3O^+$, $CHNO^+$ and/or $C_3H_7^+$)), and negative organic nitrogen ion markers (*m/z* -26 (CN^-), and -42 (CNO^-)).[1] These particles were internally mixed with nitrate (*m/z* -46 (NO_2^-) and -62 (NO_3^-)), sulfate (*m/z* -97 (HSO_4^-)), phosphate (*m/z* -97 ($H_2PO_4^-$) and -79 (PO_3^-)).[2, 3] While these particles were not classified as biomass burning, the ion peak at *m/z* 39 likely corresponds, in part, to potassium (K^+), a prominent biomass burning marker, and/or a polycyclic aromatic hydrocarbon (PAH) ion fragment ($C_3H_3^+$).[4] Additional PAH fragments present in this particle type include *m/z* 51, 63, 77, 87, 91, 102, and 115.[4, 5] Elemental carbon ion peaks (*m/z* 12 (C^+), 24 (C_2^+), C_n^+, and -24 (C_2^-), -36 (C_3^-), C_n^-)[6] were also present in these particle mass spectra.

Biomass Burning Individual Particles Peak Number Fractions

To examine the heterogeneity in the chemical composition of biomass burning particles, **Figure S6** shows the number of particles that contain different ion peaks and their relative peak intensities. As discussed in the main text, biomass burning particles are characterized by dominant potassium (*m/z* 39 (K^+)), sulfate (*m/z* -97 (HSO_4^-)), and nitrate (*m/z* -46 (NO_2^-) and -62 (NO_3^-)) peaks,[1, 7] as apparent in **Figure S6**. As shown in **Figure S6**, intense potassium, sulfate, and nitrate ion peaks were in most of the biomass burning particles. Less than 40% of the biomass burning particles had all three levoglucosan ion fragments ion (*m/z* -45 (CHO_2^+), -59

($C_2H_3O_2^+$), and -71 ($C_3H_3O_2^+$)),[1] with *m/z* peaks -45 and -59 occurring more frequently, and generally with a higher relative abundance than *m/z* peak -71. Less than 1% of biomass burning particles had minor (relative peak areas between 1 – 5%) potassium cluster salt clusters (*m/z* -163 ($K(NO_3)_2^-$), -137 (KSO_4^-), and -109 (KCl_2)). Greater than 60% of biomass burning particles had prominent organic carbon (*m/z* 27 ($C_2H_3^+$), 37 (C_3H^+), and 43 ($C_2H_3O^+$)), organic nitrogen (*m/z* 27 (NCH^+), -26 (CN^-), -42 (CNO^-)), and aromatic fragments of *m/z* 51 ($C_4H_3^+$) and 63 ($C_5H_3^+$).[4, 5] Fewer than half the particles had an aromatic fragment peak of *m/z* 77 and less than 20% of the particles had larger PAH ion peaks at *m/z* 87, 91, 102, 115, 128, 139, 152, 165, 178, 189, and 202. About 10% of biomass burning particles had the aromatic peak at *m/z* 212 ($C_{10}H_{12}O_5^+$)[4] that was prevalent in the individual particles sampled during Plume 1 (see main text).

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Table S1: Average trace gas (CO_2, CO, CH_4, C_2H_6, C_2H_2, HCN, NO, N_2O) mole ratios, and total particle (CPC) number concentrations for the background and six plume periods with the 95% confidence intervals reported.

Compound	Background	Plume 1	Plume 2	Plume 3	Plume 4	Plume 5	Plume 6
CO_2 (ppm)	391.9 ± 0.2	401 ± 5	392 ± 2	393 ± 1	392 ± 1	391 ± 1	392 ± 3
CO (ppb)	134 ± 1	190 ± 20	260 ± 20	490 ± 40	420 ± 30	290 ± 20	200 ± 10
CH_4 (ppb)	1858.3 ± 0.4	1848 ± 1	1878 ± 2	1896 ± 4	1888 ± 3	1874 ± 2	1865 ± 2
C_2H_2 (ppb)	0.17 ± 0.03	0.5 ± 0.1	0.8 ± 0.1	1.6 ± 0.1	1.2 ± 0.1	0.8 ± 0.1	0.4 ± 0.1
C_2H_6 (ppb)	1.25 ± 0.03	1.5 ± 0.1	2.4 ± 0.2	4.2 ± 0.3	3.7 ± 0.3	2.6 ± 0.2	1.8 ± 0.1
HCN (ppb)	0.03 ± 0.01	0.57 ± 0.03	0.31 ± 0.03	0.55 ± 0.04	0.43 ± 0.03	0.31 ± 0.03	0.15 ± 0.03
O_3 (ppb)	26.4 ± 0.2	24 ± 3	27 ± 1	27 ± 1	29 ± 1	27 ± 1	25 ± 1
NO (ppb)	2.17 ± 0.01	12 ± 7	3 ± 1	3.1 ± 0.3	3 ± 1	3 ± 1	5 ± 2
N_2O (ppb)	352.7 ± 0.1	353.7 ± 0.3	352.9 ± 0.1	352.9 ± 0.1	352.94 ± 0.05	352.7 ± 0.1	352.7 ± 0.2
Total Particle Concentration ($\#/cm^3$)	1500 ± 900	11000 ± 7000	10000 ± 1000	33000 ± 4000	26000 ± 3000	14000 ± 1000	7000 ± 2000

Table S2: Average SP-AMS PM_1 emission ratios (mg/g) and OA/rBC ratios for the six plume periods with the 95% confidence intervals reported.

Species	Plume 1	Plume 2	Plume 3	Plume 4	Plume 5	Plume 6
OA	80 ± 20	90 ± 10	120 ± 10	84 ± 8	74 ± 7	50 ± 10
rBC	4 ± 2	3.3 ± 0.6	4.5 ± 0.6	2.3 ± 0.2	2.3 ± 0.4	2.2 ± 0.9
SO_4^{2-}	1.1 ± 0.2	0.82 ± 0.07	0.6 ± 0.1	0.56 ± 0.05	0.8 ± 0.1	1.2 ± 0.2
NO_3^-	0.7 ± 0.2	0.8 ± 0.1	1.2 ± 0.1	0.9 ± 0.1	0.8 ± 0.1	0.4 ± 0.1
NH_4^+	0.3 ± 0.1	0.37 ± 0.07	0.5 ± 0.1	0.4 ± 0.04	0.46 ± 0.07	0.5 ± 0.1
Chl^-	0.20 ± 0.04	0.14 ± 0.01	0.12 ± 0.02	0.09 ± 0.01	0.12 ± 0.01	0.18 ± 0.02
OA/rBC	25 ± 5	33 ± 6	30 ± 3	37 ± 2	35 ± 5	31 ± 7

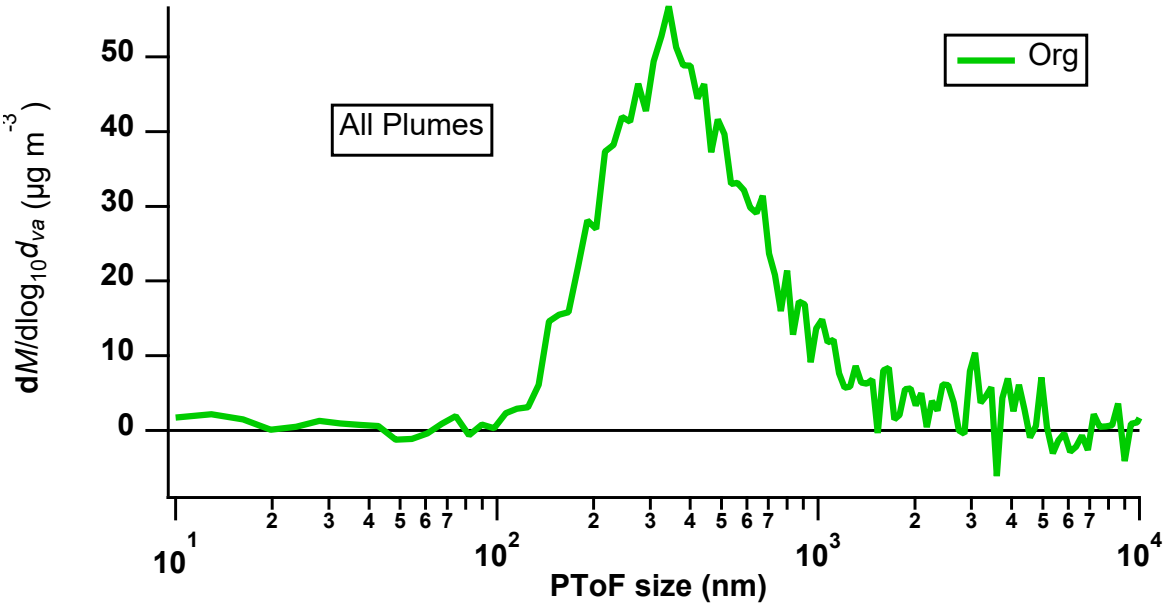

Figure S1: Average SP-AMS organic aerosol size distribution.

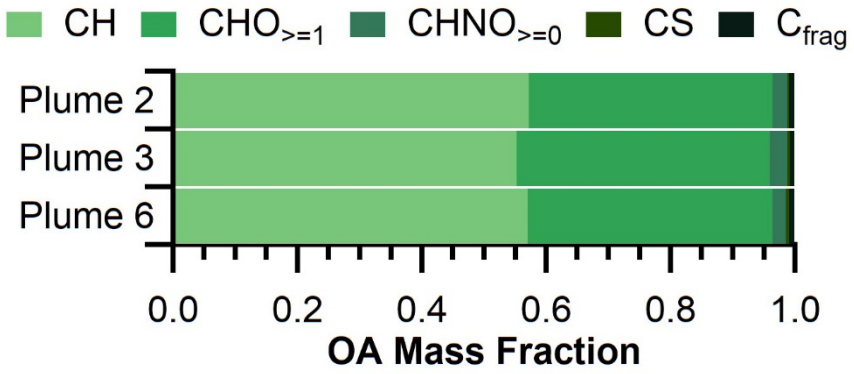

Figure S2: Fractional contributions to OA from hydrocarbon ion signal (CH), oxygenated ($CHO_{>=1}$), nitrogen-containing ($CHNO_{>=0}$), sulfur-containing (CS), and carbon fragments (C_{frag}) for Plumes 2, 3, and 6. Plume 4 is omitted due to different instrument settings.

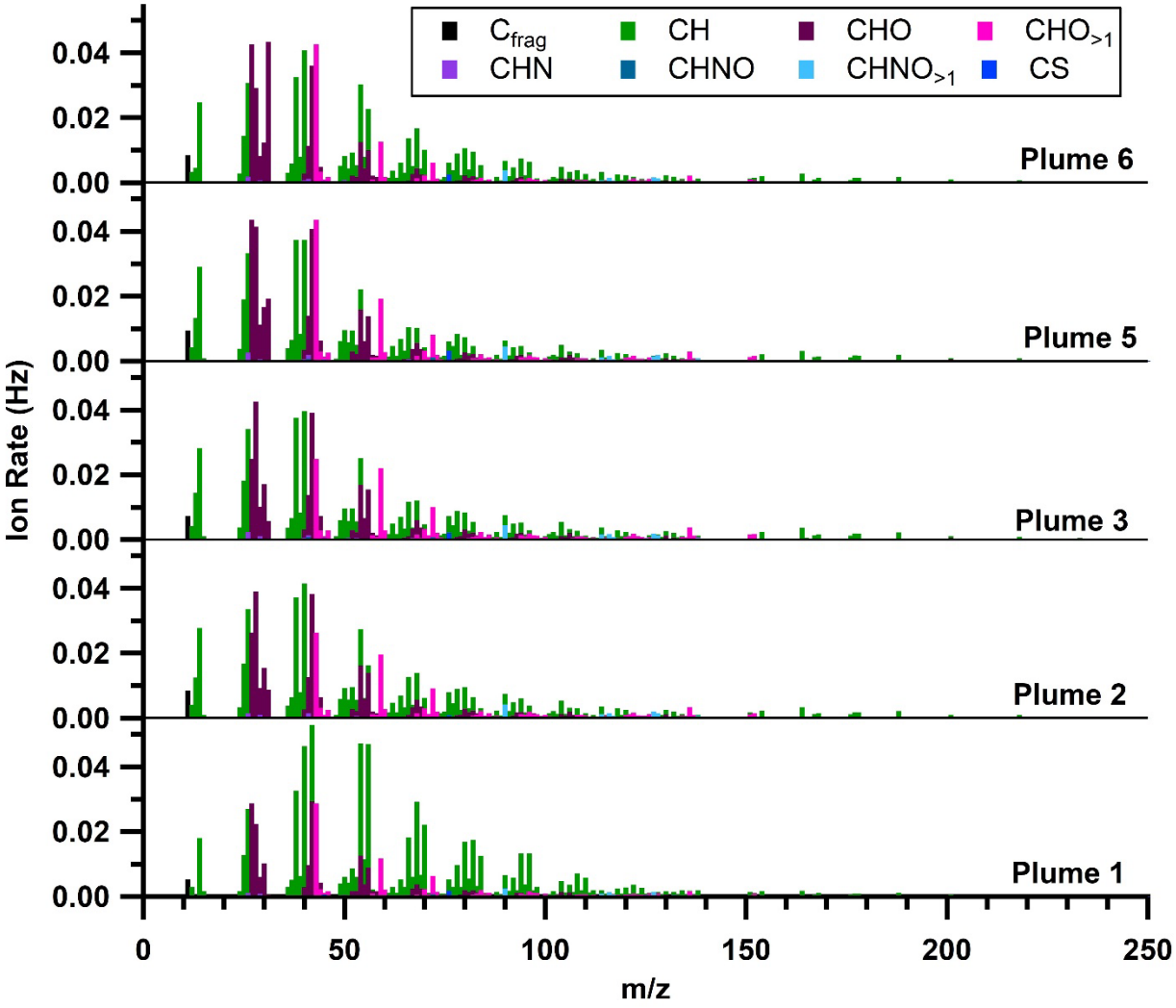

Figure S3: Average organic mass spectra for Plumes 1 – 3, 5, and 6. Plume 4 was omitted for consistency due to the SP-AMS operating with the continuous wave laser off, as only mass spectra associated with nonrefractory organics would be observed with the laser off.

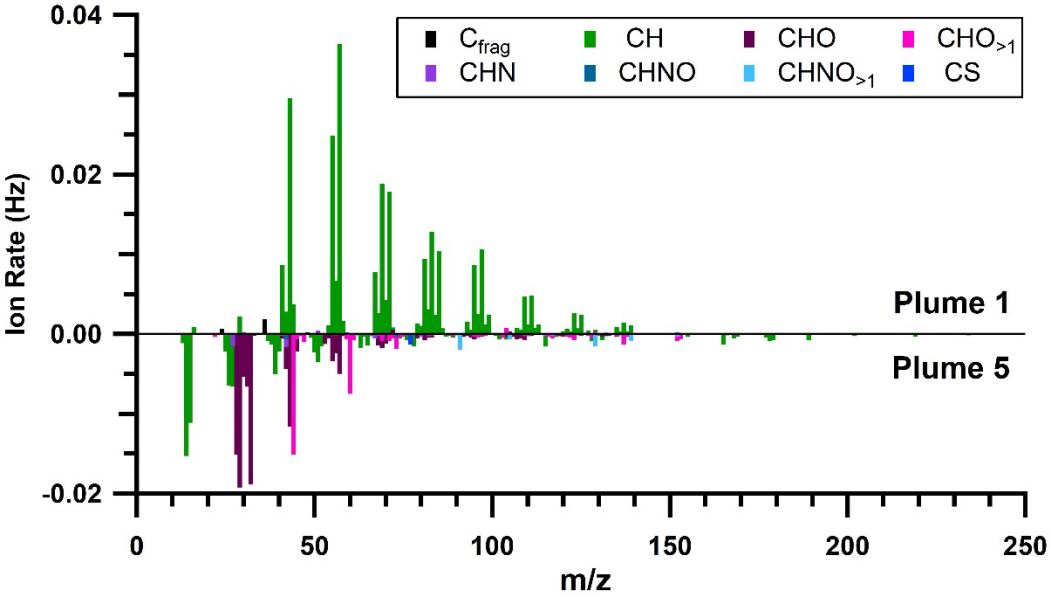

Figure S4: SP-AMS average organic aerosol mass spectrum for Plume 5 subtracted from the signal from Plume 1 with ion family peaks colored. Positive relative peak intensities correspond to greater abundance during Plume 1; negative relative peak intensities correspond to greater abundance during Plume 5.

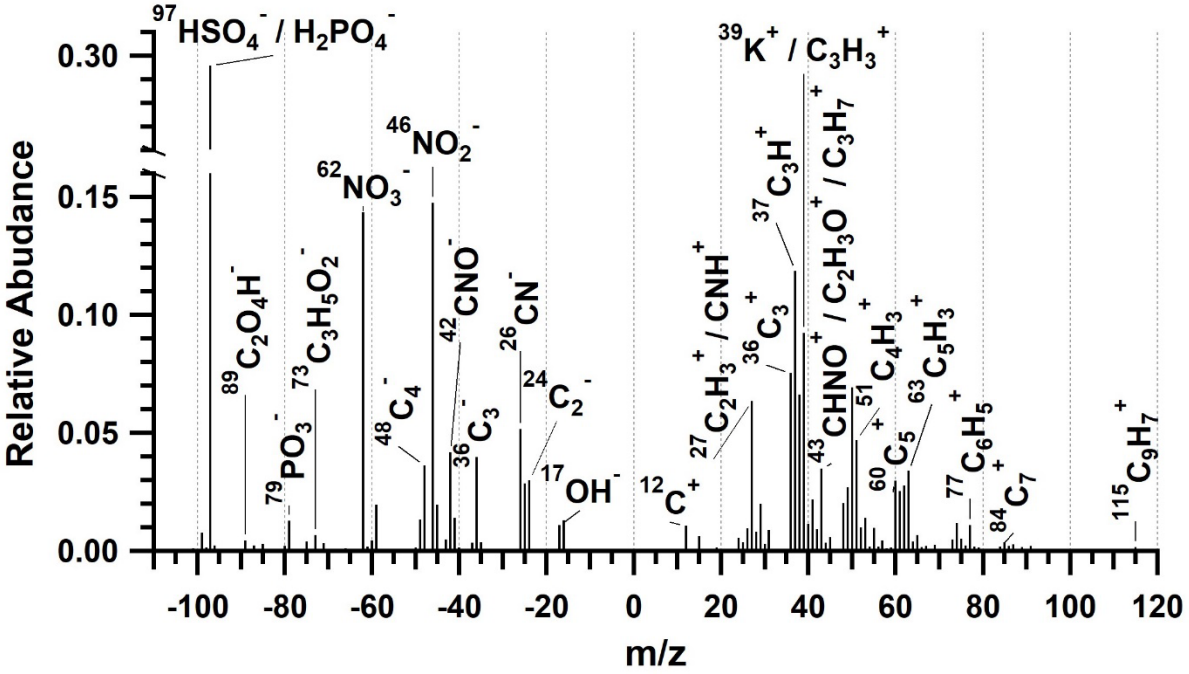

Figure S6: ATOFMS average positive and negative mass spectrum of organic carbon-nitrate-sulfate particles.

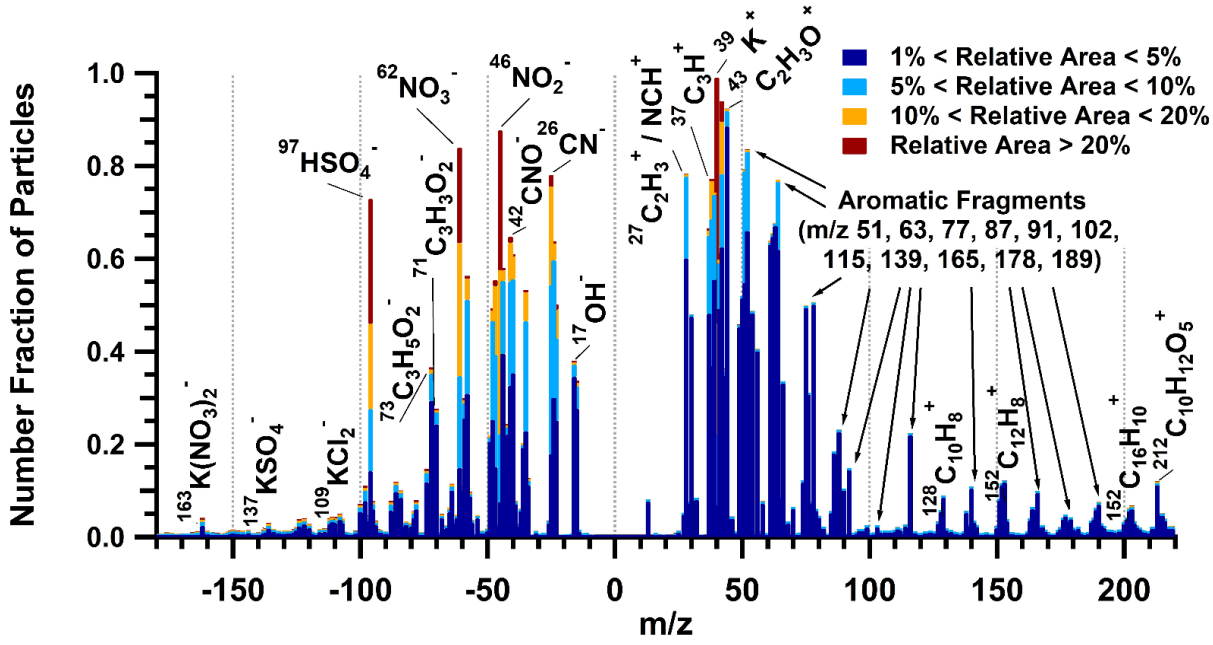

Figure S5: ATOFMS positive and negative ion digital mass spectra showing the number fractions of individual biomass burning particles (y-axis) containing each *m/z* ion (x-axis), as a function of relative peak area (color scale).

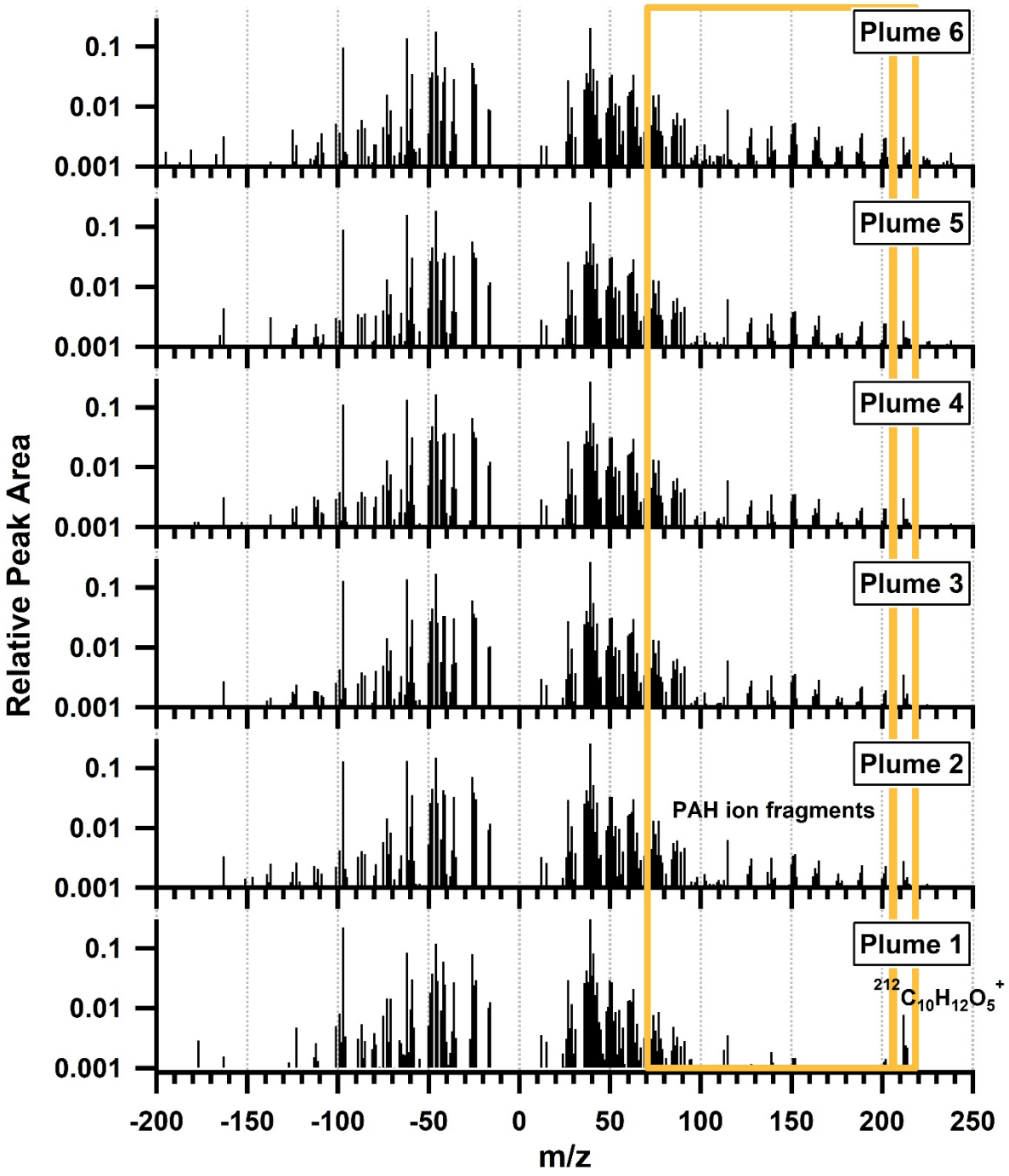

Figure S7: ATOFMS average positive and negative mass spectra of individual biomass burning particles for each plume period. Mass spectra were similar for Plumes 2 – 6. Plume 1 displayed a stronger *m/z* 212 ion peak (highlighted) and fewer PAH ion fragments (highlighted) compared to Plumes 2 – 6, further discussed in the main text.