

Figure S1. Semiquantitative C-ToF-AMS time series of K⁺ and $C_3H_3^+$ at m/z 39. Note that the measured ion signal at K⁺ is 7.1 times higher relative to $C_3H_3^+$ due to the relative ionization efficiences for K⁺ (RIE = 10) and $C_3H_3^+$ (RIE = 1.4). 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. The shaded regions correspond to: (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 for the shaded regions 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 (see Figs. S3 and S4), likely because of the production of K⁺ ions from both electron ionization and surface ionization pathways. In Fig. S2, a strong contribution from the K⁺ ion is suggested by: (1) the proximity of the "raw" peak to the K⁺ exact mass, and (2) during periods of elevated potassium (Figs. S2a and S2c), the overall fit would be improved by excluding the C₃H₃⁺ ion.



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.



Figure S5. Comparison of co-located C-ToF-AMS (unit m/z resolution) and W-ToF-AMS (high-resolution) 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 W-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 $C_3H_3^+$. Figure S5b shows that K^+ is generally below detection limit for the W-ToF, likely due to the lower overall sensitivity of that instrument. However, potassium events detected by the W-ToF correspond with C-ToF measurements of elevated potassium. Figure 5c shows that the time series of total signal measured at m/z 39 is significantly different between the two instruments. Because previous W-ToF-AMS measurements have reported K^+ and $C_3H_3^+$ as the only significant signals at m/z 39 [Aiken et al., 2009], an additional estimate of K^+ could be estimated as: (C-ToF m/z 39 total) – (W-ToF C₃H₃⁺). However, given the correlation between C-ToF $C_3H_3^+$ and W-ToF $C_3H_3^+$ evident in Fig. S5a, this estimate 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.

References

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