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Biogenic, urban, and wildfire influences on the molecular composition of dissolved organic compounds in cloud water

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Table S1. Average August-September total organic carbon (TOC) and sulfate cloud water concentrations at Whiteface Mountain, NY

Year	TOC (mg L^{-1})	SO_4^{2-} (µM)
2010	4.09	53.7
2011	3.15	47.7
2012	4.16	54.2
2013	3.00	45.8
2014	3.06	32.3
2015	4.18	50.5

Table S2. Cloud water sample TOC after SPE concentration (TOC_1) and after dilution (TOC_2), prior to ESI-FT-ICR analysis

Sample ID	TOC_1 (mg L^{-1})	TOC_2 (mg L^{-1})
A1	15	15
A2	32	32
A3	42	42
B1	37	37
B2	45	45
C1	361	30
C2	398	30
C3	153	30

Table S3. Peak assignments of cloud water samples showing the molecular formula (mf) and compound type (ct). This table can be found in "Cook_etal_2017_TableS3.xslx" The columns of the table are described below:

Column 'A' contains the observed peak *m/z* $[M-H]^-$ in the mass spectra;

Column 'B' contains the $\log_{10}$ of the peak intensity of each assigned compound in sample A1 (0 denotes not identified in sample);

Column 'C' contains the $\log_{10}$ of the peak intensity of each assigned compound in sample A2 (0 denotes not identified in sample);

Column 'D' contains the $\log_{10}$ of the peak intensity of each assigned compound in sample A3 (0 denotes not identified in sample);

Column 'E' contains the $\log_{10}$ of the peak intensity of each assigned compound in sample B1 (0 denotes not identified in sample);

Column 'F' contains the $\log_{10}$ of the peak intensity of each assigned compound in sample B2 (0 denotes not identified in sample);

Column 'G' contains the $\log_{10}$ of the peak intensity of each assigned compound in sample C1 (0 denotes not identified in sample);

Column 'H' contains the $\log_{10}$ of the peak intensity of each assigned compound in sample C2 (0 denotes not identified in sample);

Column 'I' contains the $\log_{10}$ of the peak intensity of each assigned compound in sample C3 (0 denotes not identified in sample);

Column 'J' contains the number of carbon atoms present in the assigned molecular structure of the compounds present;

Column 'K' contains the number of hydrogen atoms present in the assigned molecular structure of the compounds present;

Column 'L' contains the number of oxygen atoms present in the assigned molecular structure of the compounds present;

Column 'M' contains the number of nitrogen atoms present in the assigned molecular structure of the compounds present;

Column 'N' contains the number of sulfur atoms present in the assigned molecular structure of the compounds present;

Column 'O' contains the error (in ppm) between the peak *m/z* and the assigned formula's molecular weight;

Column 'P' contains the mf assigned to each peak;

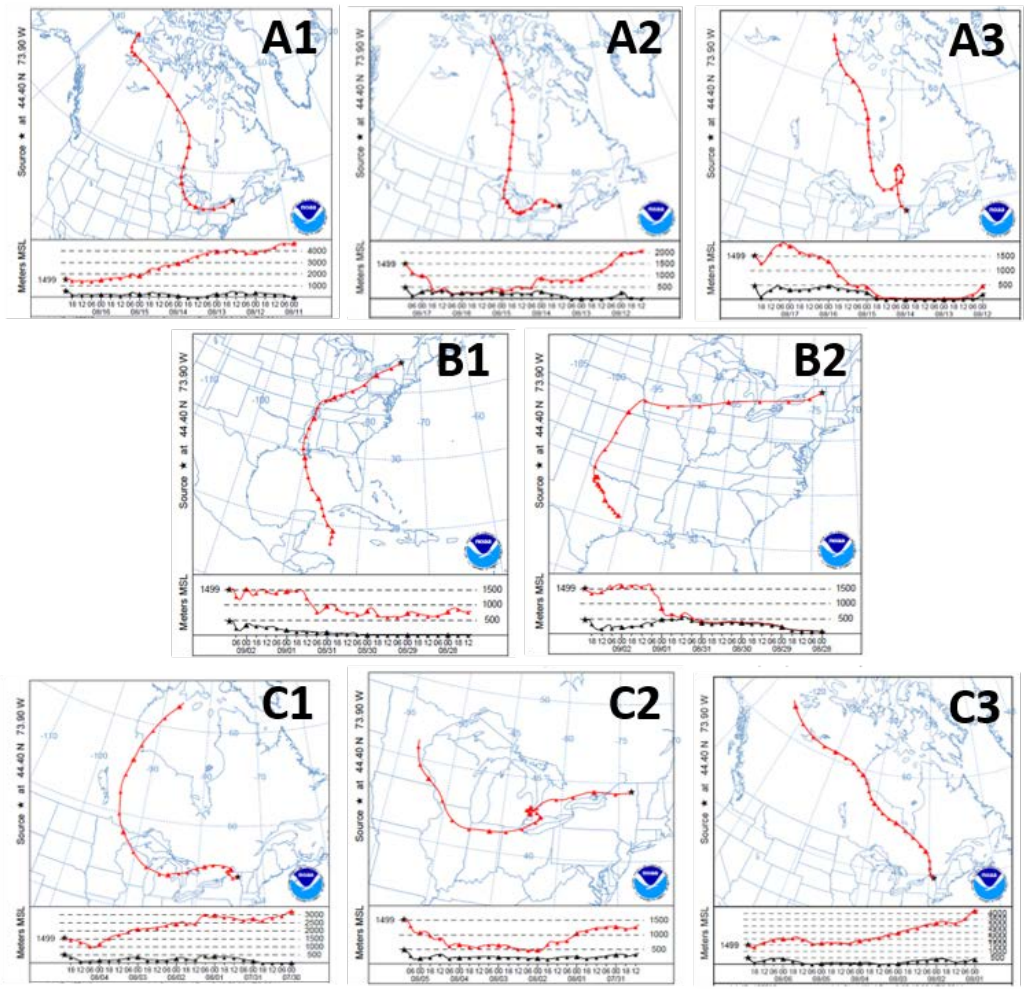
Column 'Q' contains the ct classification of the assigned mf.

Table S4. Average hydrogen-to-carbon (H:C) ratios and double bond equivalent (DBE) values, as well as 95% confidence intervals, for the Whiteface Mountain cloud water negative ion mass spectrometry data

Sample	H:C	DBE
All samples	1.466 ± 0.005	6.03 ± 0.05
Biogenic (A1-A3)	1.50 ± 0.01	5.3 ± 0.1
Urban (B1-B2)	1.504 ± 0.008	5.96 ± 0.09
Wildfire (C1-C3)	1.427 ± 0.007	6.34 ± 0.07

Table S5. Summary of cloud water molecular composition from (-)ESI-FTICR-MS (*m/z* 100-1000). The average (± 95% confidence interval) oxygen-to-carbon (O:C) and hydrogen-to-carbon (H:C) ratios, double bond equivalents (DBE), and the number of organic compounds assigned (Total), as well as numbers and percentages by (CHO, CHOS, CHNOS, CHNO) for each sample.

Event	Sample ID	O:C	H:C	DBE	Number (%)				
					CHO	CHOS	CHNOS	CHNO	Total
Biogenic	A1	0.47±0.02	1.51±0.03	4.97±0.26	225 (53)	61 (14)	31 (7)	110 (26)	427
	A2	0.47±0.01	1.49±0.02	5.49±0.19	361 (51)	102 (14)	63 (9)	181 (26)	707
	A3	0.45±0.01	1.51±0.01	5.44±0.14	397 (56)	33 (5)	7 (1)	272 (38)	709
Urban	B1	0.50±0.01	1.51±0.01	6.05±0.11	1008 (44)	227 (10)	60 (3)	981 (43)	2276
	B2	0.46±0.01	1.49±0.01	5.75±0.13	497 (53)	65 (7)	39 (4)	338 (36)	939
Wildfire	C1	0.58±0.01	1.39±0.01	6.55±0.14	712 (45)	211 (13)	28 (2)	644 (40)	1595
	C2	0.56±0.01	1.43±0.01	6.14±0.14	714 (51)	180 (13)	19 (1)	480 (35)	1393
	C3	0.47±0.01	1.46±0.01	6.32±0.11	858 (47)	93 (5)	10 (1)	866 (47)	1827



72

73 **Fig. S1.** NOAA HYSPLIT 144 h (6 day) backward air mass trajectory analysis at 1499 m
74 (red line) above mean sea level (MSL) in 6 h intervals for the cloud water samples collected
75 on (A1-3) August 16-17, 2014, (B1-2) September 2, 2014, and (C1-3) August 4-6, 2014.

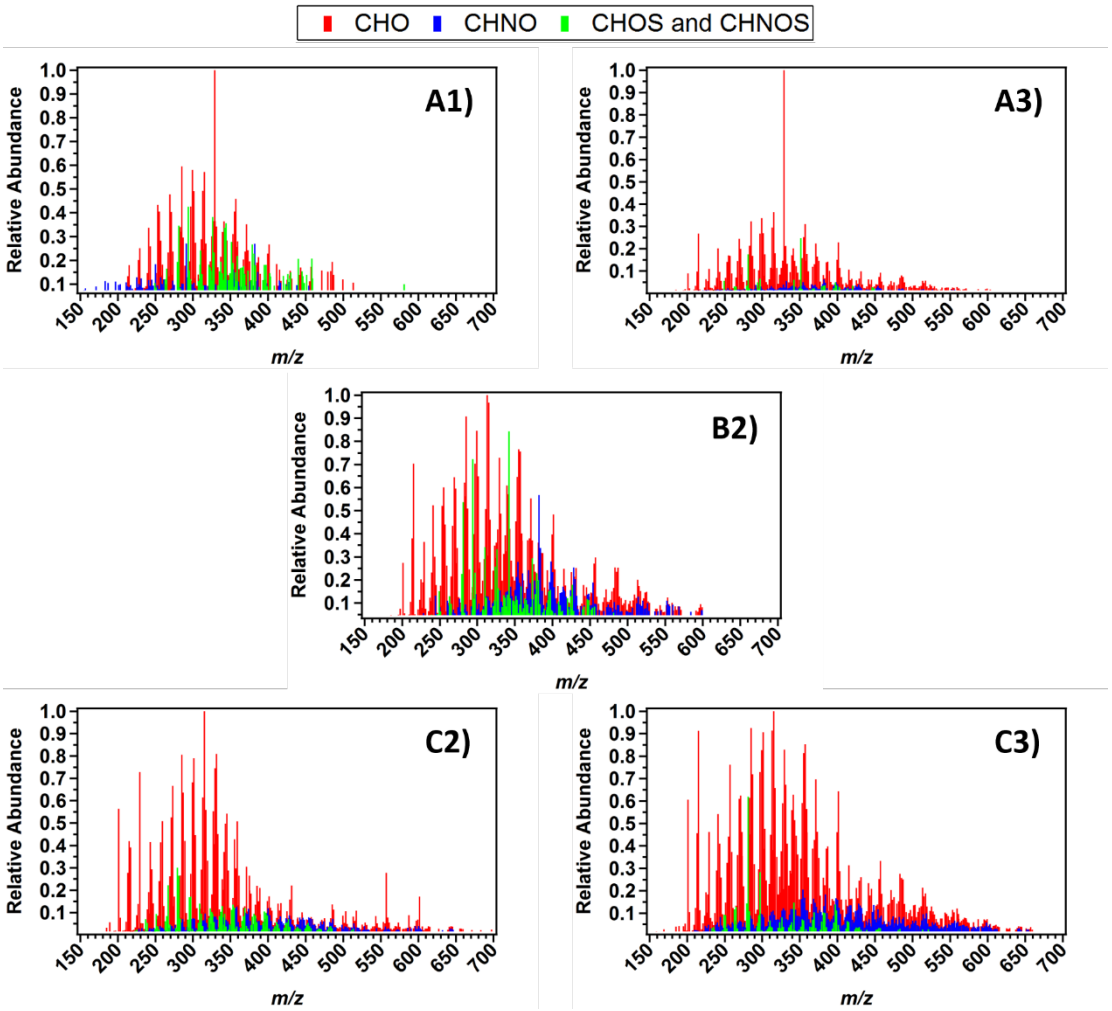


Fig. S2. Reconstructed ESI-FTICR-MS negative ion mass spectra of compound types (CHO, CHNO, CHOS, and CHNOS) for cloud water samples collected during biogenic influence (A1 and A3), urban influence (B2), and Canadian wildfire influence (C2 and C3).

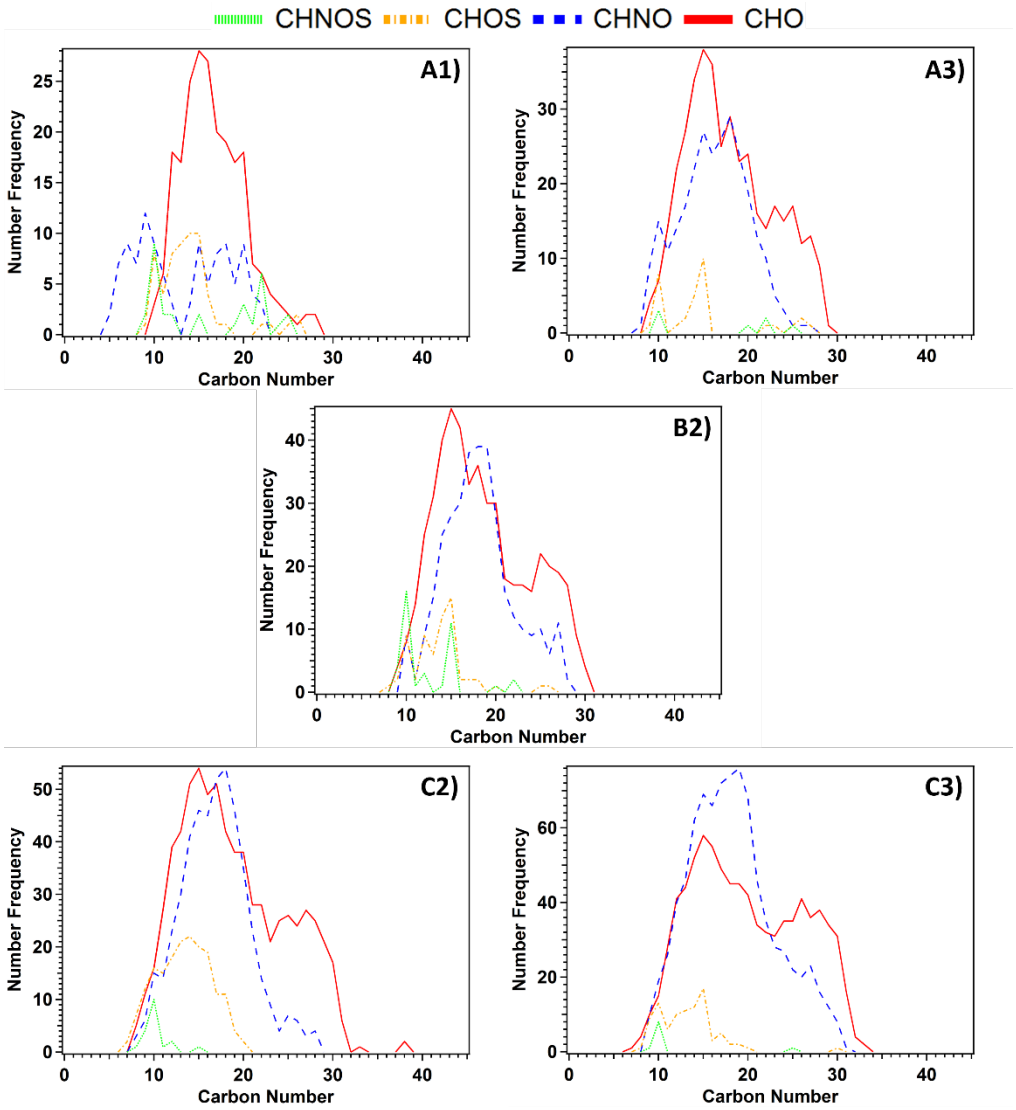


Fig. S3. Carbon number frequency distribution of organic compounds identified in cloud water collected during biogenic (A1 and A3), urban (B2), and wildfire (C2 and C3) influences.

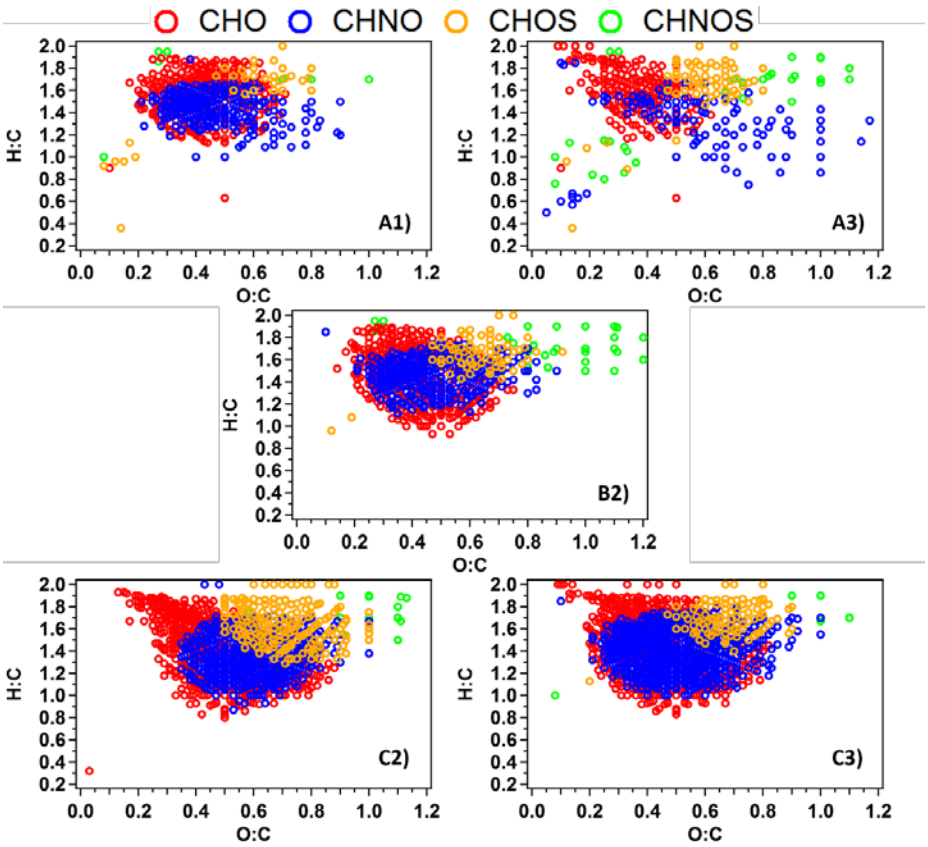


Fig. S4. Van Krevelen diagrams for the identified negative ions for the cloud water samples collected on (A1) 08/16/2014 18:00, (A3) 08/17/2014 18:00, (B2) 09/02/2014 18:00, (C2) 08/05/2014 06:00, and (C3) 08/06/2014 18:00

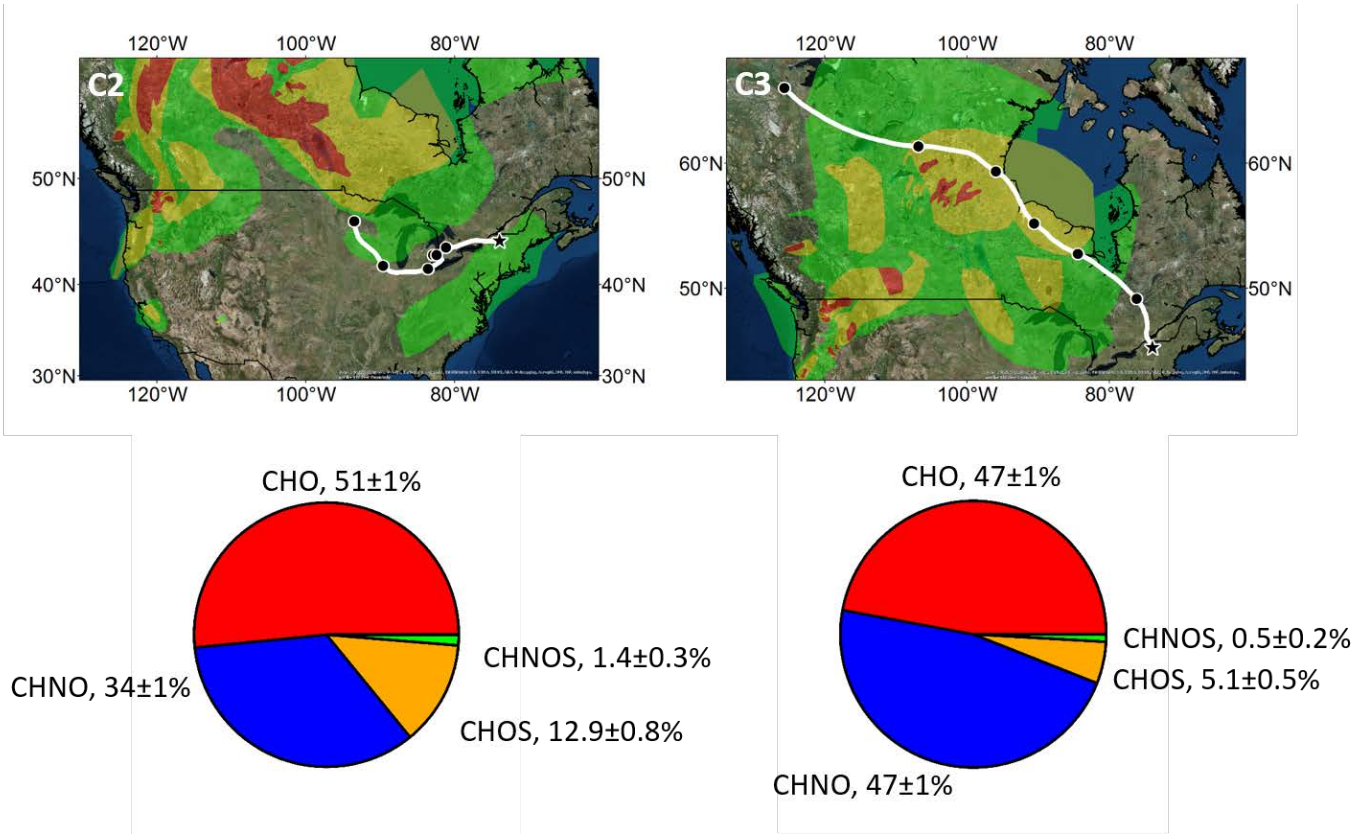
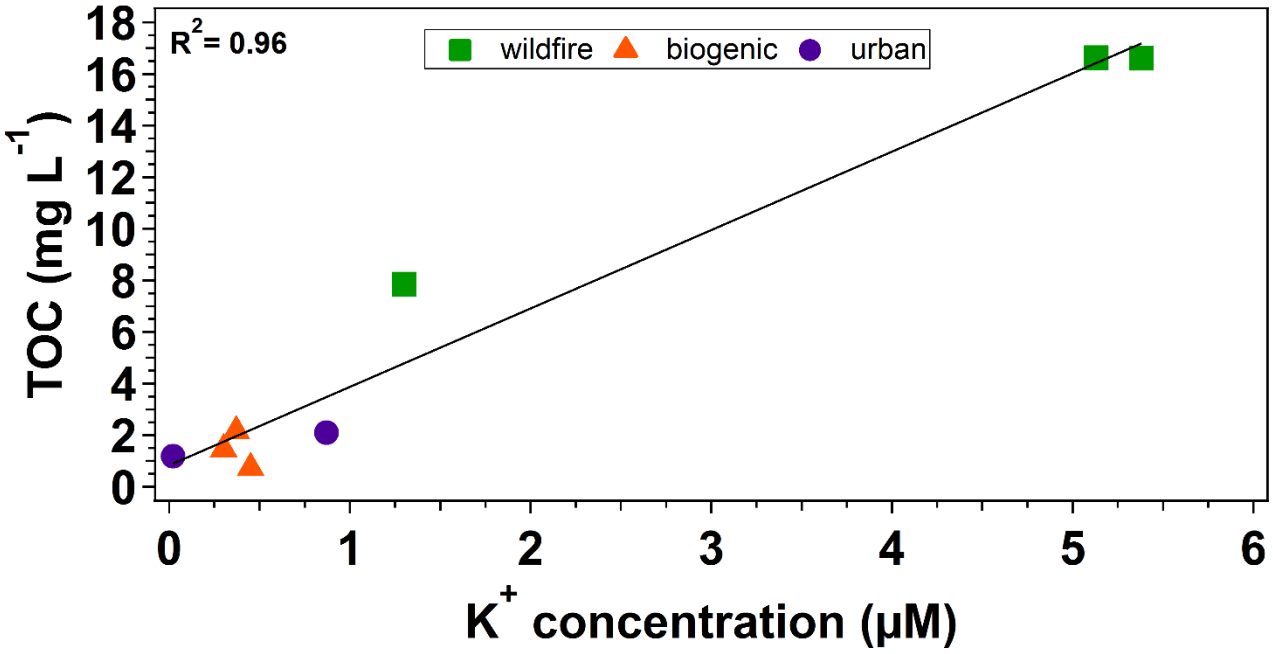


Fig. S5. NOAA HYSPLIT 144 h (6 day) backward air mass trajectories (white lines, with 6 h resolution shown as black dots) and corresponding changes in cloud water molecular composition, shown as compound type number percentages during the wildfire event (samples C2 and C3). Green, yellow, and red shading on the maps represent low, moderate, and high amounts of smoke, respectively, as defined by the NOAA Hazard Mapping System Fire and Smoke Product (http://www.ospo.noaa.gov/Products/land/hms.html).



94

95 **Fig. S6.** Correlation between cloud water total organic content (TOC) and K^+ concentration
96 for each sample, categorized by air mass source influence.