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Supplement of

A high-resolution time-of-flight chemical ionization mass spectrometer utilizing hydronium ions (H_3O^+ ToF-CIMS) for measurements of volatile organic compounds in the atmosphere

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Mass resolving power and separation of isobaric masses

The mass resolving power (m/Δm) was derived from the observed linear relationship between the full-width half maximum (FWHM) of several isolated mass peaks and their *m/z* using Tofware (Stark et al., 2015). The typical m/Δm for the H_3O^+ ToF-CIMS during the SONGNEX campaign is shown in Figure S2. The m/Δm in the range of *m/z* 30 - 200 (where most VOCs were detected), are 3900-5900 with higher resolution for heavier masses. These mass resolutions are sufficient to separate many isobaric ions. Figure S3 shows the separation of C8 aromatics ($C_8H_{10}H^+$, *m/z* 107.086) from benzaldehyde ($C_7H_6OH^+$, *m/z* 107.049) for *m/z* 107 during a flight leg (18:15-18:45 UTC) over the Permian Basin in Texas, US. The two mass spectra in A and B are 30 s averages centered around 18:25:00 and 18:35:10, respectively. The two time windows had either benzaldehyde or C8 aromatics as the higher peak between the two. The time series of benzaldehyde and C8 aromatics determined from the mass spectral fits for this 30-min period correlated well with acetone (R=0.87) and benzene (R=0.94), respectively. This is consistent with the expectation that benzaldehyde was mainly from secondary formation and C8 aromatics were dominated by primary emissions from oil and gas activities. The signals at *m/z* 107 are usually assigned to C8 aromatics in PTR-QMS studies (de Gouw and Warneke, 2007). Although the possible interference from benzaldehyde to C8 aromatics has been known, it usually constitutes a small fraction of the total signal at nominal mass 107 (Warneke et al., 2003). The example shown in Figure S3 indicates that benzaldehyde, in some environments, can contribute significantly to signals at nominal mass 107.

Based on results in previous studies (Graus et al., 2010;Stark et al., 2015), the mass resolving power of the ToF analyzer presented in this study can separate many of the isobaric masses in the mass range of *m/z*<200 by utilizing the high-resolution peak fitting algorithms. The separation of isobaric ions has several advantages over the nominal mass data of PTR-QMS: (1) reduce chemical interferences, e.g. the interference of benzaldehyde to C8 aromatics at nominal *m/z* 107 as shown above; (2) decrease background signals for several compounds of interest, e.g. for methanol (Müller et al., 2014) and acetaldehyde, the instrument backgrounds of which have interferences from O_2H^+ and CO_2H^+ at the same nominal masses, respectively; (3) increase the number of

46 species that can be measured. In general, 10-20 compounds are usually measurable by the
47 PTR-QMS explicitly without significant interference depending on the origin of the air
48 masses (de Gouw and Warneke, 2007). During the SONGNEX campaign, a total of 1055
49 peaks between *m/z* 12 and *m/z* 181 were identified and assigned to signals in the mass
50 spectra of H_3O^+ ToF-CIMS. Not all of these mass signals can be used for VOC
51 quantification. Many masses (1) are associated with large errors from high-resolution
52 peak fittings as the result of a much larger peak nearby and/or poor separation from
53 another peak; or (2) have no significant enhancement over instrument background. Over
54 260 masses had periods (at least 1 min) with signal to background ratios larger than three
55 during the flight over the Permian Basin on April 23, 2015. Although not all of these
56 masses are attributable to specific compounds, chemical formulas of the masses give
57 more detailed information on the chemical composition than just the nominal *m/z*.
58 Detailed interpretation of the mass spectra in various air masses during the SONGNEX
59 campaign will be presented in a separate publication (Koss et al., in prep).
60

Figures

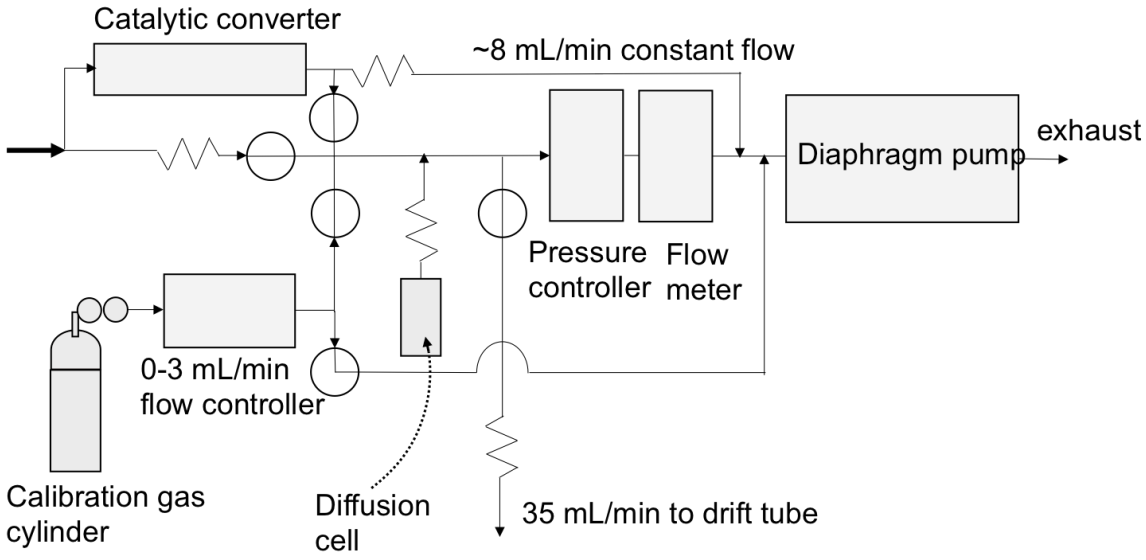


Figure S1. Inlet diagram used during the SONGNEX campaign

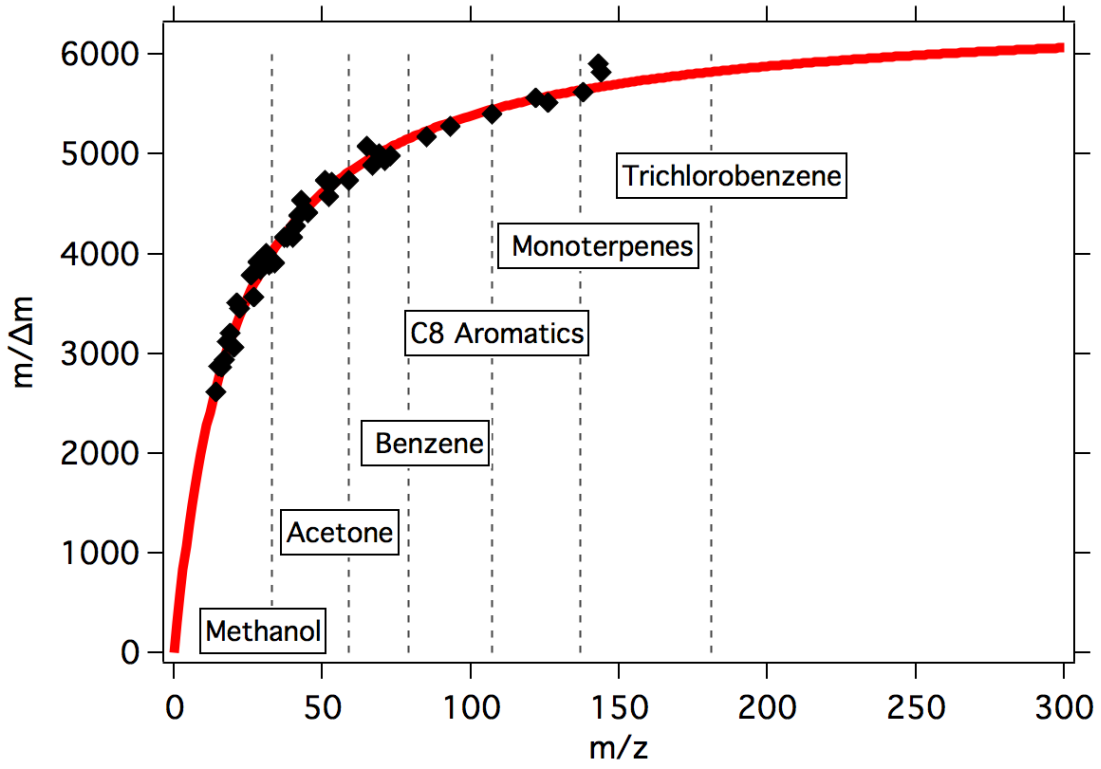


Figure S2. Mass resolution (m/Δm) of the ToF analyzer from measured data in the flight on April 13, 2015. The black markers are the calculated m/Δm from isolated *m/z* peaks. The red curve indicates the fitted line in the range of *m/z* 0-300. Vertical dashed lines indicate the positions of several VOC species (methanol, acetone, benzene, C8 aromatics, monoterpenes and trichlorobenzenes).

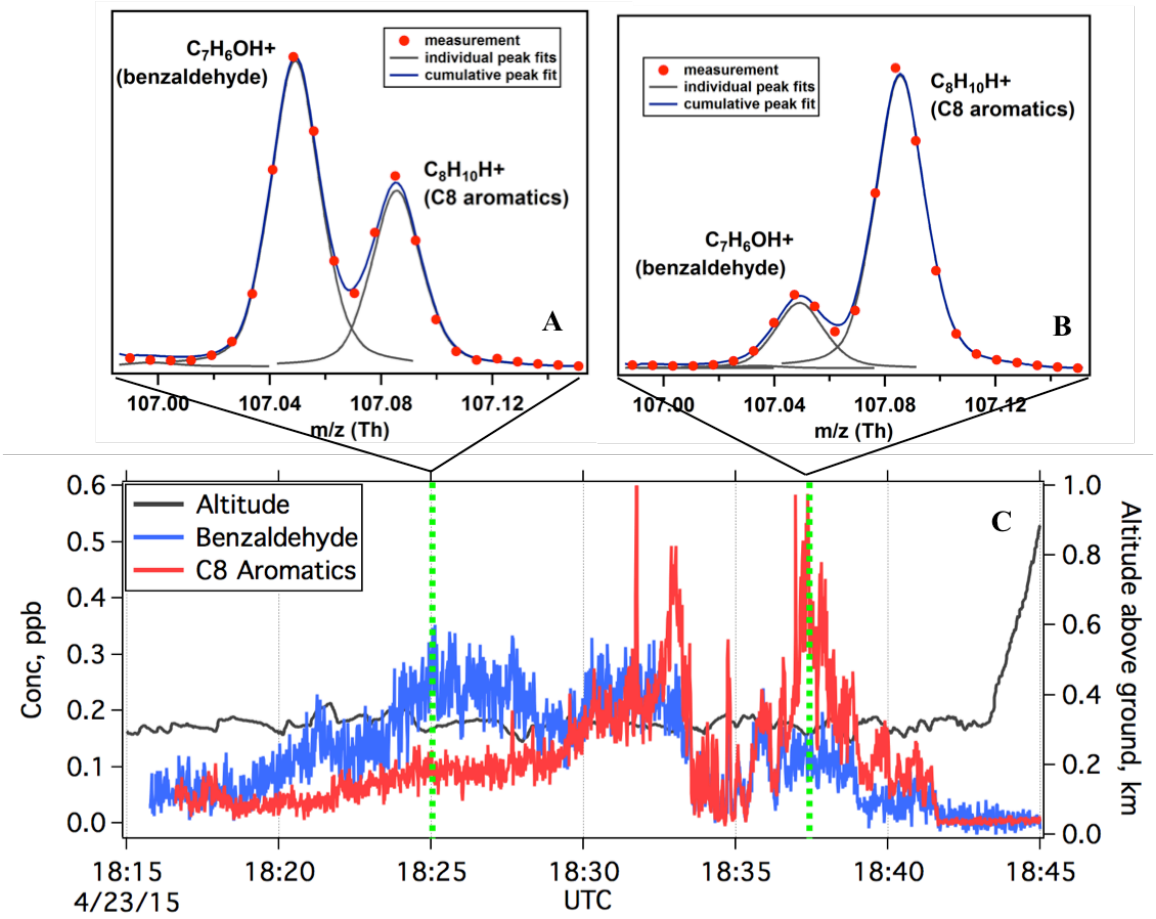


Figure S3. Separation of benzaldehyde and C8 aromatics from the nominal mass at *m/z* 107 in a period (18:15-18:45 UTC) during the flight over the Permian Basin on April 23, 2015. (A and B) HR peak fittings of mass spectra at *m/z* 107 at 18:25 and 18:37, respectively. (C) Time series of benzaldehyde and C8 aromatics during the period. Flight altitude of the NOAA WP-3D aircraft is included in C.

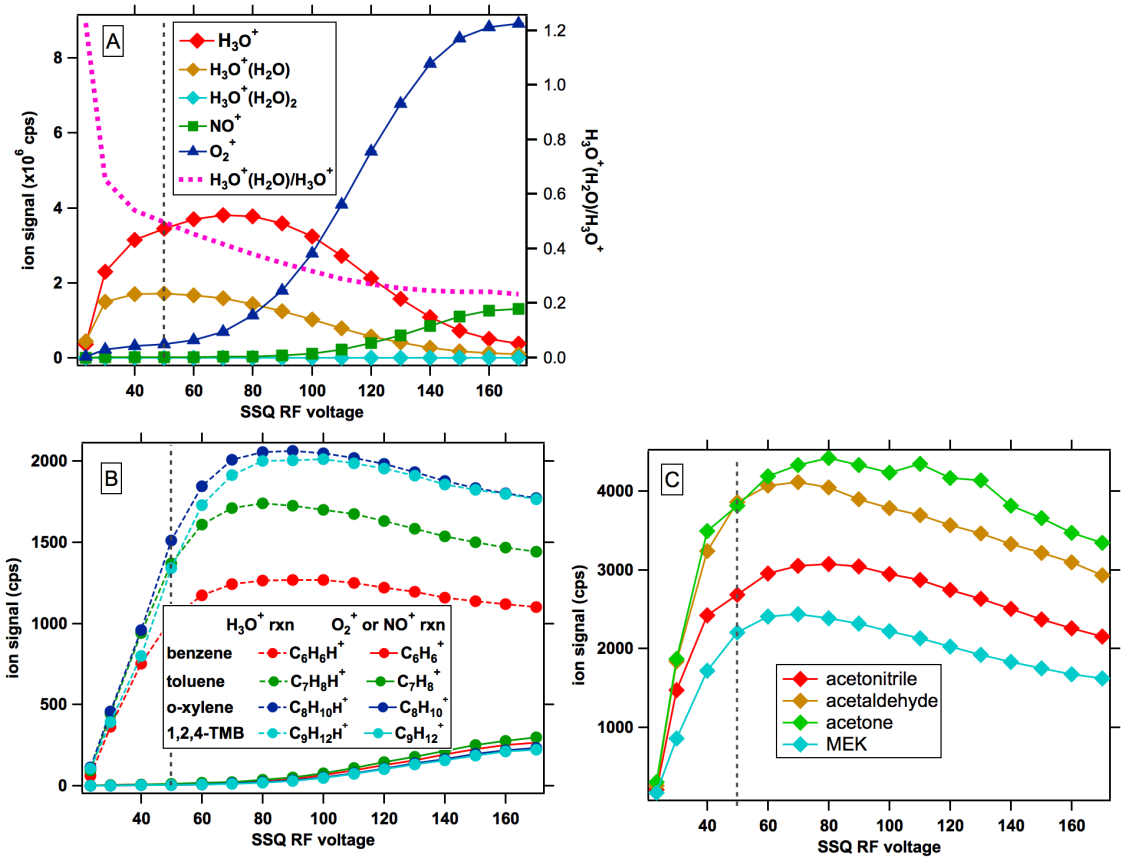


Figure S4. Signals of the reagent ions and VOC product ions as a function of the RF amplitudes in the SSQ. (A) Signals of H_3O^+, $H_3O^+(H_2O)$, $H_3O^+(H_2O)_2$, NO^+ and O_2^+ as a function of RF amplitudes of the SSQ. $H_3O^+(H_2O)/ H_3O^+$ ratios as a function of RF amplitudes are also shown in A. (B) Product ions from proton transfer and charge transfer reactions of aromatics (benzene, toluene, o-xylene and 1,2,4-trimethylbenzene) as a function of RF amplitudes of the SSQ. (C) Product ions of acetonitrile, acetaldehyde, acetone and MEK as a function of RF amplitudes of the SSQ. The vertical dashed lines indicate the RF amplitudes of the SSQ (50 V) used during the SONGNEX campaign.

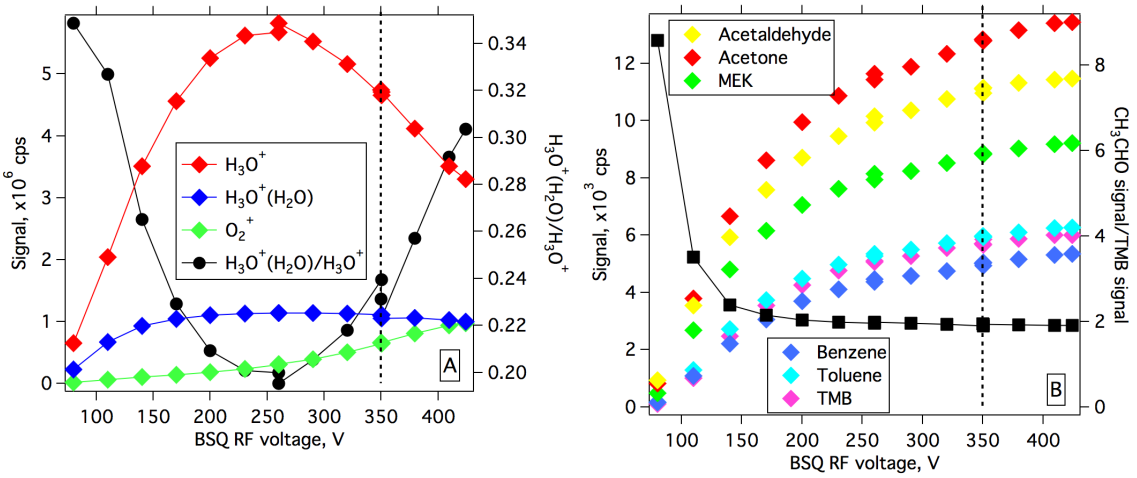


Figure S5. (A) Signals of H_3O^+, $H_3O^+(H_2O)$ and O_2^+ as a function of RF amplitudes of the BSQ. $H_3O^+(H_2O)/ H_3O^+$ ratios as a function of RF amplitudes of the BSQ are also shown in A. (B) Product ions of several VOCs (acetaldehyde, acetone, MEK, benzene, toluene and 1,2,4-trimethylbenzene) as a function of RF amplitudes of the BSQ. The ratios of acetaldehyde signals to 1,2,4-trimethylbenzene signals as a function of RF amplitudes of the BSQ are included. The vertical dashed lines indicate the RF amplitudes of BSQ (350 V) used during the SONGNEX campaign.

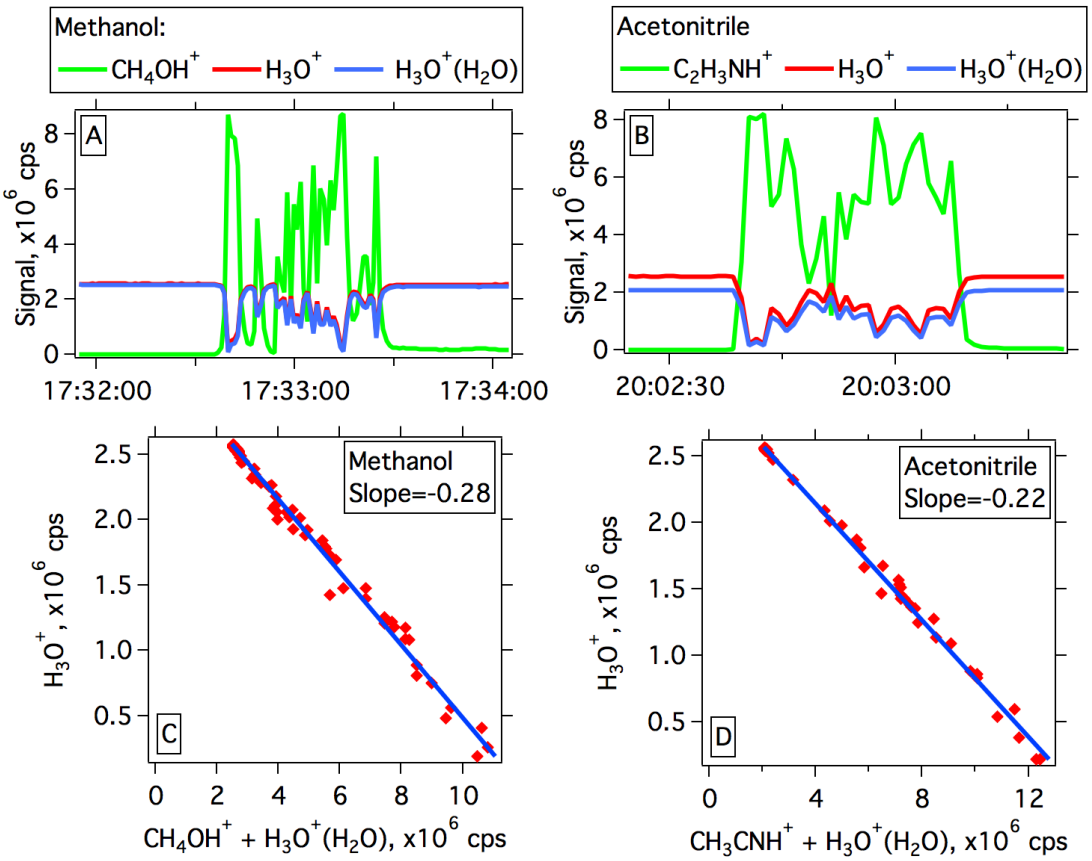
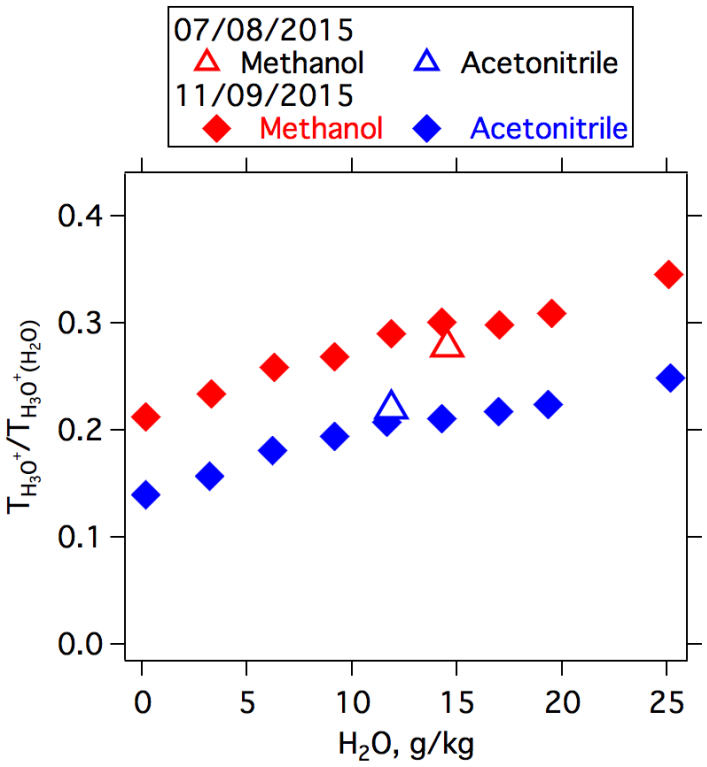


Figure S6. (A and B) Time series of the signals of the reagent ions and protonated product ions when large amounts of methanol (A) and acetonitrile (B) were introduced into the instrument. (C and D) Scatterplots of H_3O^+ ions versus the sums of protonated product ions and $H_3O^+(H_2O)$ ions from methanol and acetonitrile experiments shown in (A) and (B), respectively. The blue lines are linear fits to the data points. The slopes of linear fits represent the ratios of transmission efficiency between H_3O^+ and $H_3O^+(H_2O)$ ($T_{H_3O^+}/T_{H_3O^+(H_2O)}$).



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113 Figure S7. The determined ratios of transmission efficiency between H_3O^+ and
114 $H_3O^+(H_2O)$ ($T_{H_3O^+}/T_{H_3O^+(H_2O)}$) as a function of water vapor mixing ratios of the sampled
115 air from the experiments of introducing large concentrations of methanol and acetonitrile,
116 respectively (Figure S4). Experiments were performed on July 8 and November 9, with
117 measurements at different humidity levels on November 9, 2015. Consistent estimates
118 were derived from the experiments in July and November.

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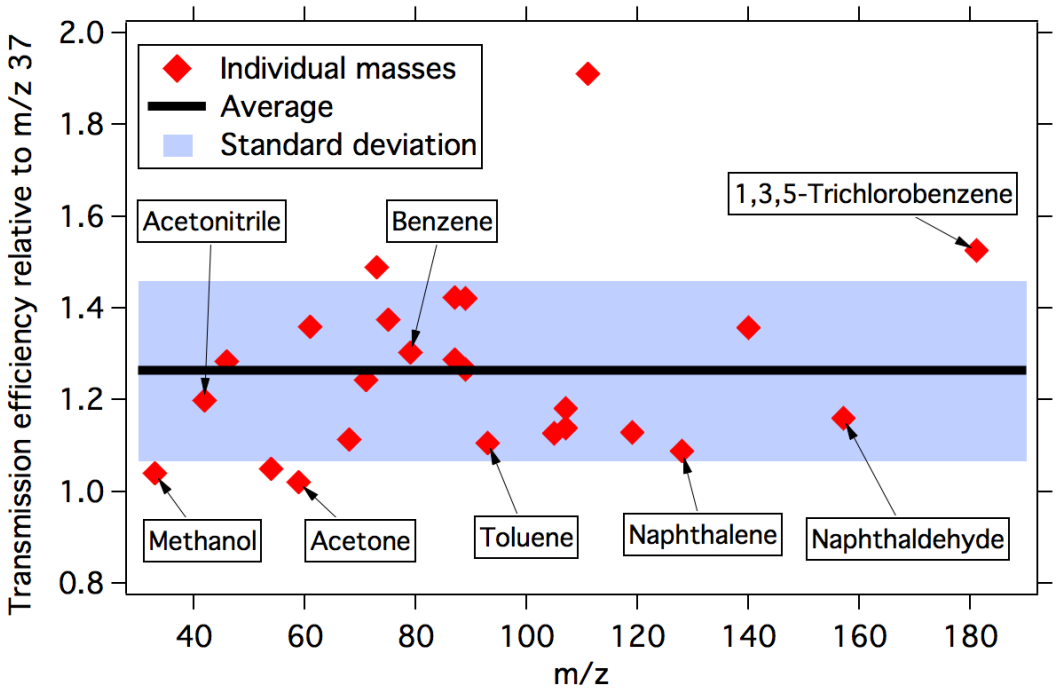
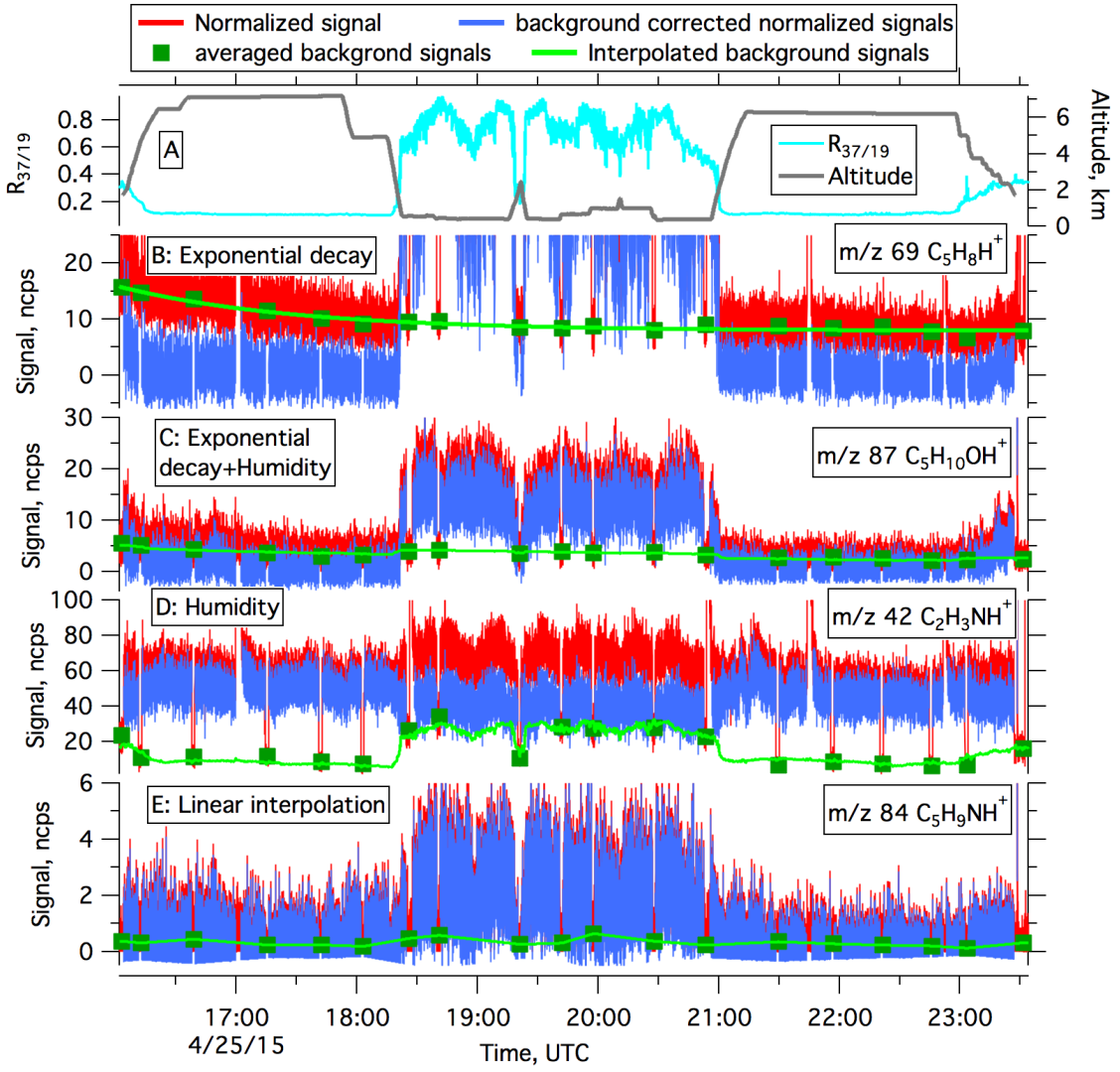


Figure S8. Determined ratios of the transmission efficiency of various VOC masses relative to $H_3O^+(H_2O)$. Excess concentrations of different VOCs were introduced into the instrument in a similar way as shown in Figure S4. The ratios of the transmission efficiency between the masses and $H_3O^+(H_2O)$ are estimated from the depletion of the reagent ions and increase of the product ions. The average for the data points (1.26±0.20) is also shown in the graph.



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130 Figure S9. Background correction for several ions for the flight on April 25, 2015 over
131 the Haynesville during SONGNEX. (A) Time series of $H_3O^+(H_2O)/H_3O^+$ ($R_{37/19}$) and
132 aircraft altitude during the flight. (B-E) Time series of the normalized signals, averaged
133 background signals, interpolated background signals and the background corrected
134 signals for the ions of $C_5H_8H^+$ (m/z 69.070), $C_5H_{10}OH^+$ (m/z 87.080), $C_2H_3NH^+$ (m/z
135 42.034) and $C_5H_9NH^+$ (m/z 84.081) to illustrate background correction algorithms with
136 exponential decay, exponential decay+humidity, humidity dependence and linear
137 interpolation, respectively.

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