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Supplement of

Evaluation of NO^+ reagent ion chemistry for online measurements of atmospheric volatile organic compounds

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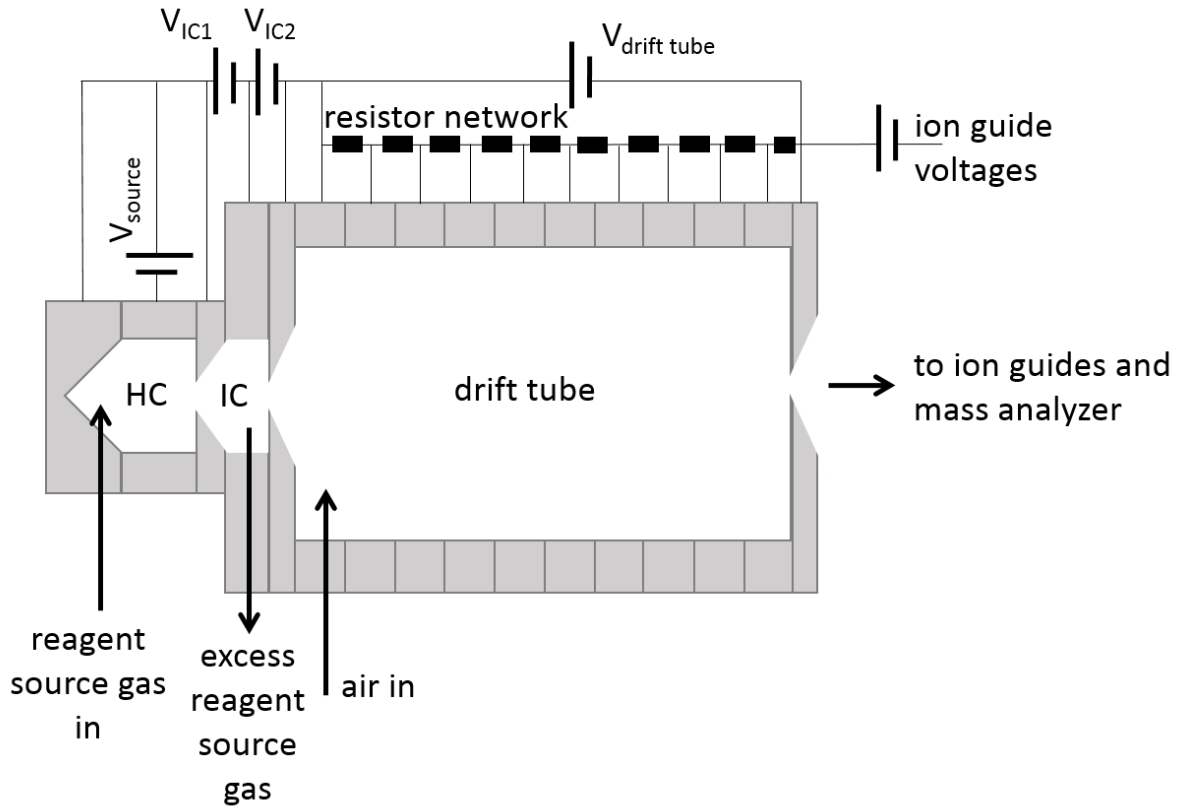

Figure S1. Ion source and drift tube schematic.

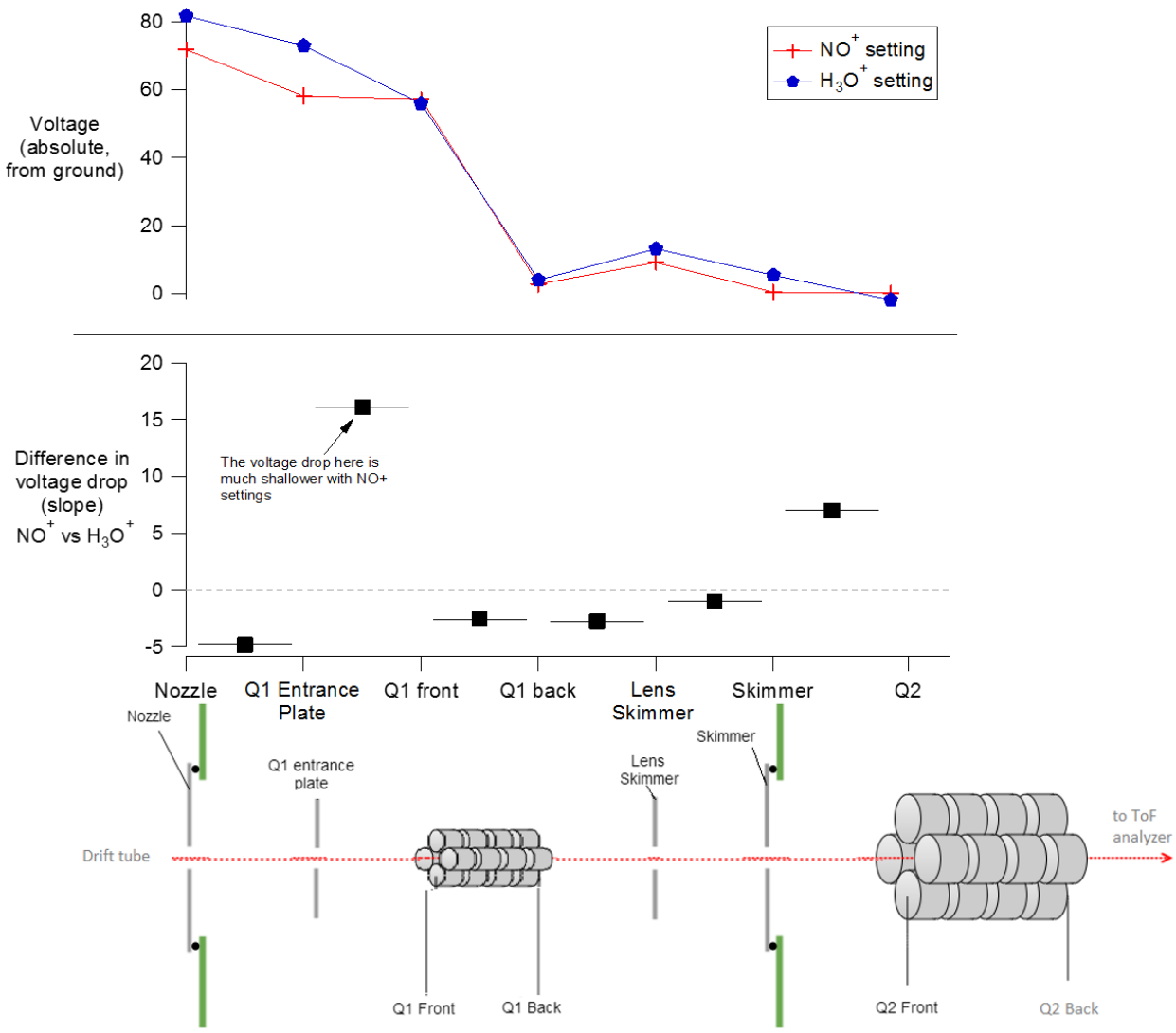

Figure S2. Ion guide voltage settings. The top panel shows the absolute voltage setting (from ground); the middle panel highlights the changes in voltage potential between H_3O^+ and NO^+ settings, and the bottom panel is a cartoon of the ion guide section taken from the CI-API manual (Aerodyne Inc./Tofwerk AG). The horizontal (axial) distances are not to scale.

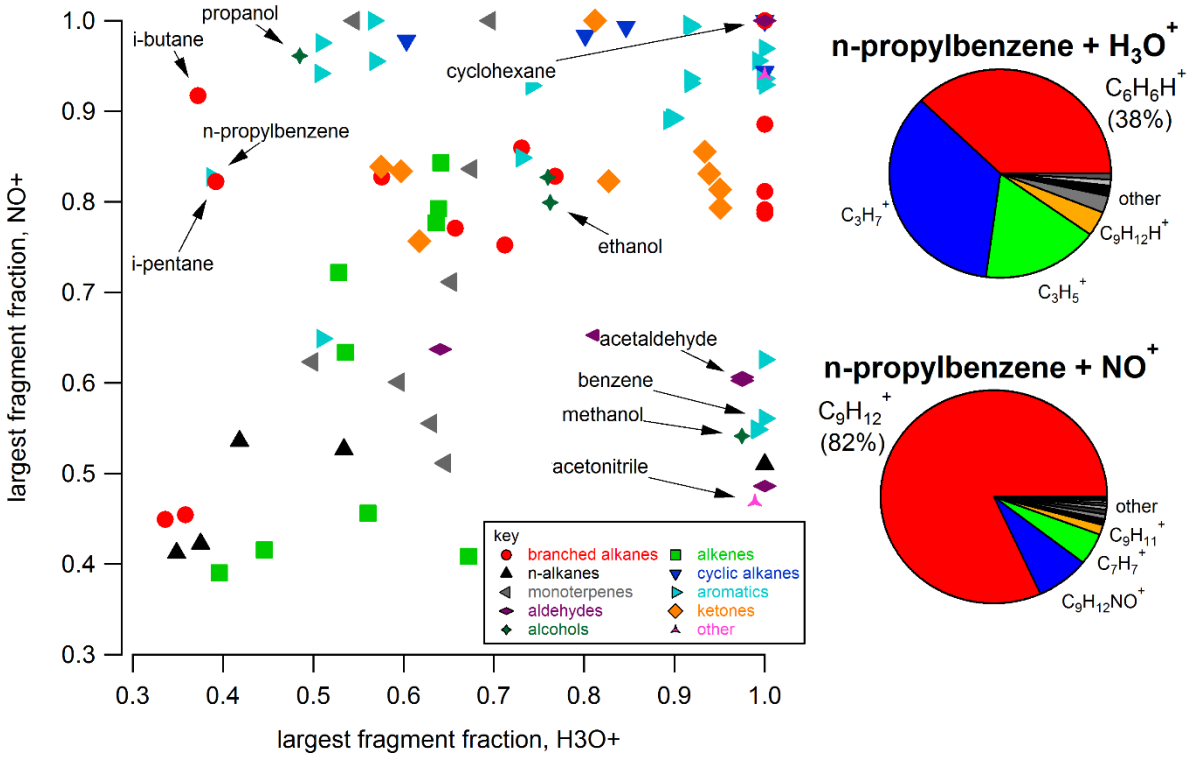

Figure S3. Comparison of product ion distributions between NO^+ CIMS and H_3O^+ CIMS. The complete product ion distribution of n-propylbenzene is shown as an example of a compound with a complex mass spectrum resulting from H_3O^+ chemistry, and a simple mass spectrum resulting from NO^+ chemistry.

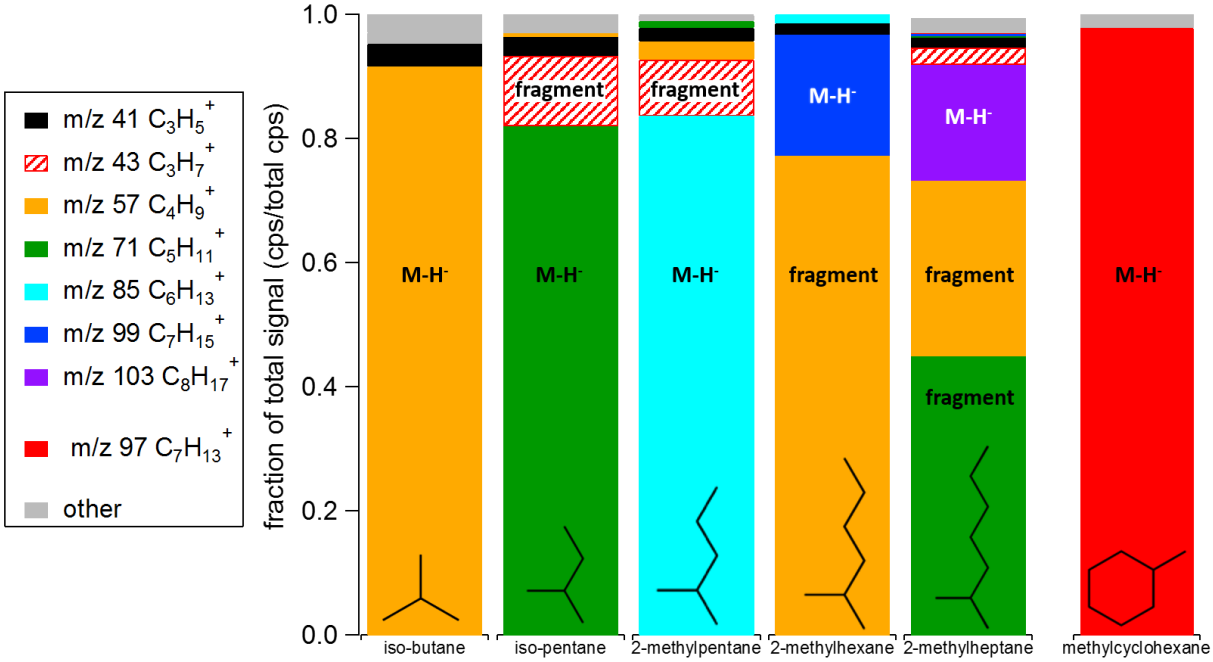

Figure S4. Product ion distributions of selected aliphatic hydrocarbons, at a relative humidity of 20%.

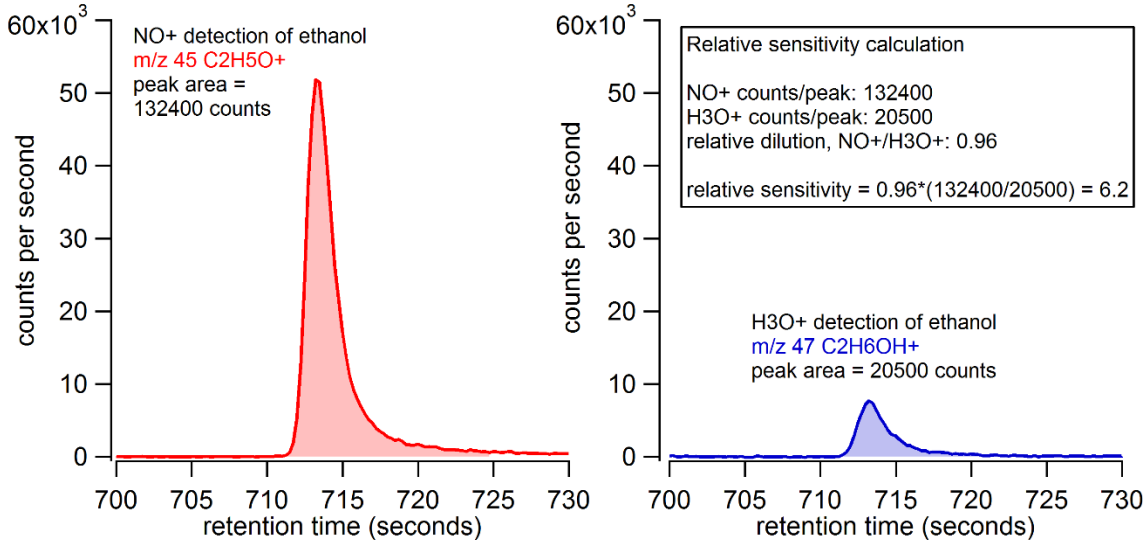

Figure S5. Example chromatograms and relative sensitivity calculation of ethanol for Table 2.

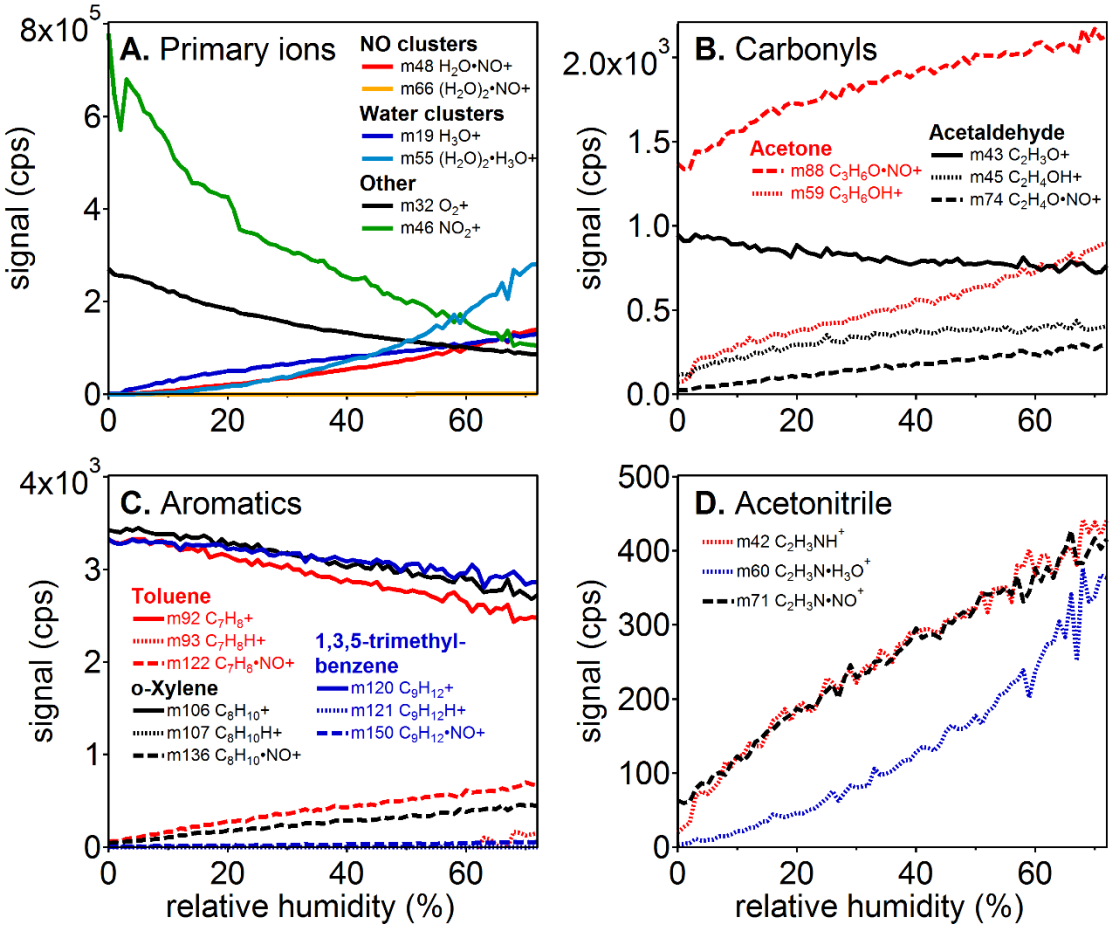

Figure S6. Humidity dependence of primary ions and VOCs. (a) Impurity ions and water clusters. (b) Carbonyls. (c) Aromatics. (d) Acetonitrile. Acetonitrile is detected with poor sensitivity using NO^+; the NO^+ and H_3O^+ products are approximately equal in magnitude.

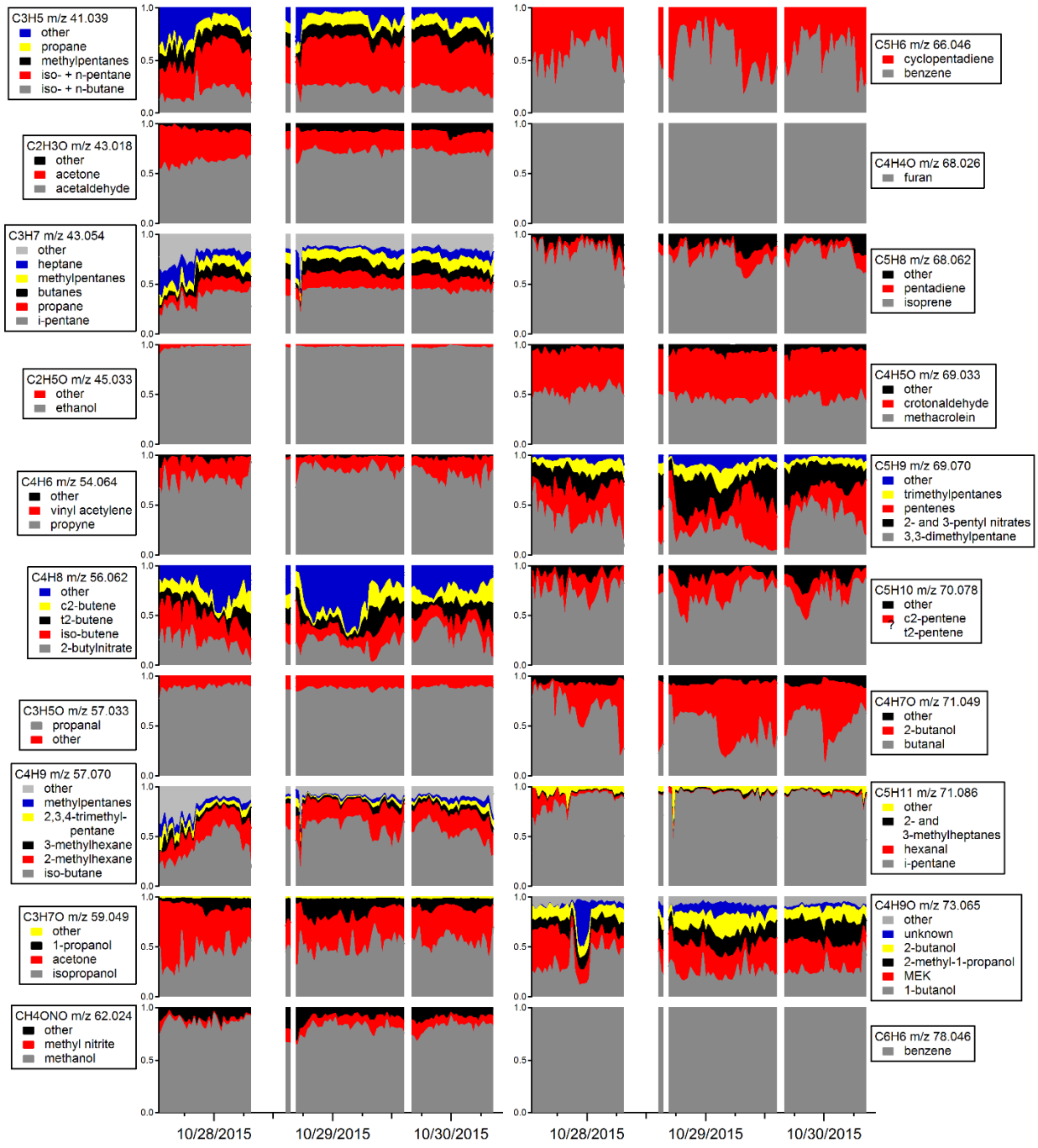

Figure S7. Speciated contributions to various NO^+ CIMS masses, in urban air. Values on Y-axes are the fractional contribution of each VOC to total signal. Includes m/z 41-m/z 78.

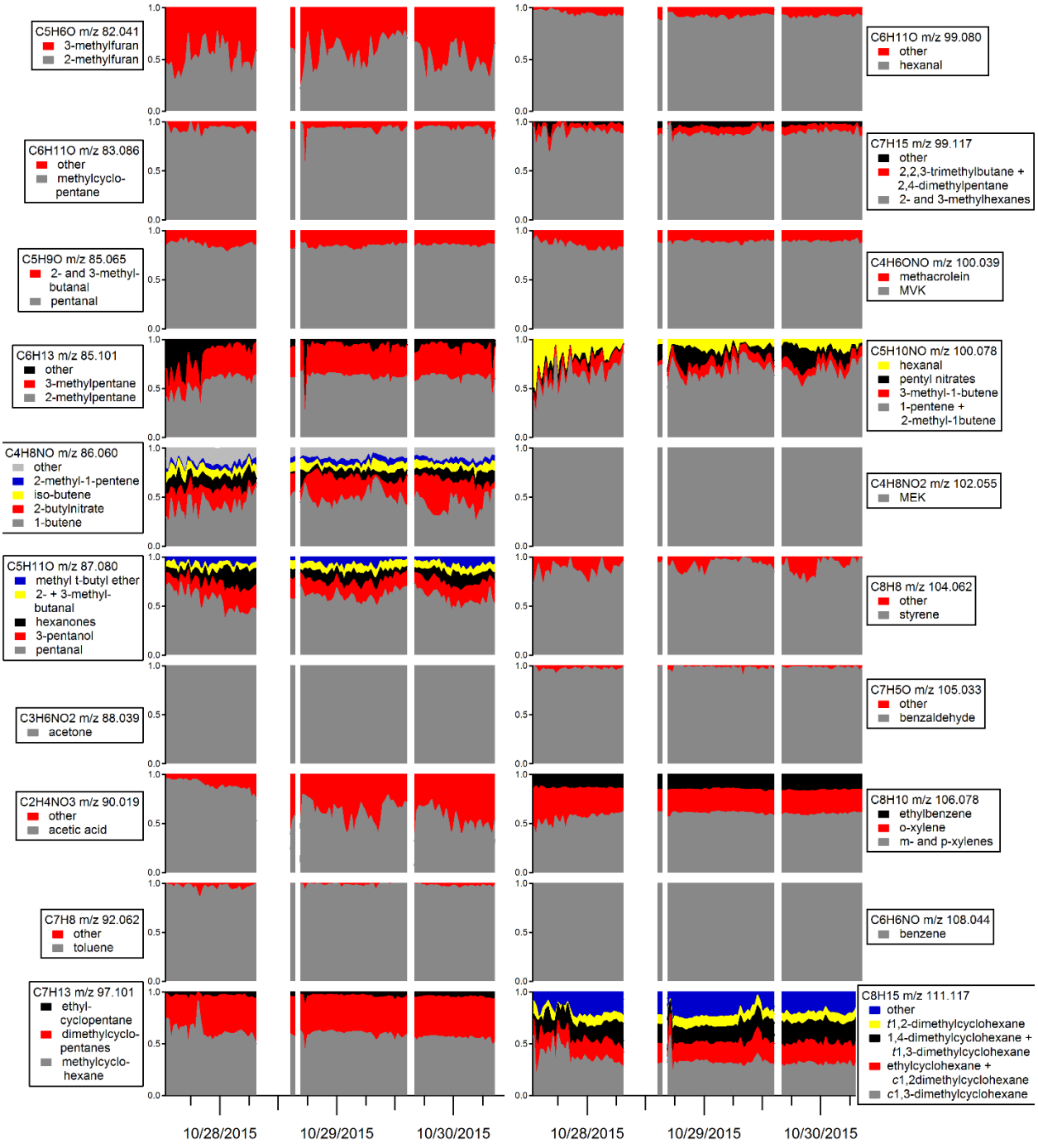

Figure S8. Figure S7, continued. Includes m/z 82-m/z 111.

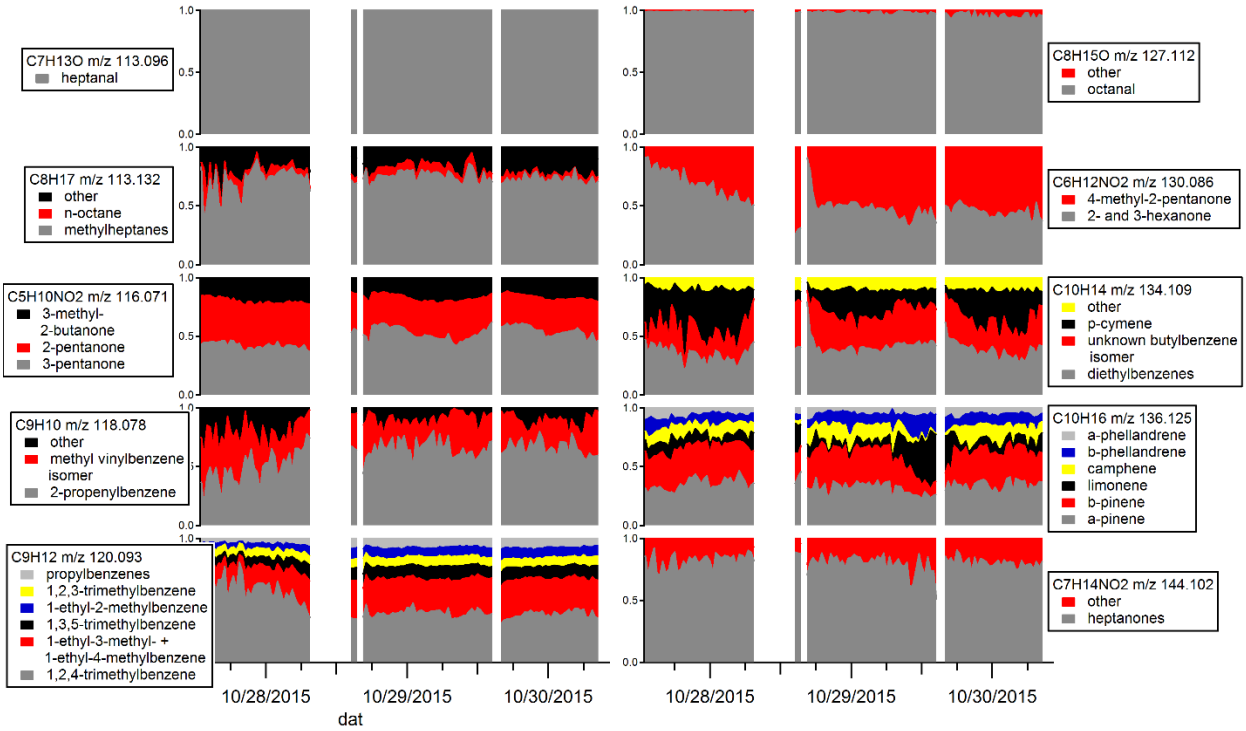

Figure S9. Figure S7, continued. Includes m/z 113-m/z 144.

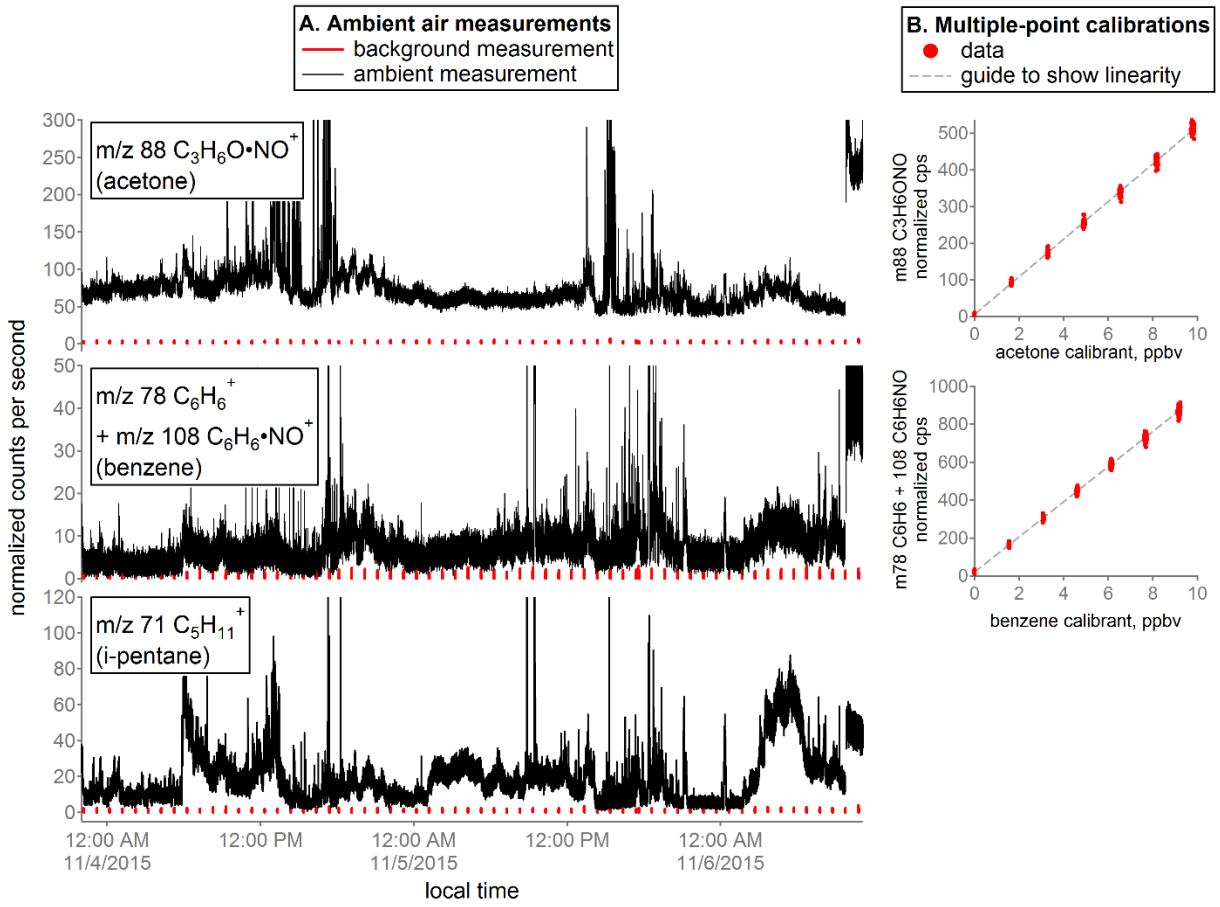

Figure S10. A. Background and ambient measurements taken during urban air sampling with the NO^+ ToF-CIMS. B. Example multiple-point calibrations of the NO^+ ToF-CIMS showing sensitivity linear with concentration.

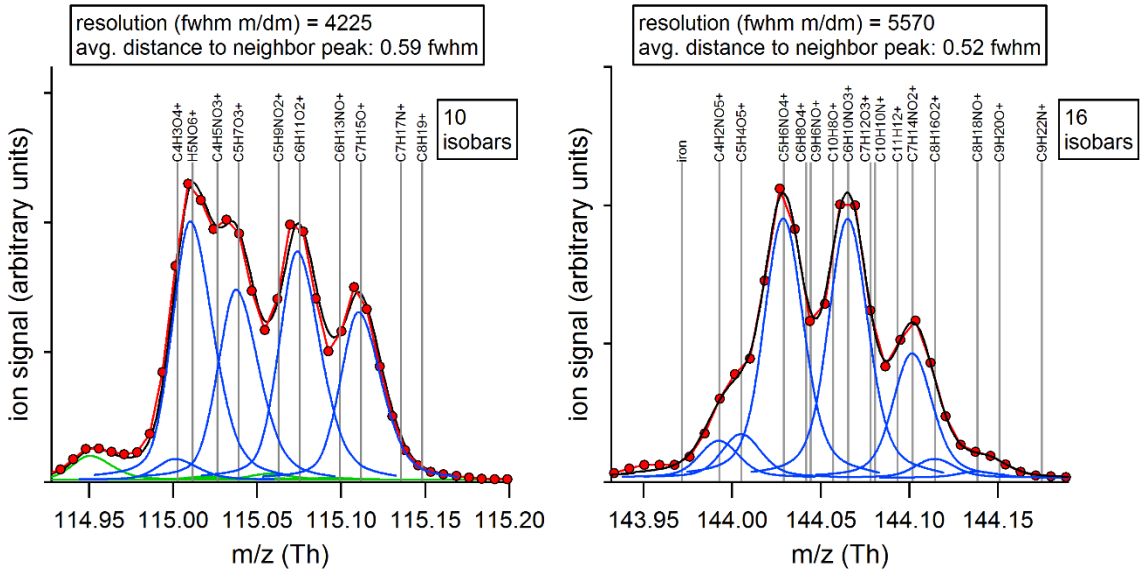

Figure S11. Example isobaric interferences for heptanone measured with H_3O^+ CIMS, at m/z 115 $C_7H_{14}OH^+$, and with NO^+ CIMS, at m/z 144 $C_7H_{14}ONO^+$. Although the resolution m/dm is better at m/z 144, there are more possible isobaric interferences and the average distance to neighboring peaks is smaller. The m/z range of each window is 10 FWHM. H_3O^+ ToF-CIMS mass spectrum courtesy of M. Coggon, collected in Boulder, CO in Dec. 2015.

Table S1. VOCs sampled in series GC-ToFCIMS laboratory experiments.

VOC name	Formula
alkanes	
ethane	C_2H_6
propane	C_3H_8
n-butane	C_4H_{10}
n-pentane	C_5H_{12}
n-hexane	C_6H_{14}
n-octane	C_8H_{18}
n-decane	$C_{10}H_{22}$
n-undecane	$C_{12}H_{26}$
i-butane (2-methylpropane)	C_4H_{10}
i-pentane (2-methylbutane)	C_5H_{12}
2,2-dimethylbutane	C_6H_{14}
2-methylpentane	C_6H_{14}
2,3-dimethylbutane	C_6H_{14}
3-methylpentane	C_6H_{14}
2,4-dimethylpentane	C_7H_{16}
2-methylhexane	C_7H_{16}
2,3-dimethylpentane	C_7H_{16}
3,3-dimethylpentane	C_7H_{16}
3-methylhexane	C_7H_{16}
2,2,4-trimethylpentane	C_8H_{18}
2,3,4-trimethylpentane	C_8H_{18}
2-methylheptane	C_8H_{18}
3-methylheptane	C_8H_{18}
4-methylheptane	C_8H_{18}
alkenes	
ethene	C_2H_4
propene	C_3H_6
ethyne	C_2H_2
trans-2-butene	C_4H_8
1-butene	C_4H_8
iso-butene (2-methylpropene)	C_4H_8
cis-2-butene	C_4H_8
1-pentene	C_5H_{10}
trans-2-pentene	C_5H_{10}
cis-2-pentene	C_5H_{10}
1-hexene	C_6H_{12}
isoprene	C_5H_8
cycloalkanes	
cyclopentane	C_5H_{10}
methylcyclopentane	C_6H_{12}
cyclohexane	C_6H_{12}
methylcyclohexane	C_7H_{14}
ethylcyclohexane	C_8H_{16}
1,1-dimethylcyclopentane	C_7H_{14}
ethylcyclopentane	C_7H_{14}
monoterpenes	
α-pinene	$C_{10}H_{16}$
β-pinene	$C_{10}H_{16}$
limonene	$C_{10}H_{16}$
camphene	$C_{10}H_{16}$
γ-terpinene	$C_{10}H_{16}$
α-phellandrene	$C_{10}H_{16}$
1,8-cineol	$C_{10}H_{16}$
3-carene + myrcene	$C_{10}H_{16}$
aromatics	
benzene	C_6H_6
toluene	C_7H_8
ethylbenzene	C_8H_{10}
m-xylene + p-xylene	C_8H_{10}
o-xylene	C_8H_{10}
vinylbenzene (styrene)	C_8H_8
isopropylbenzene	C_9H_{12}
n-propylbenzene	C_9H_{12}
1-ethyl,3-methylbenzene + 1-ethyl,4-methylbenzene	C_9H_{12}
1,3,5-trimethylbenzene	C_9H_{12}
1-ethyl,2-methylbenzene	C_9H_{12}
1,2,4-trimethylbenzene	C_9H_{12}
1,2,3-trimethylbenzene	C_9H_{12}
1,3-diethylbenzene	$C_{10}H_{14}$
1,4-diethylbenzene	$C_{10}H_{14}$
aldehydes	
acetaldehyde	C_2H_4O
propanal	C_3H_6O
butanal	C_4H_8O
pentanal	$C_5H_{10}O$
hexanal	$C_6H_{12}O$
heptanal	$C_7H_{14}O$
octanal	$C_8H_{16}O$
methacrolein	C_4H_6O
ketones	
acetone	C_3H_6O
2-butanone (MEK)	C_4H_8O
3-methyl-2-butanone	$C_5H_{10}O$
2-pentanone	$C_5H_{10}O$
3-pentanone	$C_5H_{10}O$
3-hexanone	$C_6H_{12}O$
methyl vinyl ketone (MVK)	C_4H_6O
other	
methanol	CH_4O
ethanol	C_2H_6O
2-propanol	$C3H_8O$
methyl-*t*-butyl ether (MTBE)	$C_5H_{12}O$
acetonitrile	C_2H_3N
3-methyfuran	C_5H_6O