Supporting information for

"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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Figures

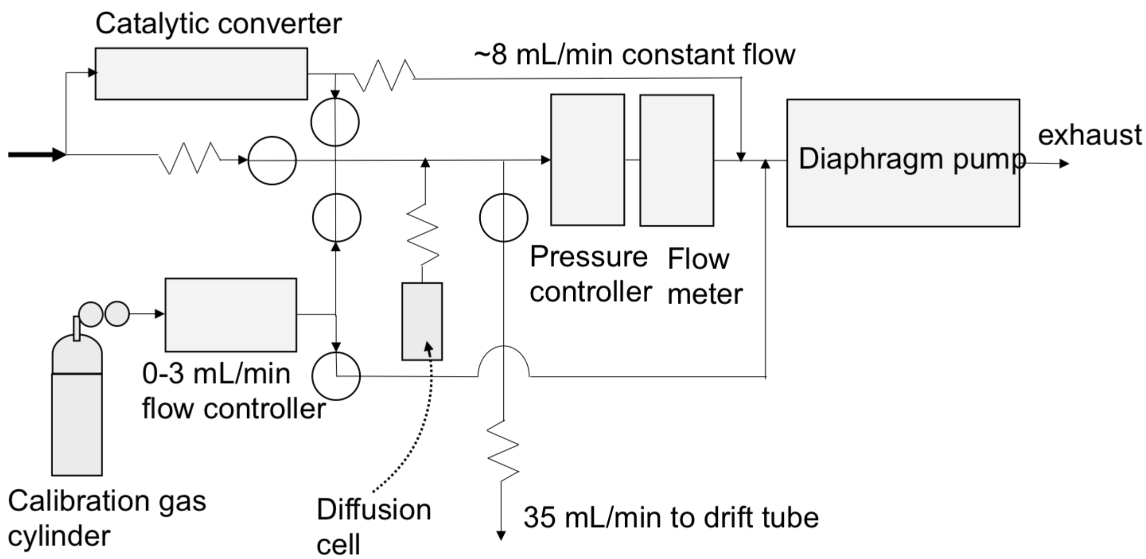

Figure S1. Inlet diagram used during the SONGNEX campaign

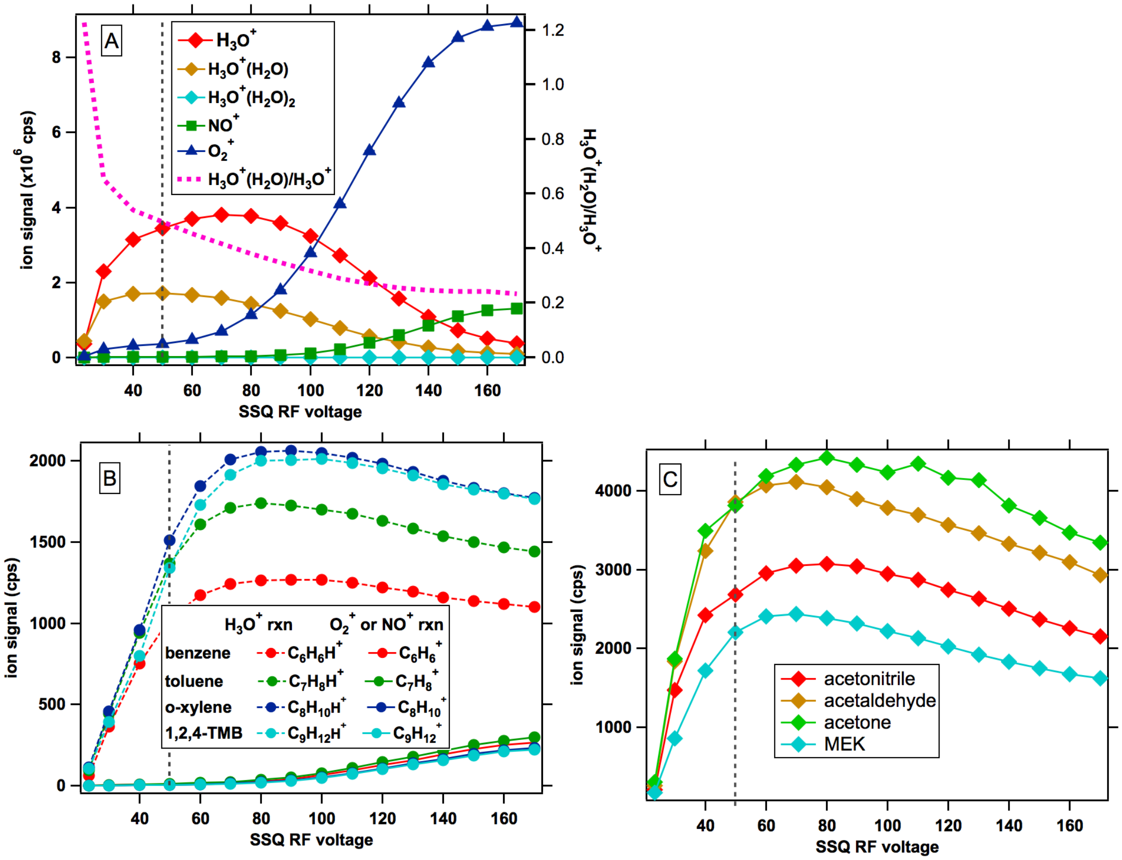

Figure S2. Signals of the reagent ions and VOC product ions as a function of the RF amplitudes in the SSQ. (A) Signals of H_3O^+, $H_3O^+(H_2O)$, $H_3O^+(H_2O)_2$, NO^+ and O_2^+ as a function of RF amplitudes of the SSQ. $H_3O^+(H_2O)/ H_3O^+$ ratios as a function of RF amplitudes are also shown in 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.

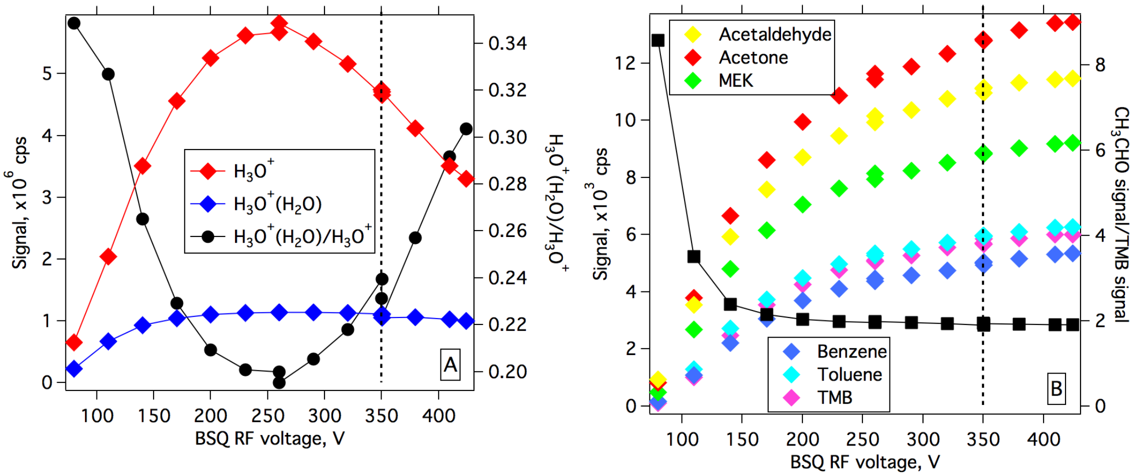

Figure S3. (A) Signals of H_3O^+ and $H_3O^+(H_2O)$ as a function of RF amplitudes of the BSQ. $H_3O^+(H_2O)$/ H_3O^+ ratios as a function of RF amplitudes of the BSQ are also shown in A. (B) Product ions of several VOCs (acetaldehyde, acetone, MEK, benzene, toluene and 1,2,4-trimethylbenzene) as a function 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.

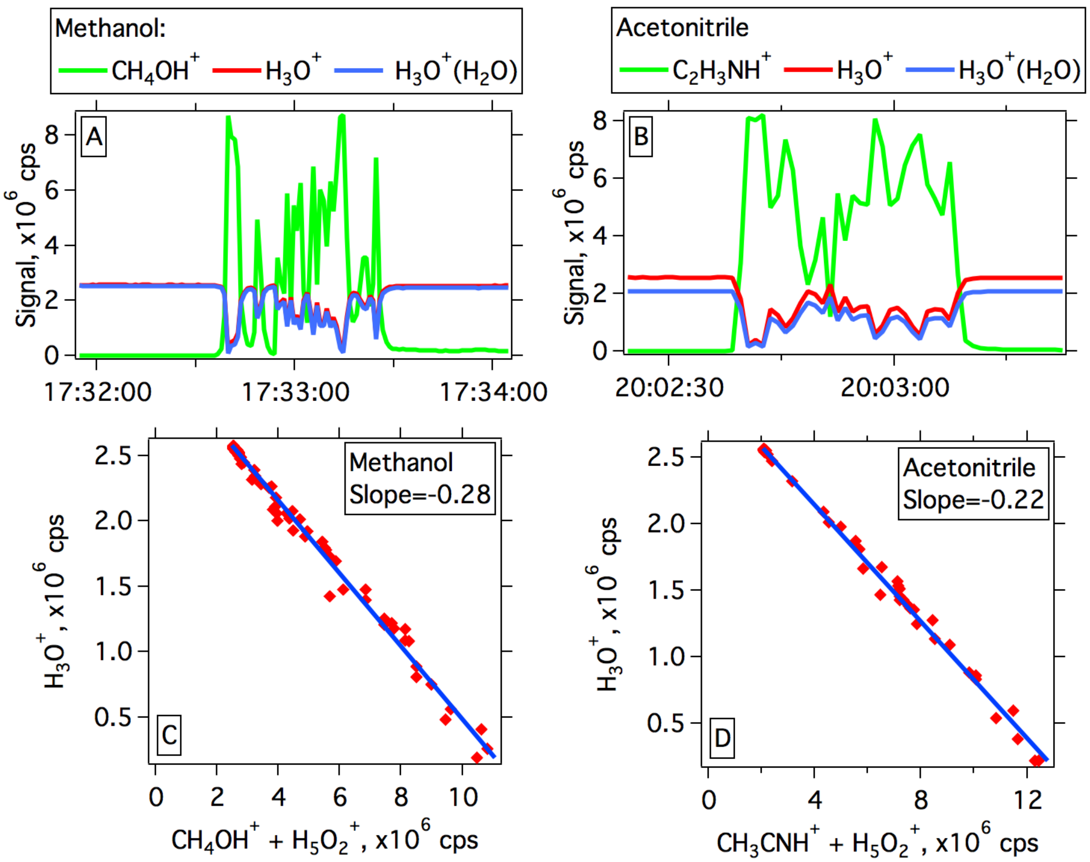

Figure S4. (A and B) Time series of the signals of the reagent ions and protonated product ions when large amounts of methanol (A) and acetonitrile (B) were introduced into the instrument. (C and D) Scatterplots of H_3O^+ ions versus the sums of protonated product ions and $H_3O^+(H_2O)$ ions from methanol 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 $H_3O^+(H_2O)$ $(T_{H_3O^+}/T_{H_3O^+(H_2O)})$.

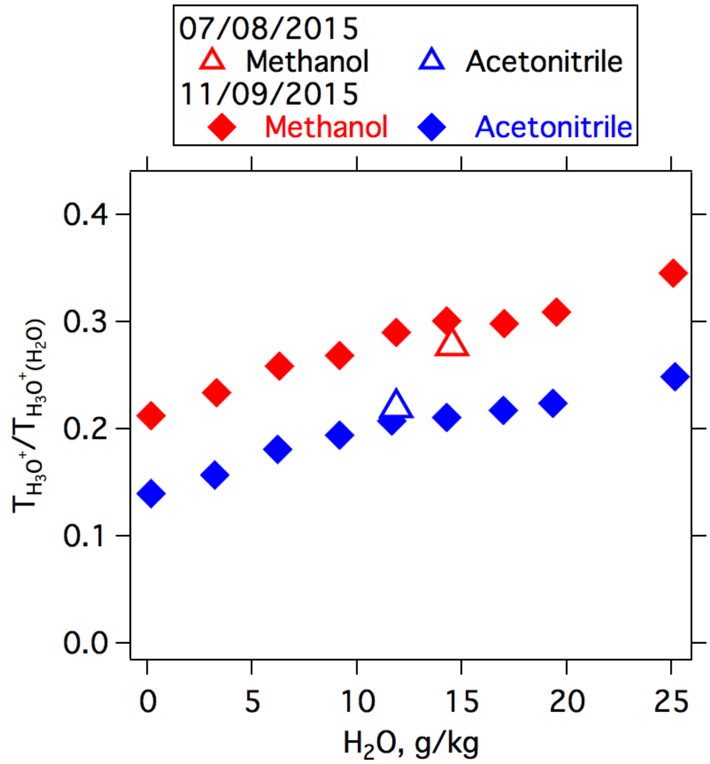

Figure S5. The determined ratios of transmission efficiency between H_3O^+ and $H_3O^+(H_2O)$ ($T_{H_3O^+}/T_{H_3O^+(H_2O)}$) as a function of water vapor mixing ratios of the sampled air from the experiments of introducing large concentrations of methanol and acetonitrile, respectively (Figure S4). Experiments were performed on July 8 and November 9, with measurements at different humidity levels on November 9, 2015. Consistent estimates were derived from the experiments in July and November.

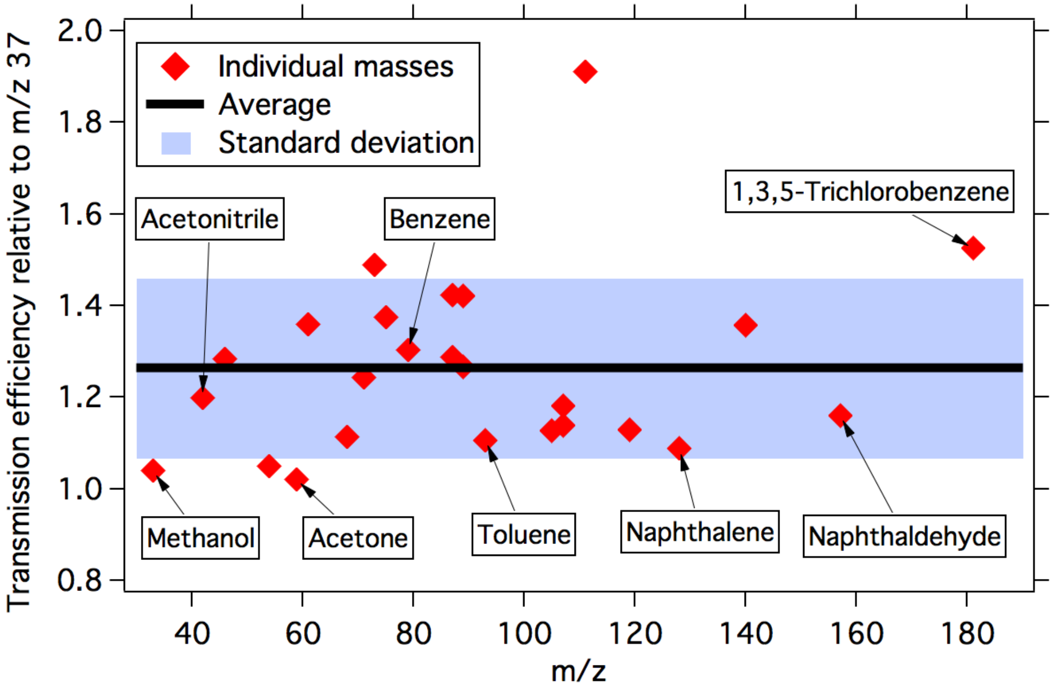

Figure S6. Determined ratios of the transmission efficiency of various VOC masses relative to $H_3O^+(H_2O)$. Excess concentrations of different VOCs were introduced into the instrument in a similar way as shown in Figure S4. The ratios of the transmission efficiency between the masses and $H_3O^+(H_2O)$ 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.

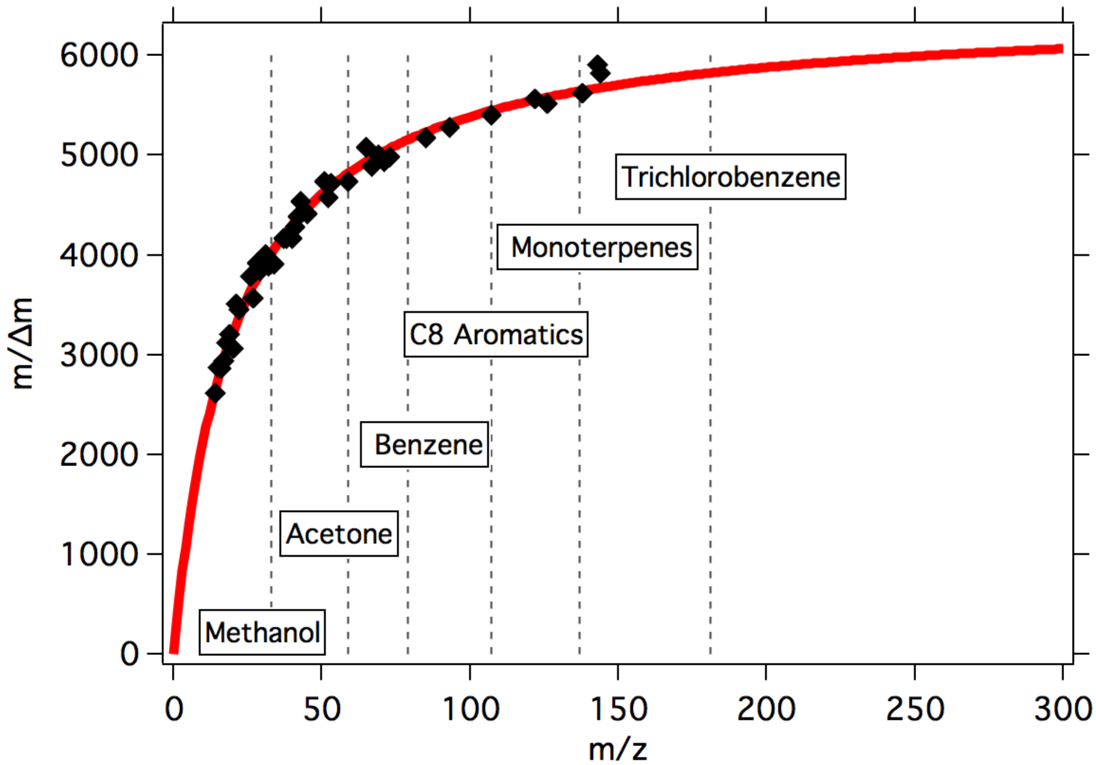

Figure S7. Mass resolution (m/Δm) of the ToF analyzer from measured data in the flight on April 13, 2015. The black markers are the calculated m/Δm from isolated *m/z* peaks. The red curve indicates the fitted line in the range of *m/z* 0-300. Vertical dashed lines indicate the positions of several VOC species (methanol, acetone, benzene, C8 aromatics, monoterpenes and trichlorobenzenes).

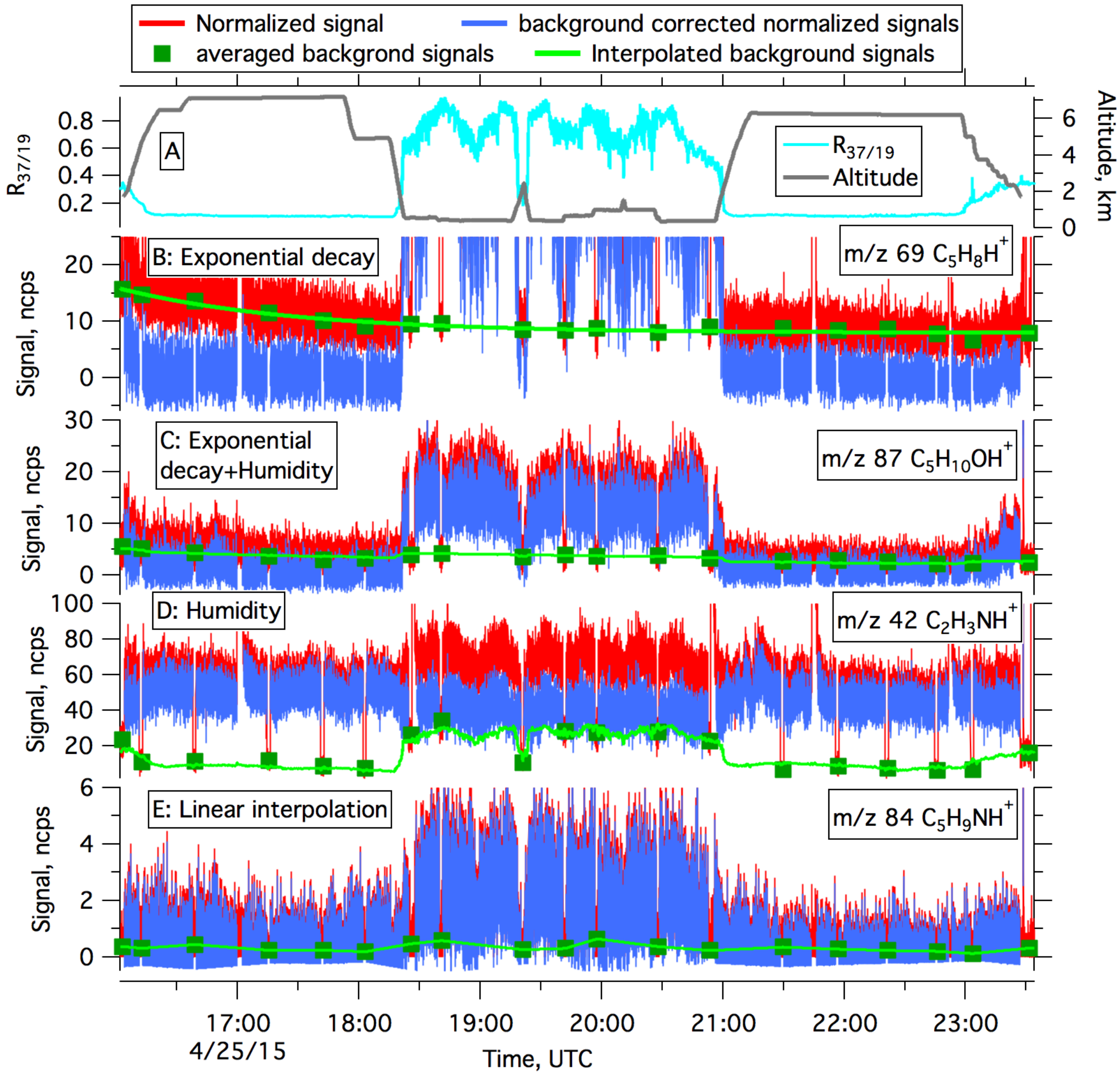

Figure S8. Background correction for several ions for the flight on April 25, 2015 over the Haynesville during SONGNEX. (A) Time series of $H_3O^+(H_2O)/H_3O^+$ ($R_{37/19}$) and aircraft altitude during the flight. (B-E) Time series of the normalized signals, averaged background signals, interpolated background signals and the background corrected signals for the ions of $C_5H_8H^+$ (m/z 69.0699), $C_5H_{10}OH^+$ (m/z 87.0804), $C_2H_3NH^+$ (m/z 42.0338) and $C_5H_9NH^+$ (m/z 84.0808) to illustrate background correction algorithms with exponential decay, exponential decay+humidity, humidity dependence and linear interpolation, respectively.