Supplement for:

<u>Characterization of a Large Biogenic Secondary Organic Aerosol Event</u> <u>from Eastern Canadian Forests</u>

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Figure S1. C-ToF-AMS time series (semiquantitative) of K^+ and $C_3H_3^+$ at m/z 39. Reported intensities are corrected for the estimated relative ionization efficiencies for K^+ (RIE = 10) and $C_3H_3^+$ (RIE = 1.4); therefore the measured raw K^+ ion signal is 7.1 times higher relative to $C_3H_3^+$ than indicated in the figure. Time traces and peak fits were obtained using the AMS high-resolution analysis software (PIKA v.1.06A) as discussed in section 2.2.1. Peak fits at selected m/z for the shaded periods are shown in Figs S2 to S4. These periods consist of: (a) period of elevated potassium; (b) anthropogenic case study; (c) biomass burning case study; (d) biogenic case study.



Figure S2. Peak fits at m/z 39 for the C-ToF-AMS during the periods designated in Fig. S1: (a) period of elevated potassium; (b) anthropogenic case study; (c) biomass burning case study; (d) biogenic case study. Fits are obtained using the AMS high-resolution analysis software and depend on calibration of m/z, peak width, and peak shape, which may be evaluated in Figs. S3 (m/z 40) and S4 (m/z 64). The overall fit quality is lower at m/z 39 than at other m/z, likely caused by the production of K⁺ ions from both electrion ionization and surface ionization pathways. In Fig. S2, the proximity of the "raw" peak to the K⁺ exact mass indicates a dominant contribution from that ion. During periods of elevated potassium (Figs. S2a and S2c), the overall fit would be improved by excluding the C₃H₃⁺ ion.

Fit quality is better on the leading edge (dominated by K^+) than the trailing edge (dominated by $C_3H_3^+$), suggesting that the K^+ time series may be more reliable. However, as shown in Fig. S5a, the C-ToF-AMS $C_3H_3^+$ time series agrees well with $C_3H_3^+$ from a co-located high-resolution HR-ToF-AMS, except during periods of elevated potassium.



Figure S3. Peak fits at m/z 40 (Ar⁺ and C₃H₄⁺) for the C-ToF-AMS for: (a) period of elevated potassium; (b) anthropogenic case study; (c) biomass burning case study; (d) biogenic case study. Agreement between raw and fitted peaks indicates the validity of m/z, peak shape, and peak width calibrations used to fit m/z 39 in Fig. S2.



Figure S4. Peak fits at m/z 64 (SO₂⁺ and C₅H₄⁺) for the C-ToF-AMS for: (a) period of elevated potassium; (b) anthropogenic case study; (c) biomass burning case study; (d) biogenic case study. Agreement between raw and fitted peaks indicates the validity of m/z, peak shape, and peak width calibrations used to fit m/z 39 in Fig. S2.



Date and Time

Figure S5. Comparison of co-located C-ToF-AMS and (high-resolution) HR-ToF-AMS time series for (a) $C_3H_3^+$, (b) K^+ , and (c) total signal at m/z 39. As shown in Fig. S5a, the C-ToF and HR-ToF $C_3H_3^+$ time series are correlated except during periods of elevated potassium. Note from Fig. S2 that the m/z fit quality is better on the leading edge (dominated by K^+) than the trailing edge (dominated by $C_3H_3^+$), suggesting that the C-ToF K^+ time series is more reliable than C-ToF $C_3H_3^+$. Fig. S5b shows that K^+ is generally below detection limit for the HR-ToF, likely due to the lower overall sensitivity of that instrument. However, periods where the HR-ToF detects potassium correspond to periods of elevated potassium as measured by the C-ToF. Fig. 5c shows that the time series of total signal measured at m/z 39 is significantly different between the two instruments. Previous HR-ToF-AMS measurements have reported K^+ and $C_3H_3^+$ as the only significant signals at m/z 39 [Aiken et al., 2009]. Note that K⁺ could therefore be estimated as: (C-ToF m/z 39 total) – (HR-ToF C₃H₃⁺). However, given the correlation between C-ToF $C_3H_3^+$ and HR-ToF $C_3H_3^+$ evident in Fig. S5a, such a calculation would yield a K^+ time series similar to that obtained using the peak fits shown in Fig. S2 and presently reported in the manuscript.



Figure S6. Factor mass spectra (a) and time series (b) for the 5-factor solution to the AMS dataset. Mass spectra are normalized such that the sum of each spectrum across all m/z's is equal to 1. Time series are plotted for both AMS PMF factors (red traces, left axis) and selected tracer species (black and blue traces, right axis).



Figure S7. Factor mass spectra (a) and time series (b) as a function of fPeak for the 4-factor PMF solution to the AMS dataset. Mass spectra are normalized such that the sum of each spectrum across all m/z's is equal to 1.



Figure S8. Factor mass spectra (a) and time series (b) for the 4-factor PMF solution to the AMS dataset for 98 convergent runs generated from 100 random starting points. The mean, maximum, and minimum values for each m/z and time point are shown.



Figure S9. Factor mass spectra (a) and time series (b) for 100 bootstrapping runs for the 4-factor solution. Solution standard deviations are denoted as error bars (a) for the mass spectra and red traces (b) for the time series,



Figure S10. Factor mass spectra (a) and time series (b) for 100 bootstrapping runs for the 5-factor solution. Solution standard deviations are denoted as error bars (a) for the mass spectra and red traces (b) for the time series,