Supplementary information for Evaluation of NO^+ reagent ion chemistry for on-line measurements of atmospheric volatile organic compounds

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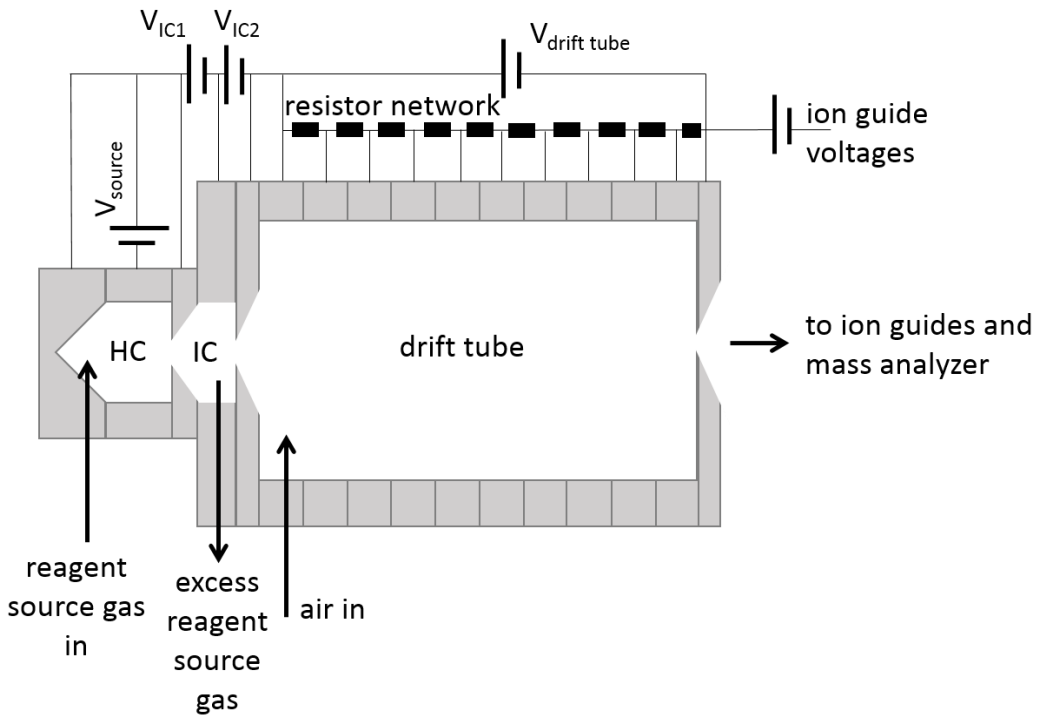

Figure S1. Ion source and drift tube schematic.

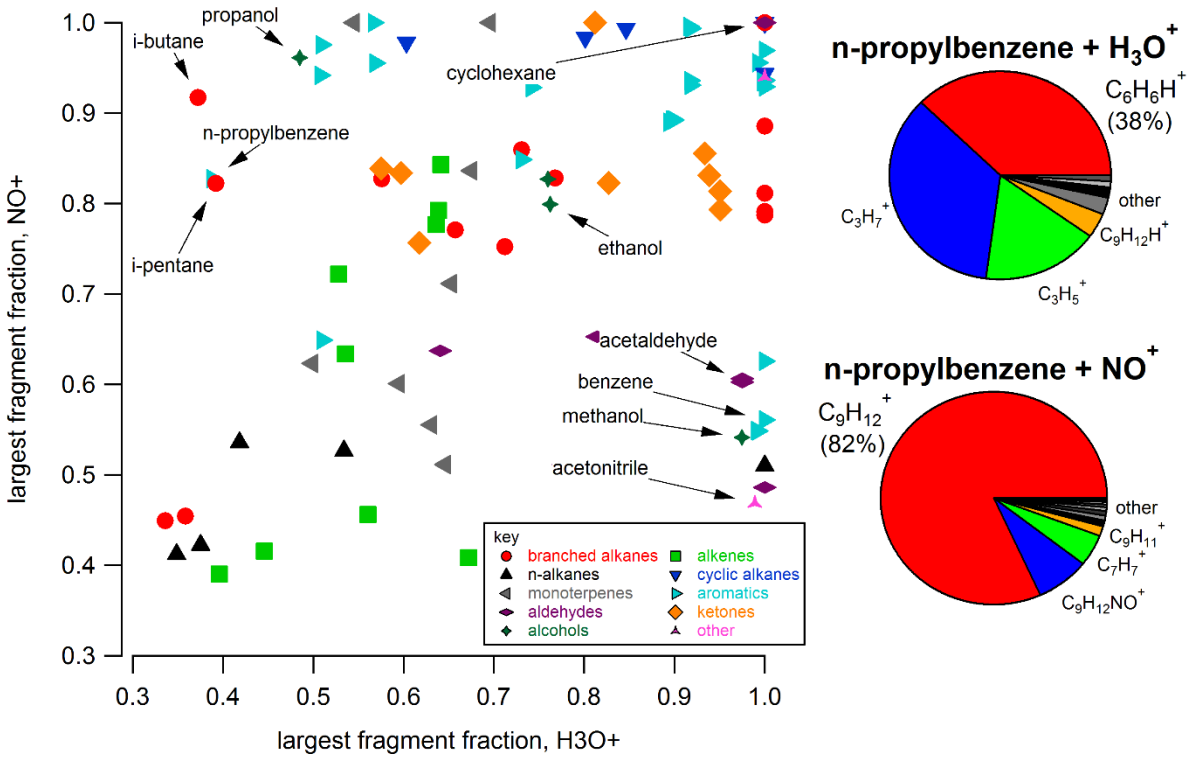

Figure S2. Comparison of product ion distributions between NO^+ CIMS and H_3O^+ CIMS. The complete product ion distribution of n-propylbenzene is shown as an example of a compound with a complex mass spectrum resulting from H3O+ chemistry, and a simple mass spectrum resulting from NO+ chemistry.

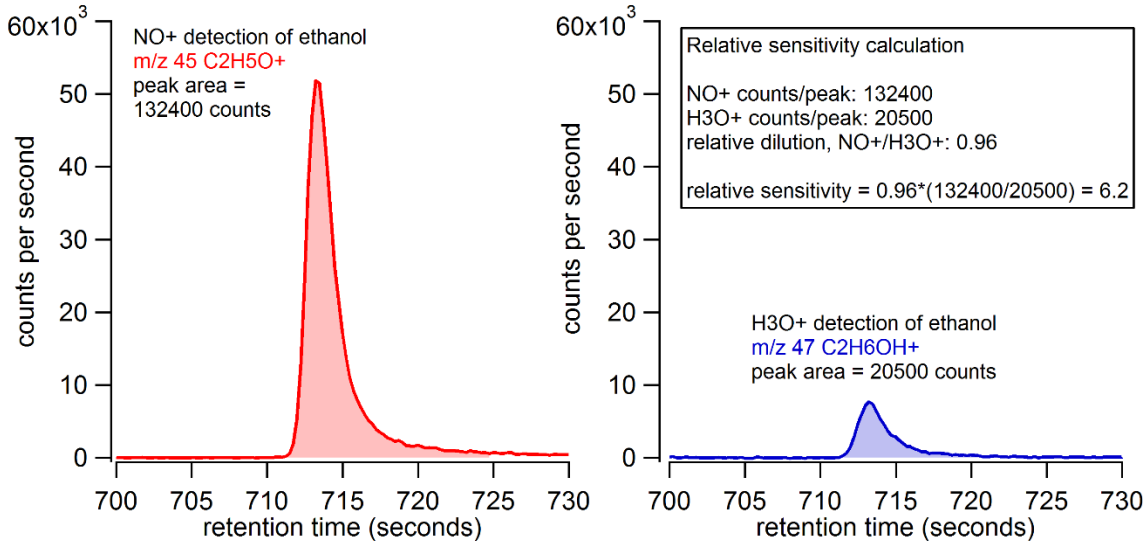

Figure S3. Example chromatograms and relative sensitivity calculation of ethanol for Table 2.

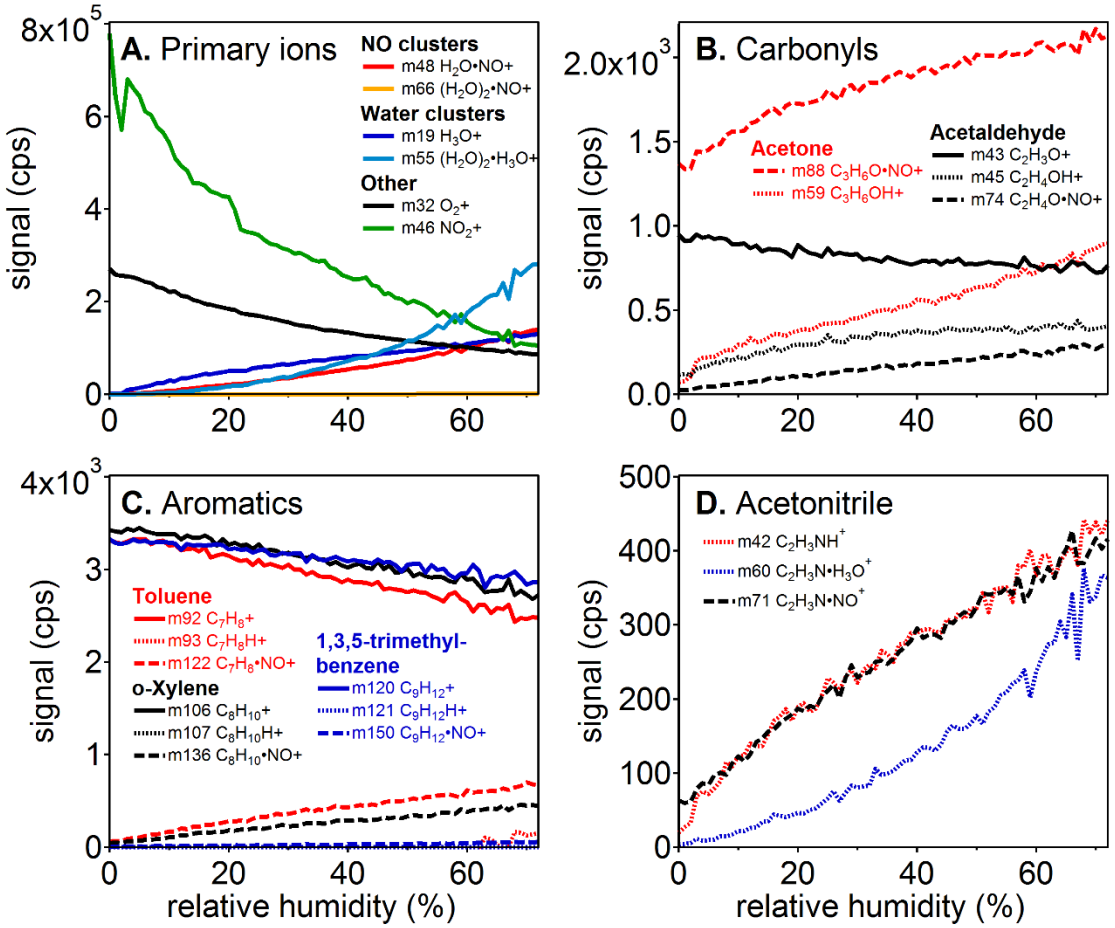

Figure S4. Humidity dependence of primary ions and VOCs. (a) Impurity ions and water clusters. (b) Carbonyls. (c) Aromatics. (d) Acetonitrile. Acetonitrile is detected with poor sensitivity using NO^+; the NO^+ and H_3O^+ products are approximately equal in magnitude.

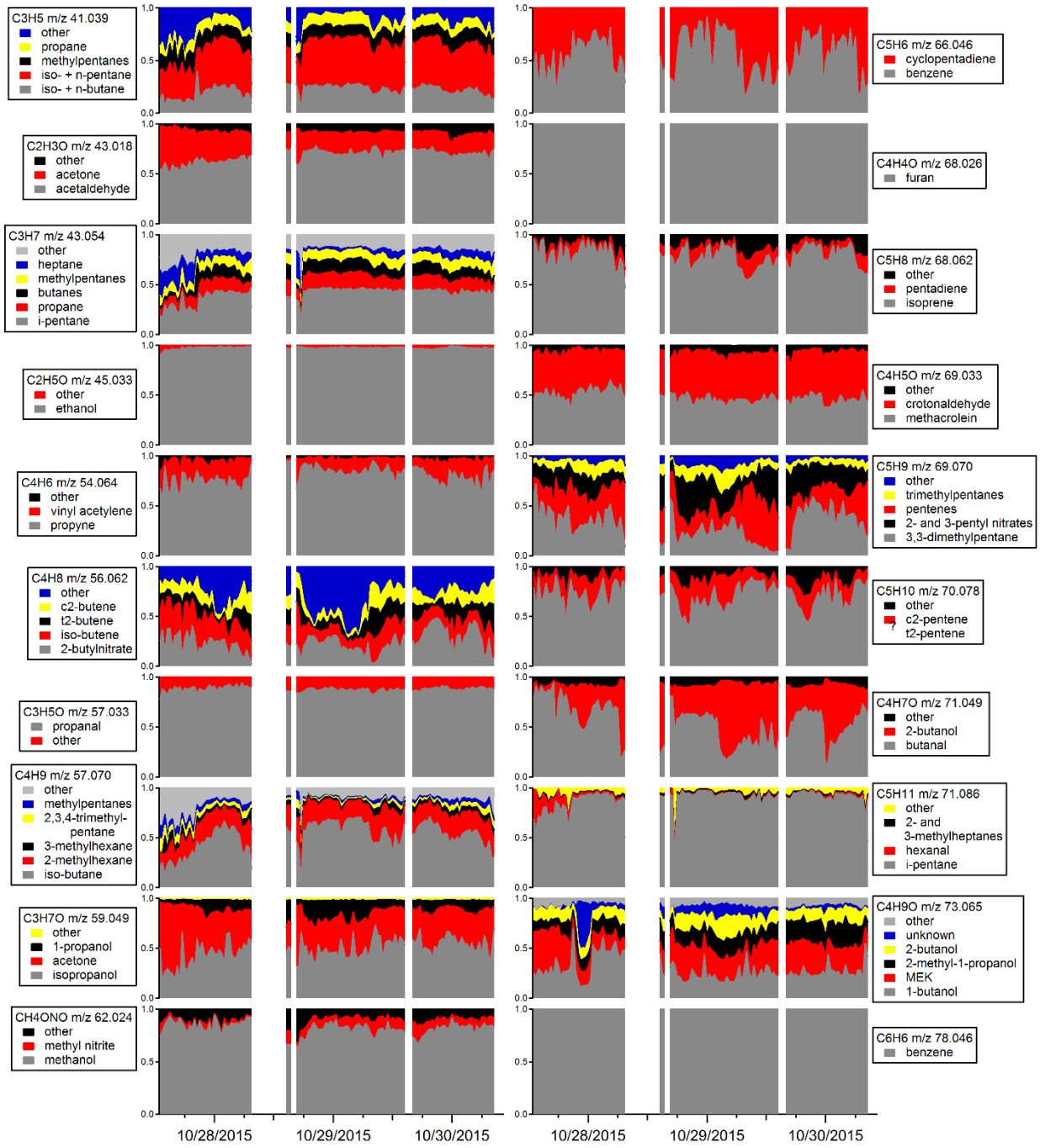

Figure S5. Speciated contributions to various NO+ CIMS masses, in urban air. Values on Y-axes are the fractional contribution of each VOC to total signal. Includes m/z 41-m/z 78.

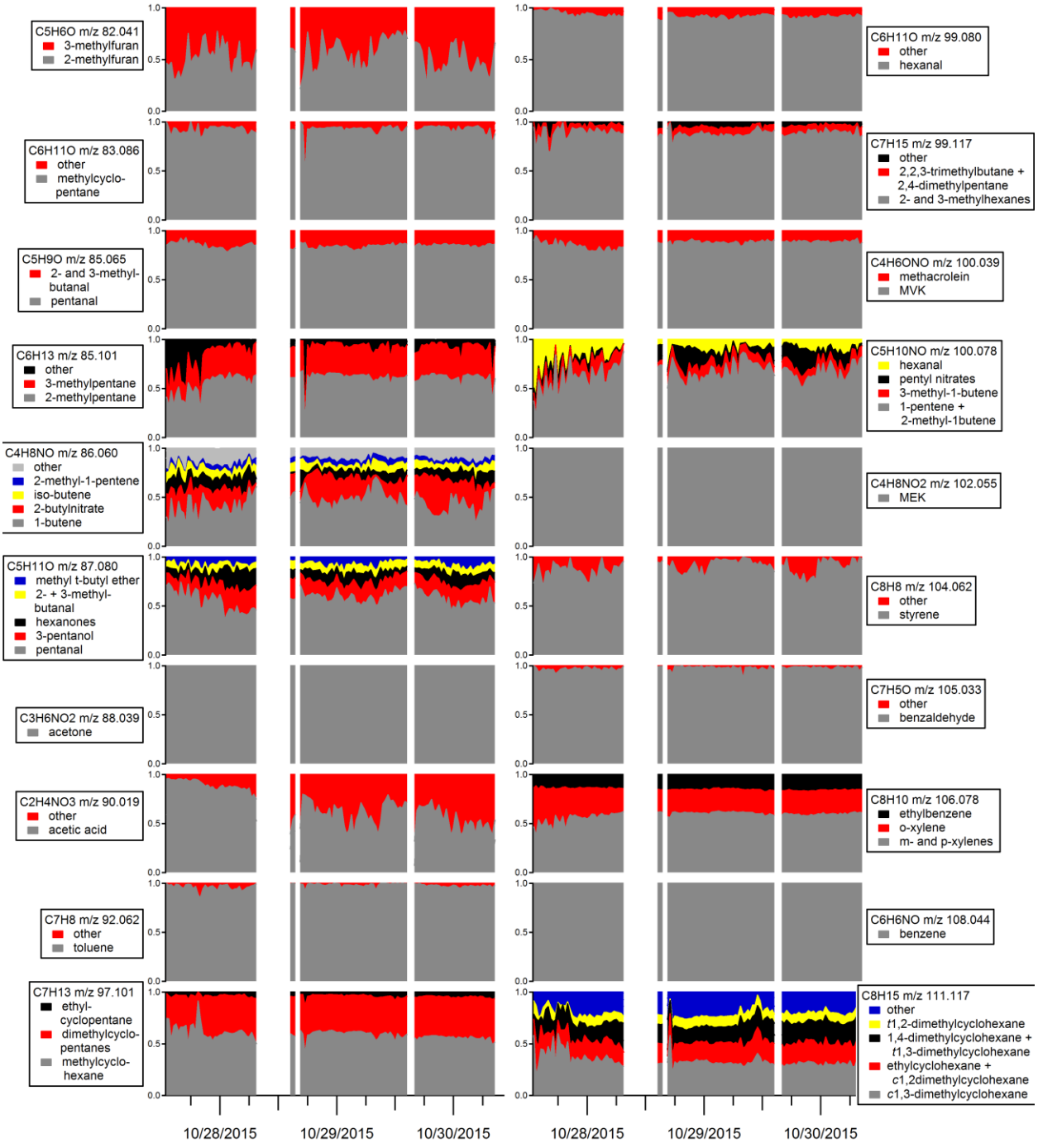

Figure S6. Figure S5, continued. Includes m/z 82-m/z 111.

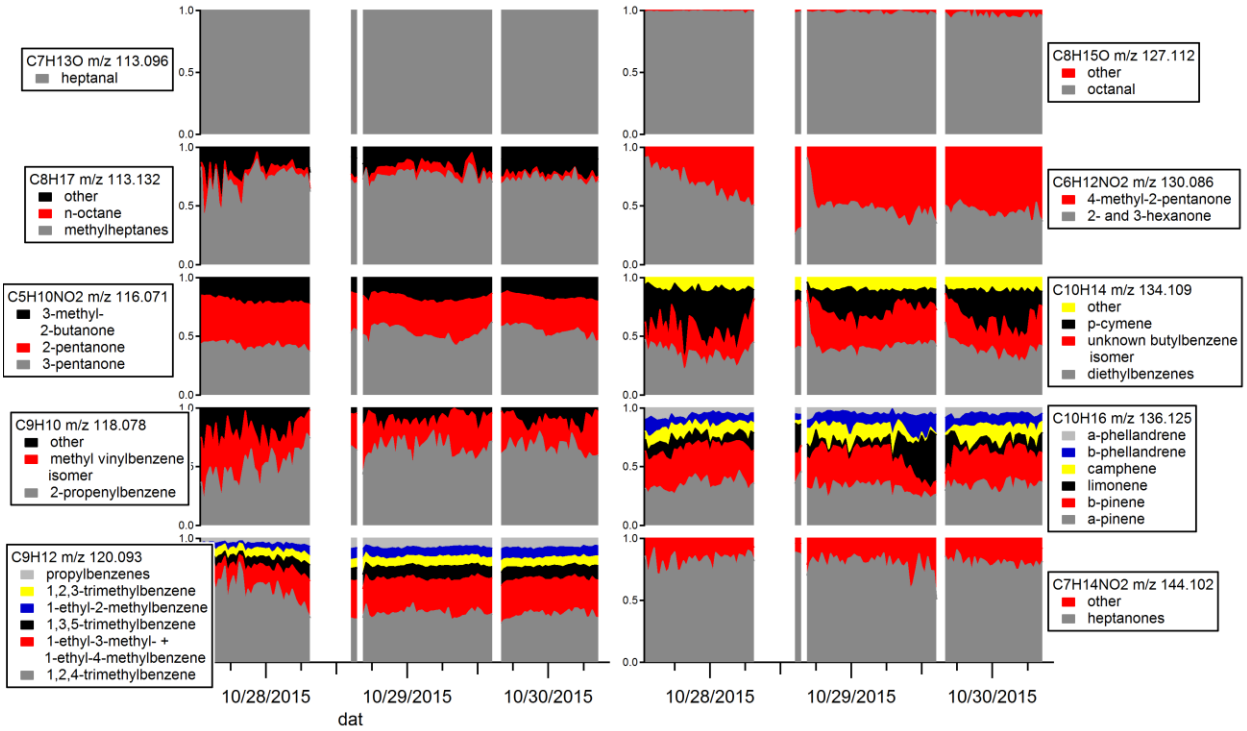

Figure S7. Figure S5, continued. Includes m/z 113-m/z 144.

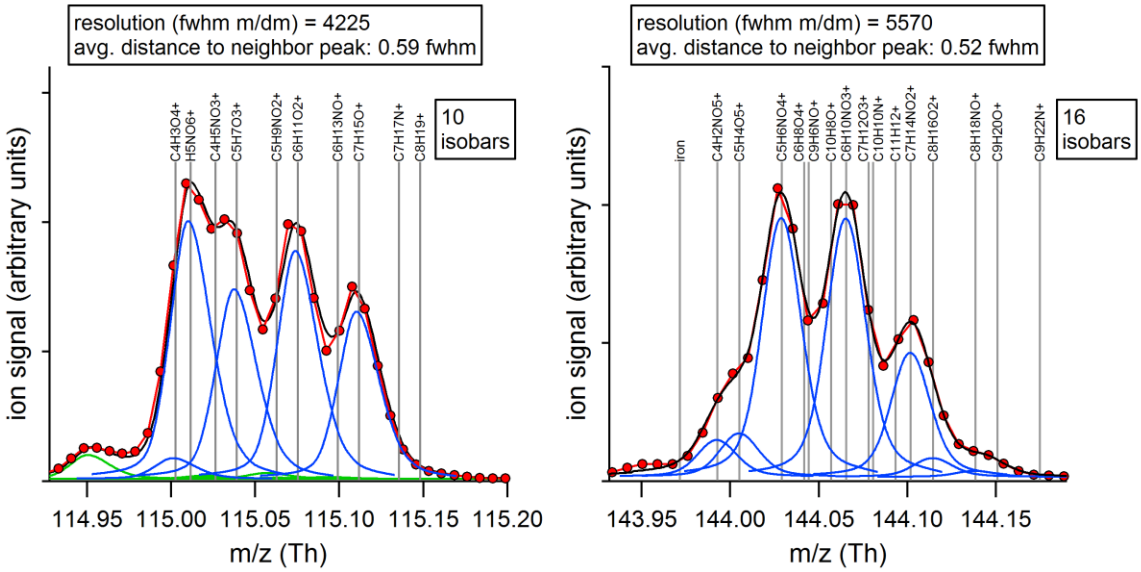

Figure S8. Example isobaric interferences for heptanone measured with H_3O^+ CIMS, at m/z 115 $C_7H_{14}OH^+$, and with NO^+ CIMS, at m/z 144 $C_7H_{14}ONO^+$. Although the resolution m/dm is better at m/z 144, there are more possible isobaric interferences and the average distance to neighboring peaks 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