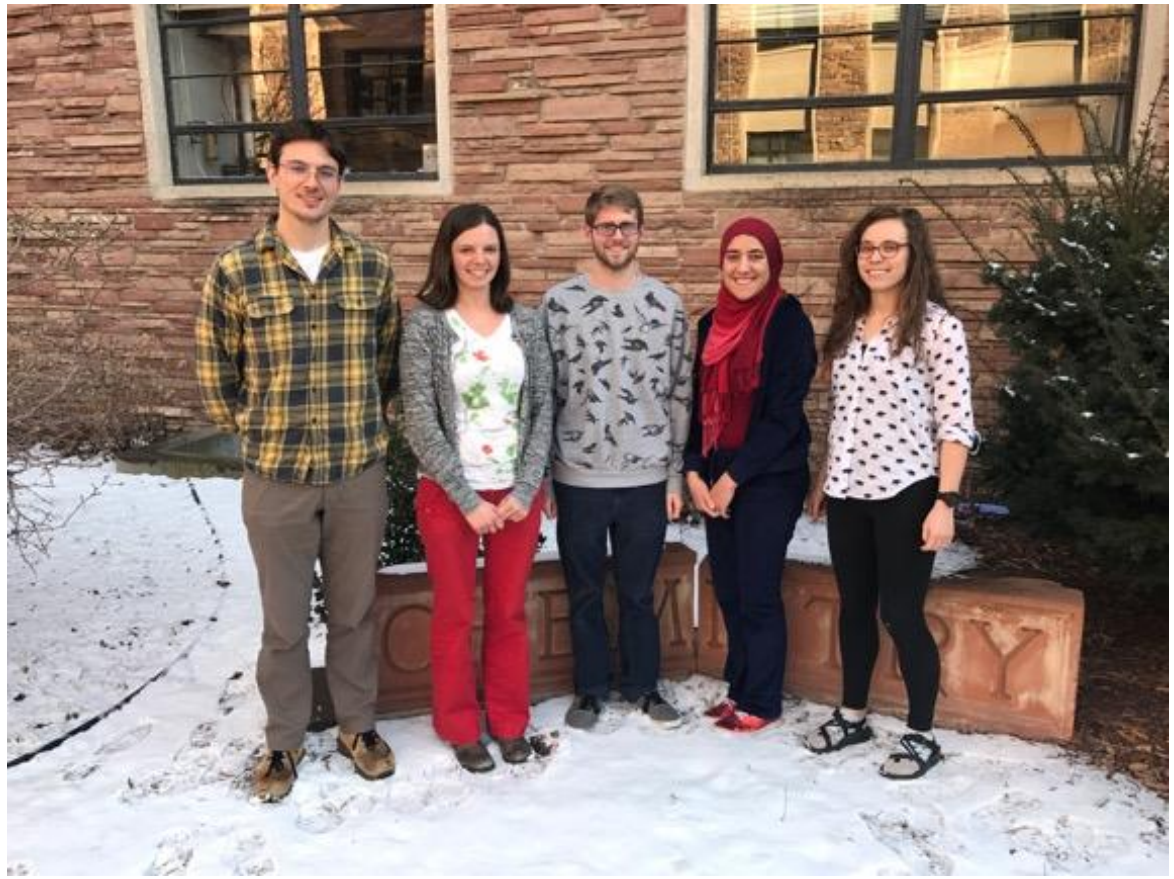
Detection of Novel Organic Nitrogen Compounds with Protonated Ethanol Cluster Chemical Ionization Mass Spectrometry



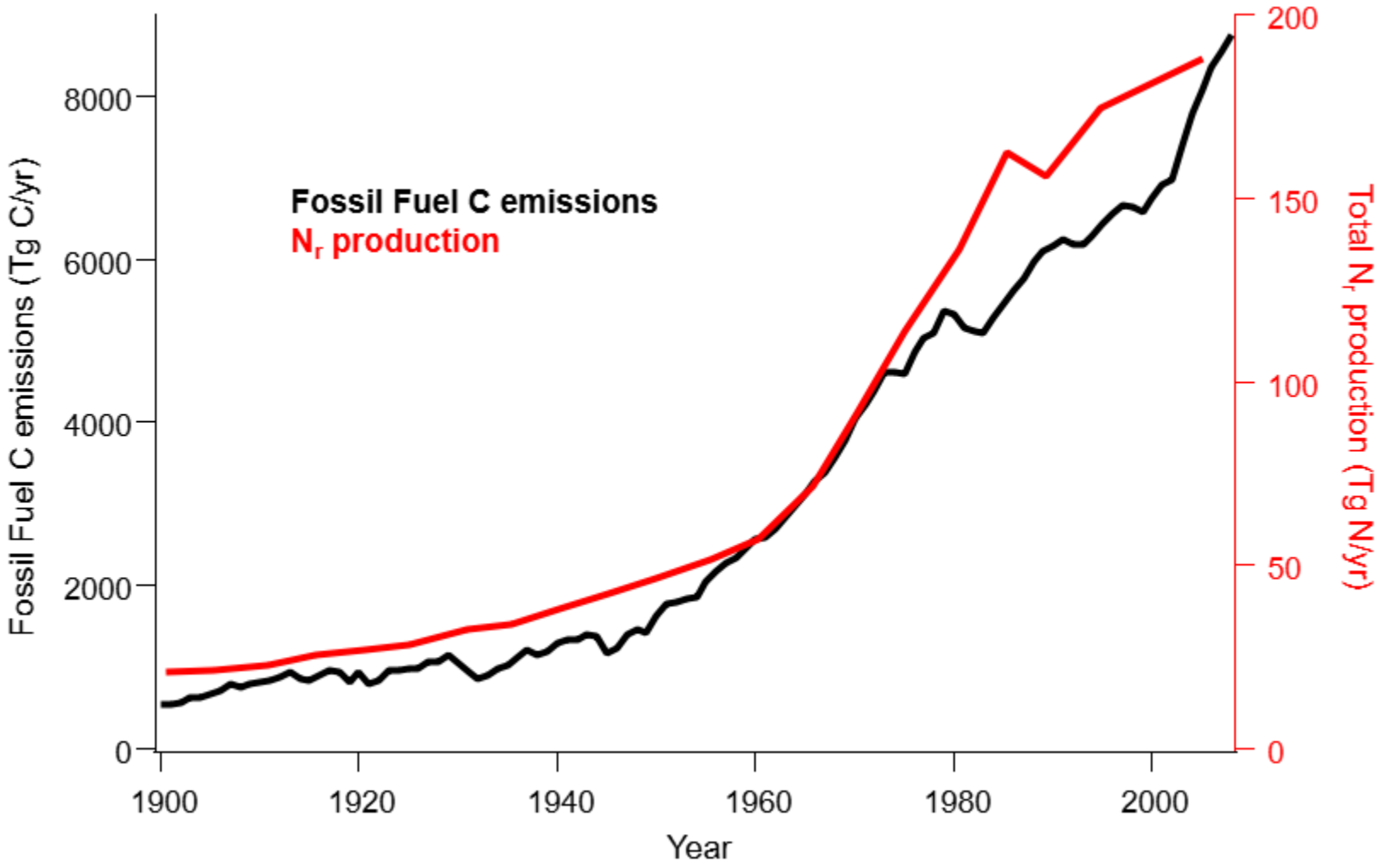
Ellie Browne

Mitchell Alton, Aroob Abdelhamid, Jennifer Berry

University of Colorado Boulder

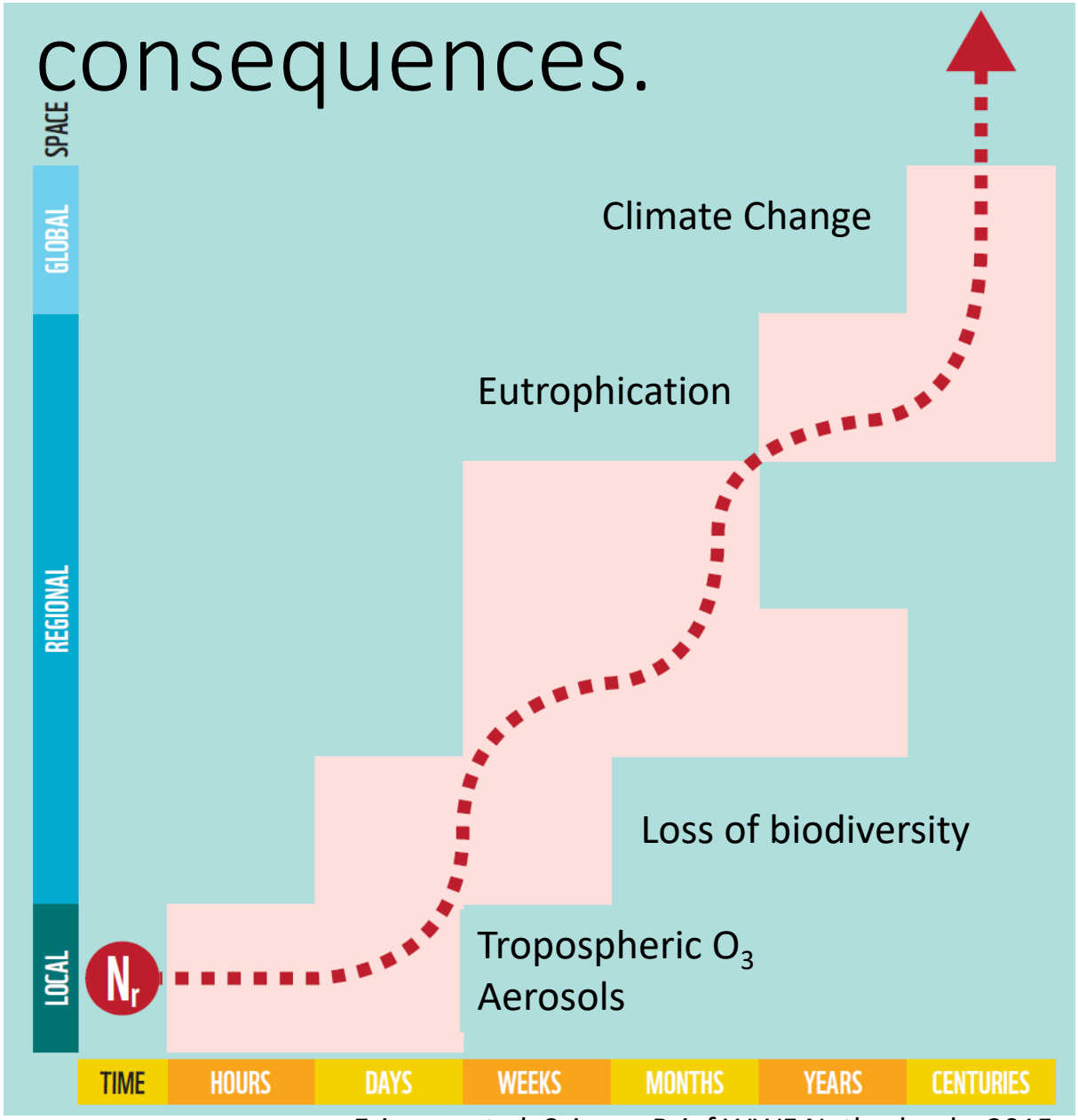
CIRES

Anthropogenic activities have radically altered the N cycle.

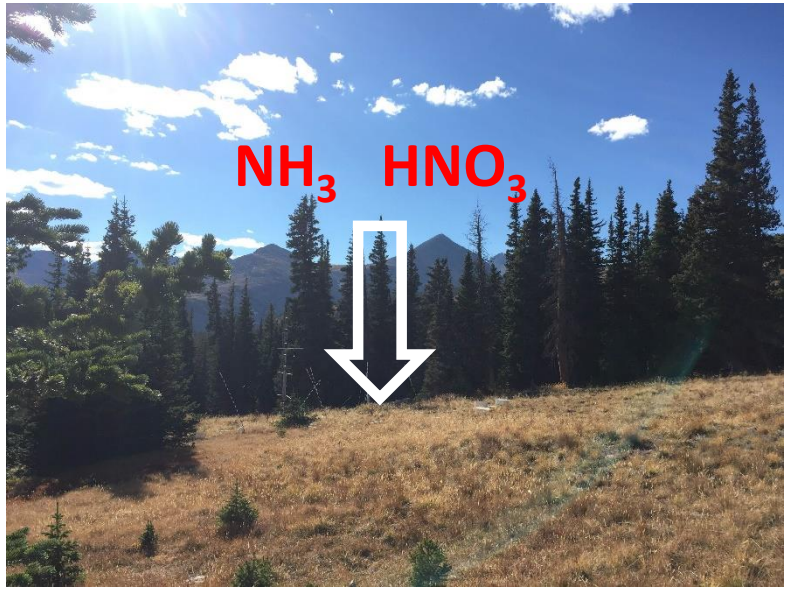


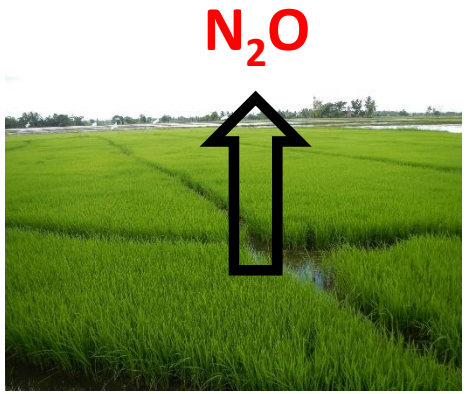
Adapted from Erisman et al, Curr. Opin. Environ. Sustain., 2011.

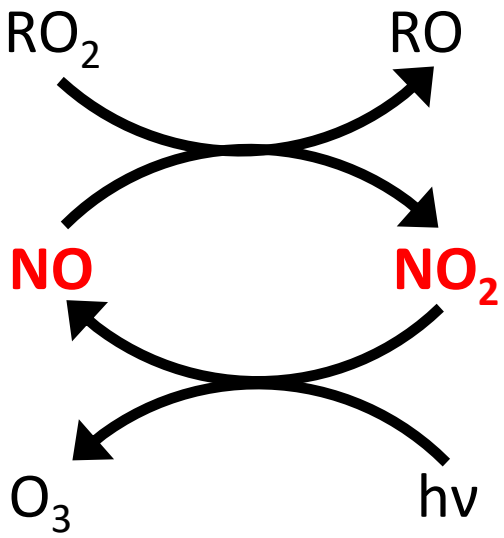
N cycle modifications have led to unintended consequences.



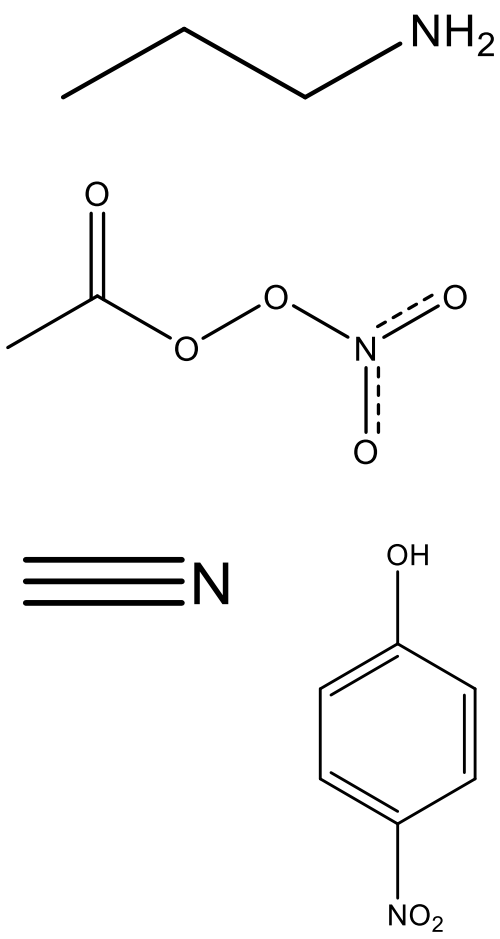
Erisman et al, Science Brief WWF Netherlands, 2015.

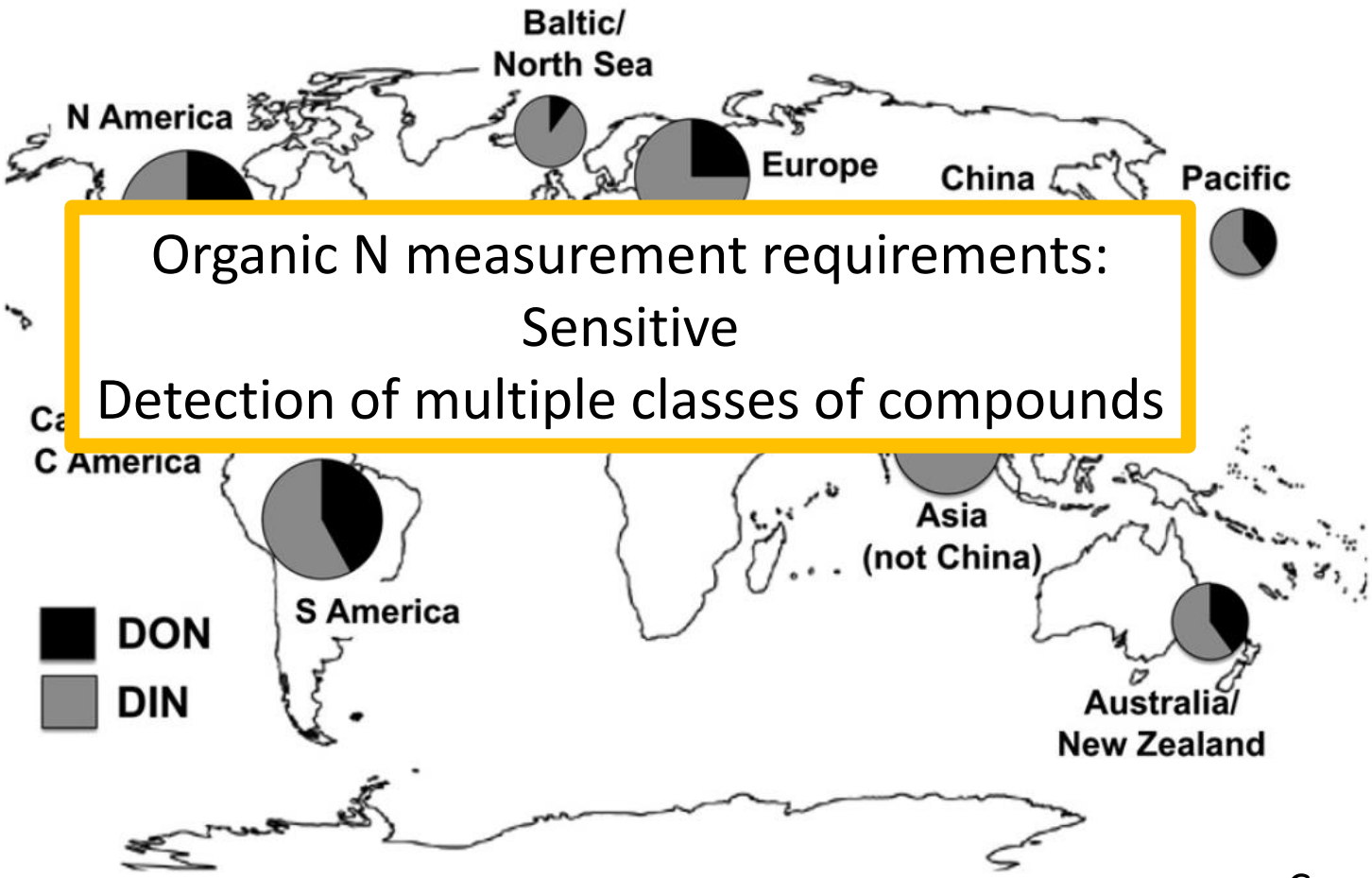




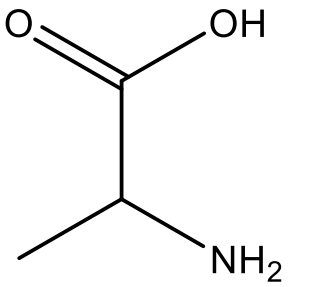


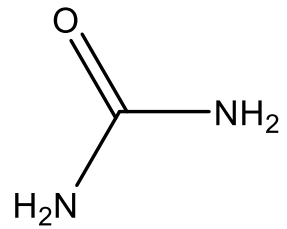
Organic N compounds account for a large fraction of dissolved Nr around the world.

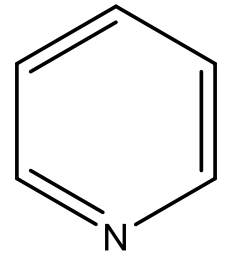




Organic N measurement requirements:
Sensitive
Detection of multiple classes of compounds







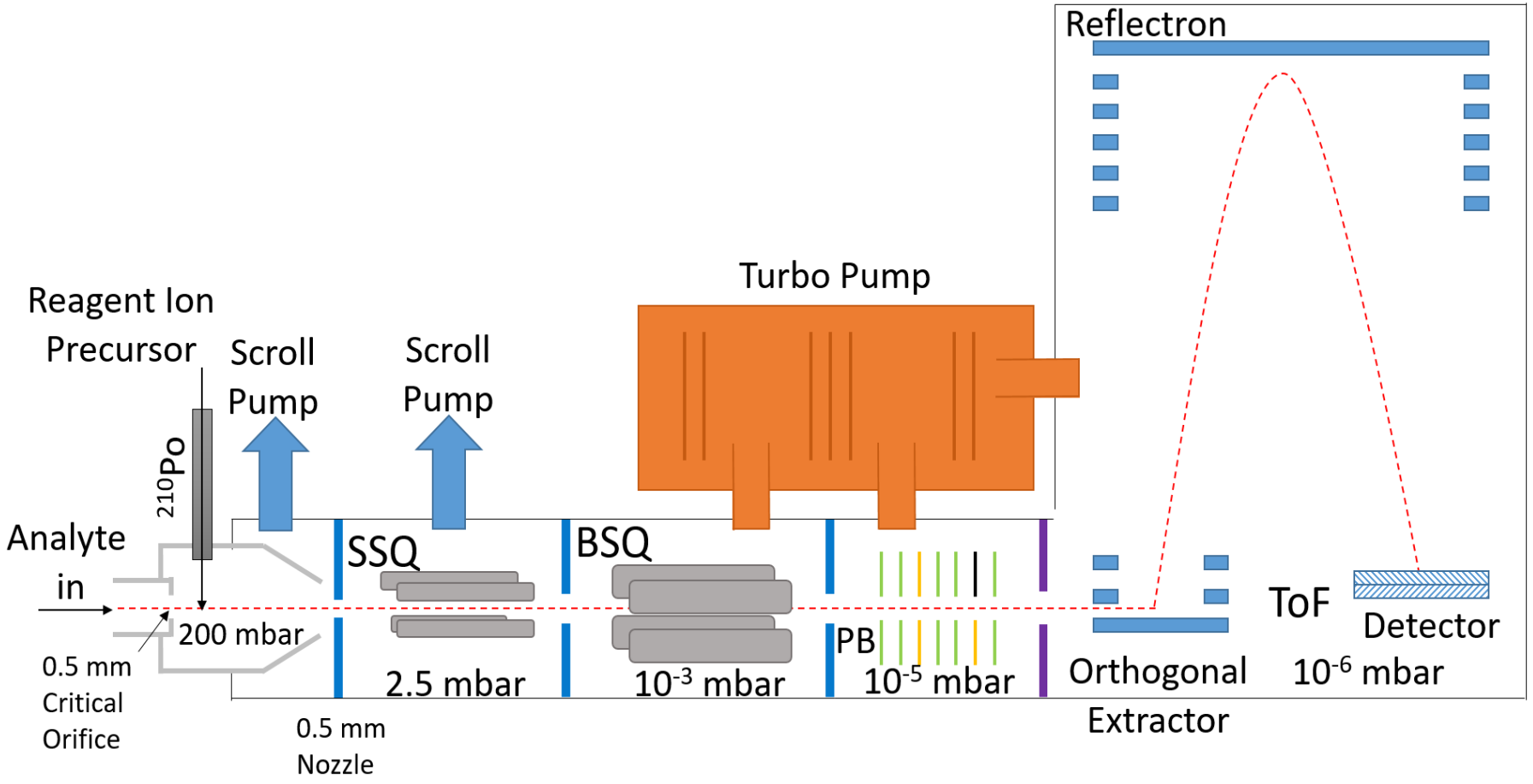
Cornell, *Environ. Poll.*, 2011.

Protonated Ethanol CIMS (EtOH-CIMS)

$$(C_2H_5OH)_nH^+ + B \rightarrow (C_2H_5OH)_yBH^+ + (n-y)C_2H_5OH$$

Ligand Switching

Proton Transfer



EtOH-CIMS provides sensitive measurement of organic N compounds.

$$(C_2H_5OH)_nH^+ + B \rightarrow (C_2H_5OH)_yBH^+ + (n-y)C_2H_5OH$$ Ligand Switching

$$(C_2H_5OH)_nH^+ + B \rightarrow BH^+ + nC_2H_5OH$$ Proton Transfer

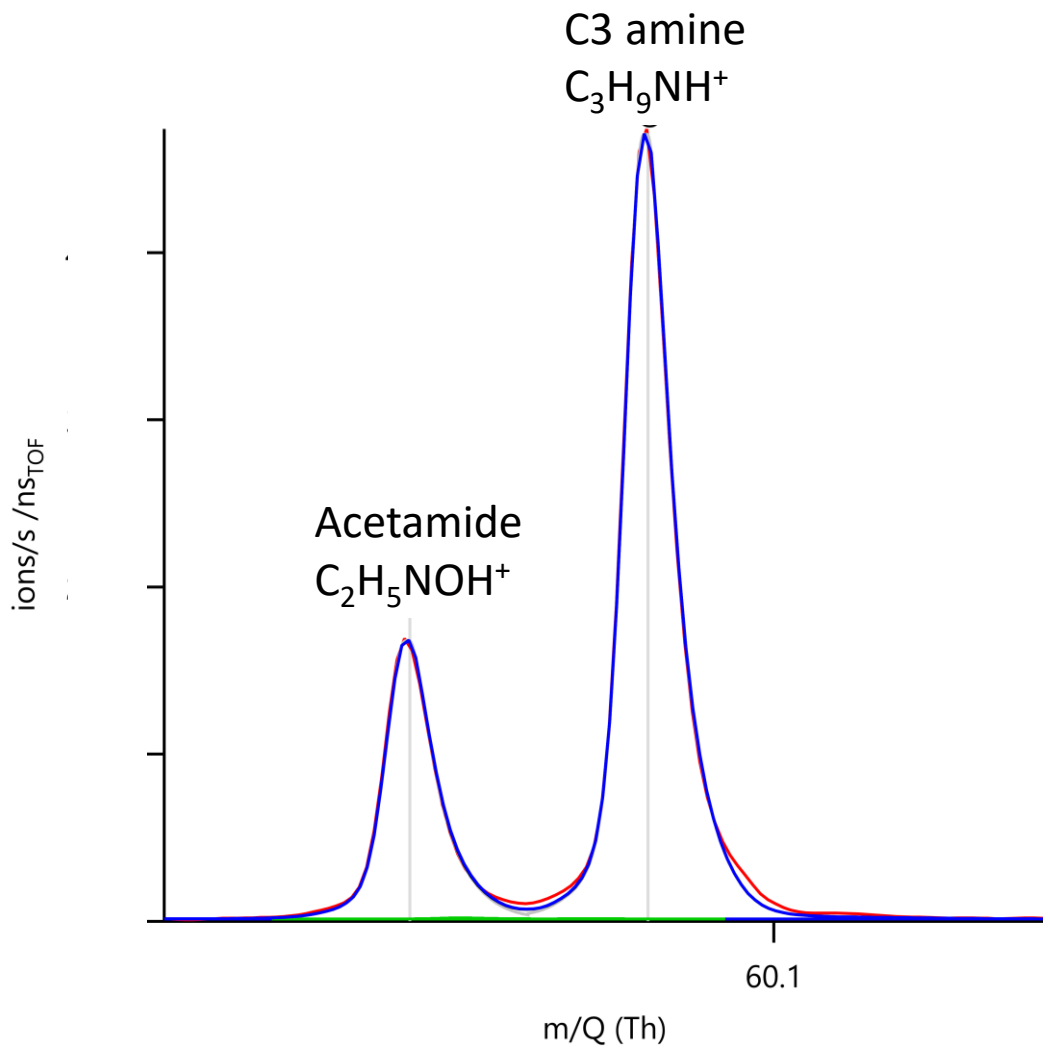
Quad-MS for detection of amines and NH_3

Nowak et al., *J. Geophys. Res.,* 2002.

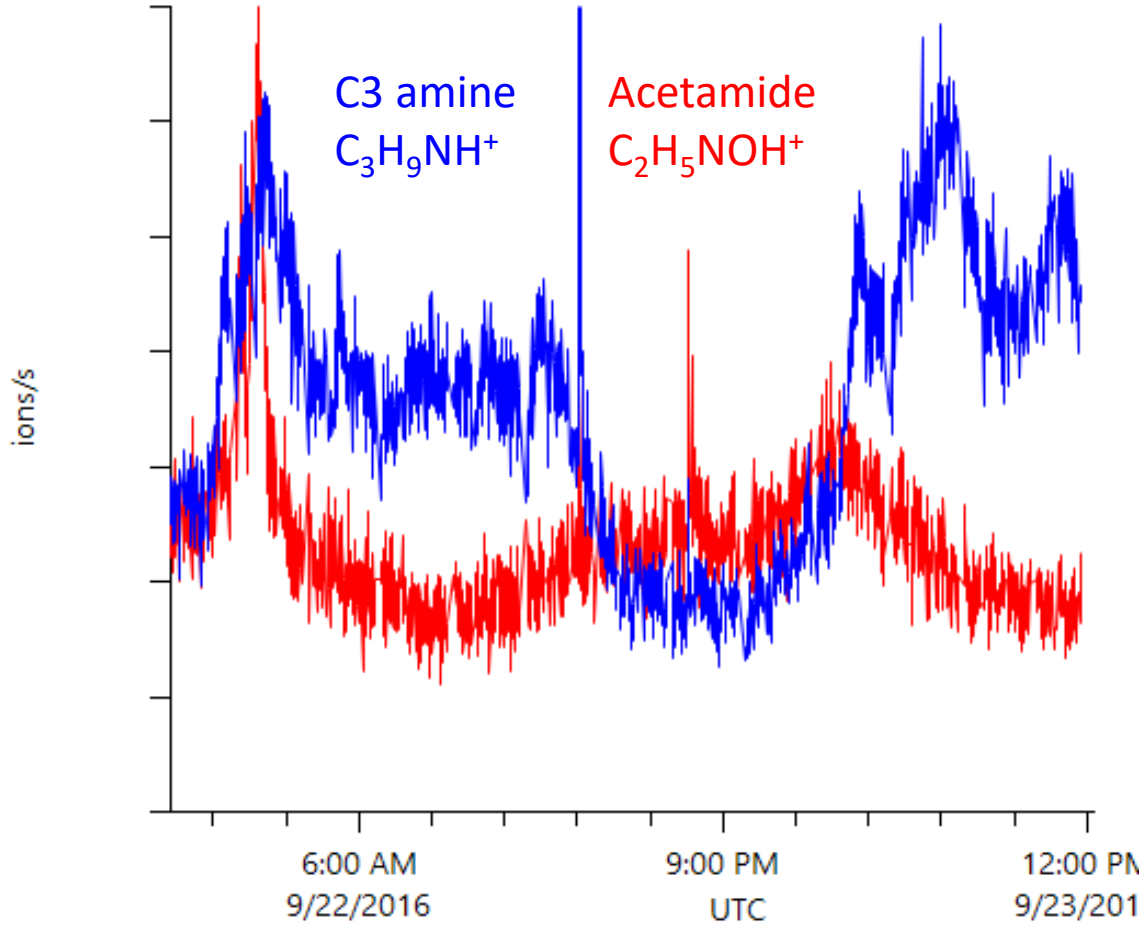
Yu and Lee, *Environ. Chem.,* 2012.

Compound	Sensitivity (Hz/ppt/MHz)	LOD (ppt)
Dimethyl amine	4.0	25
Methyl amine	1.6	56
Diethyl amine	6.5	5.4
Pyridine	148	1.7
Imidazole	33	24

High resolving power MS is necessary for organic N measurement.

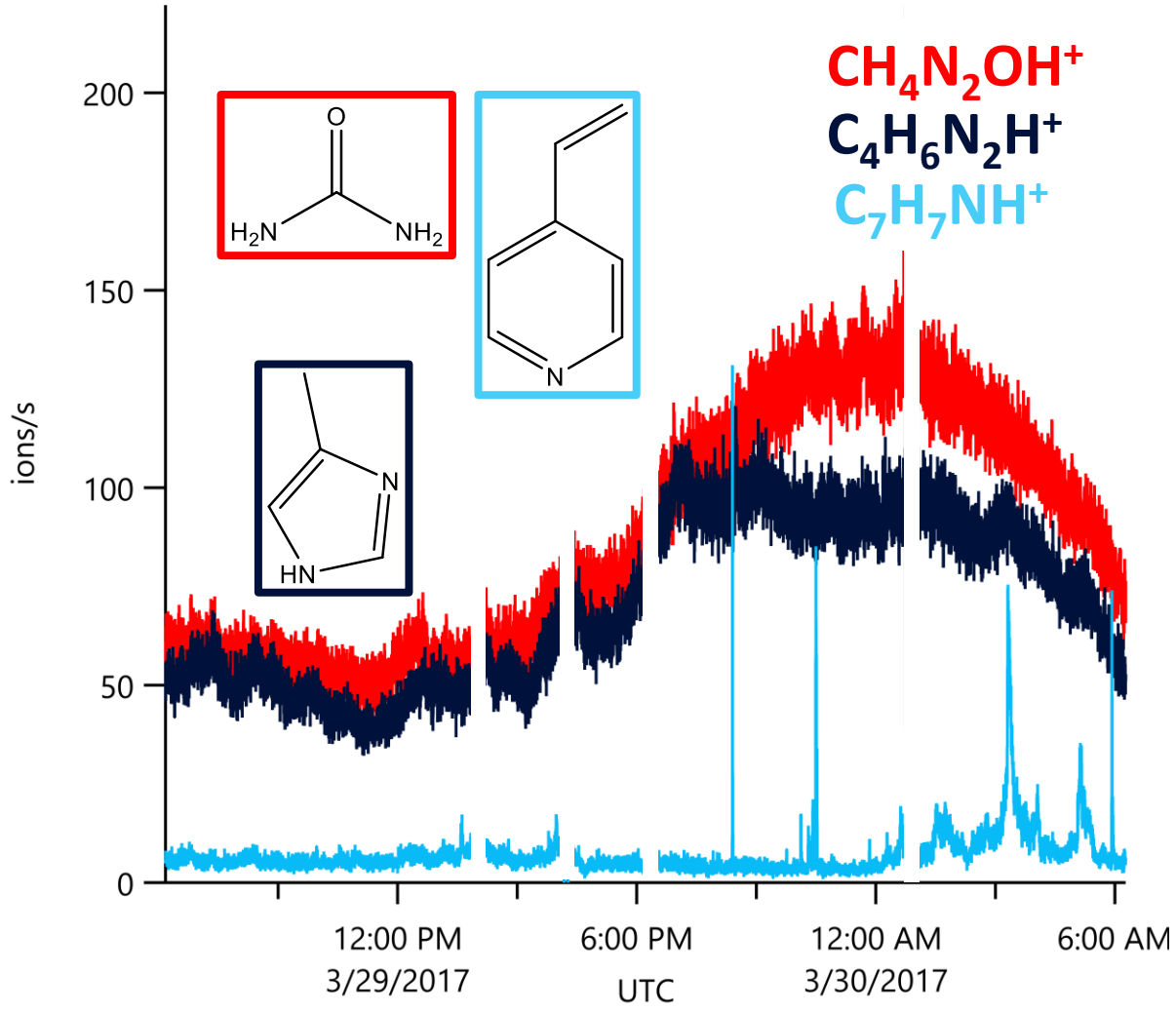


Ambient measurements
Lamont, Oklahoma



Also Yao et al., *Atmos. Chem. Phys.,* 2015.

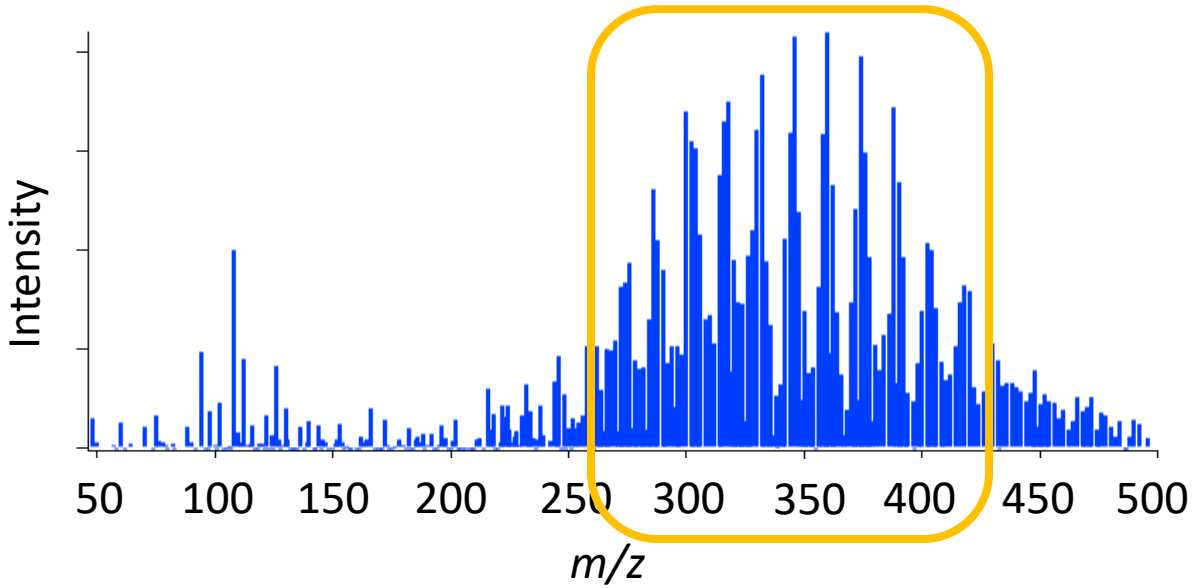
Detection of multiple classes of compounds.

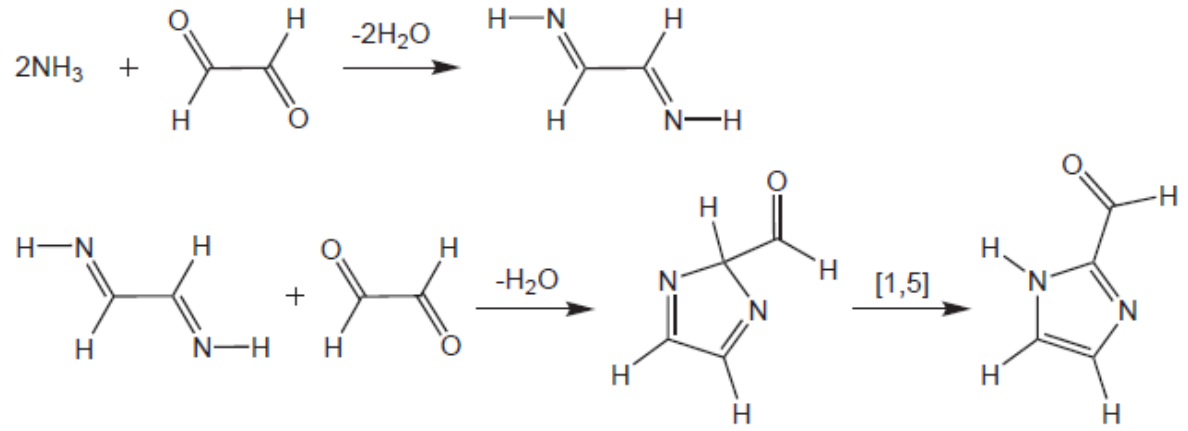


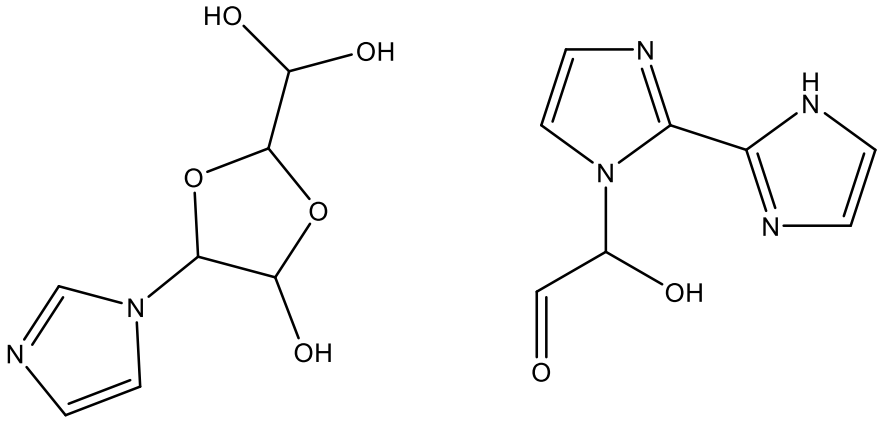
Ambient measurements
Boulder, CO

Application of EtOH CIMS

N, NO, NO_2, NO_3
C17-C29
DBE of 7+







Galloway et al., *Atmos. Chem. Phys.*, 2009.
Kampf et al., *Atmos. Chem. Phys.*, 2012.

Application of EtOH CIMS

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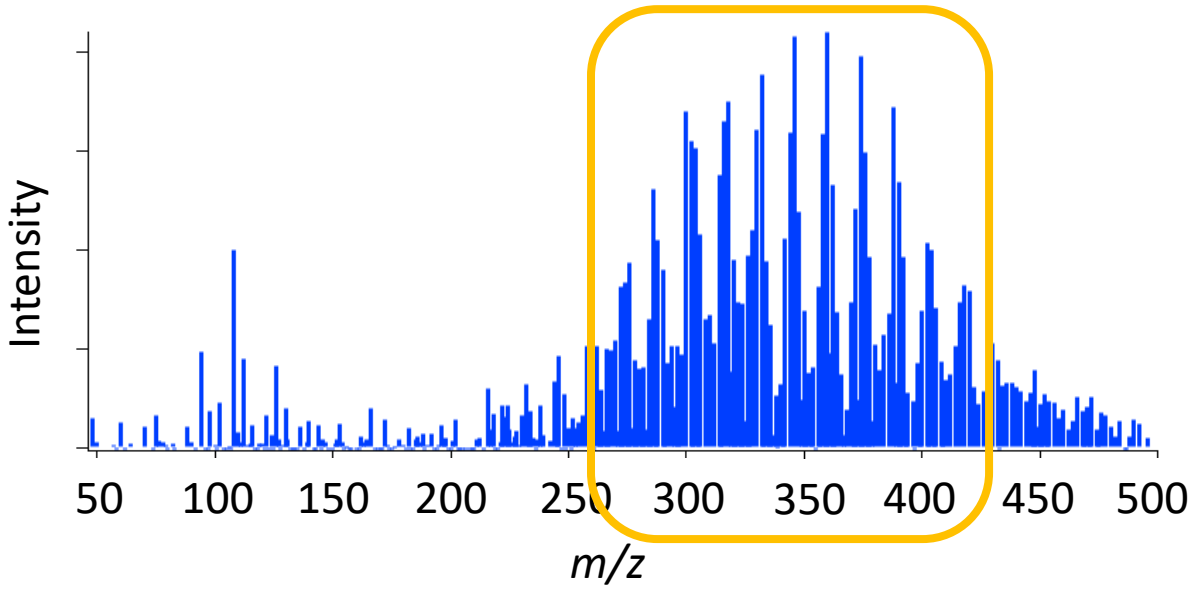
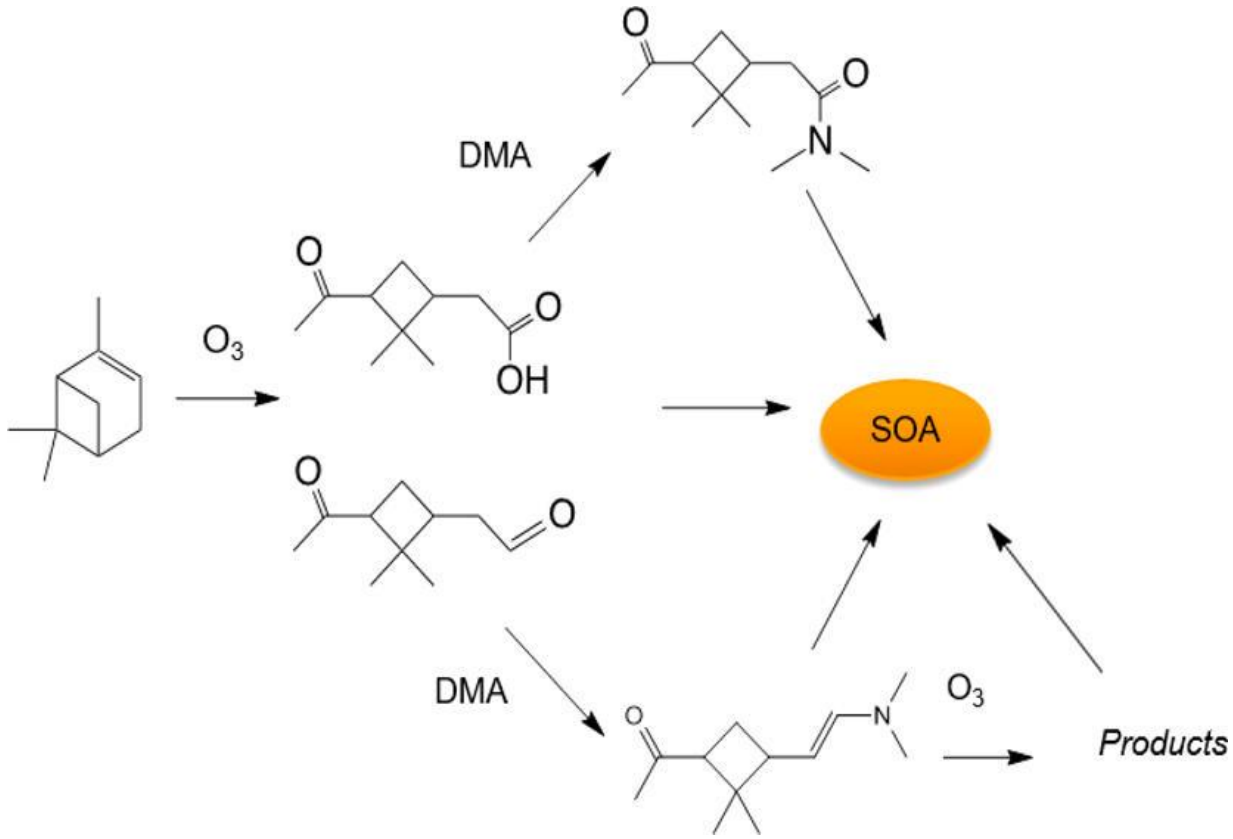


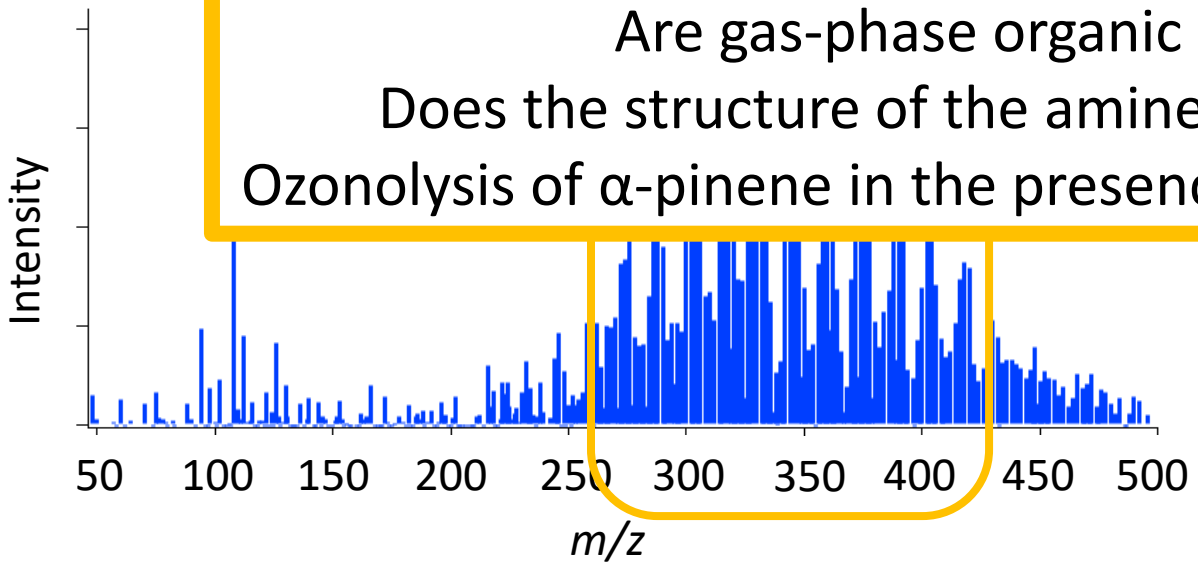


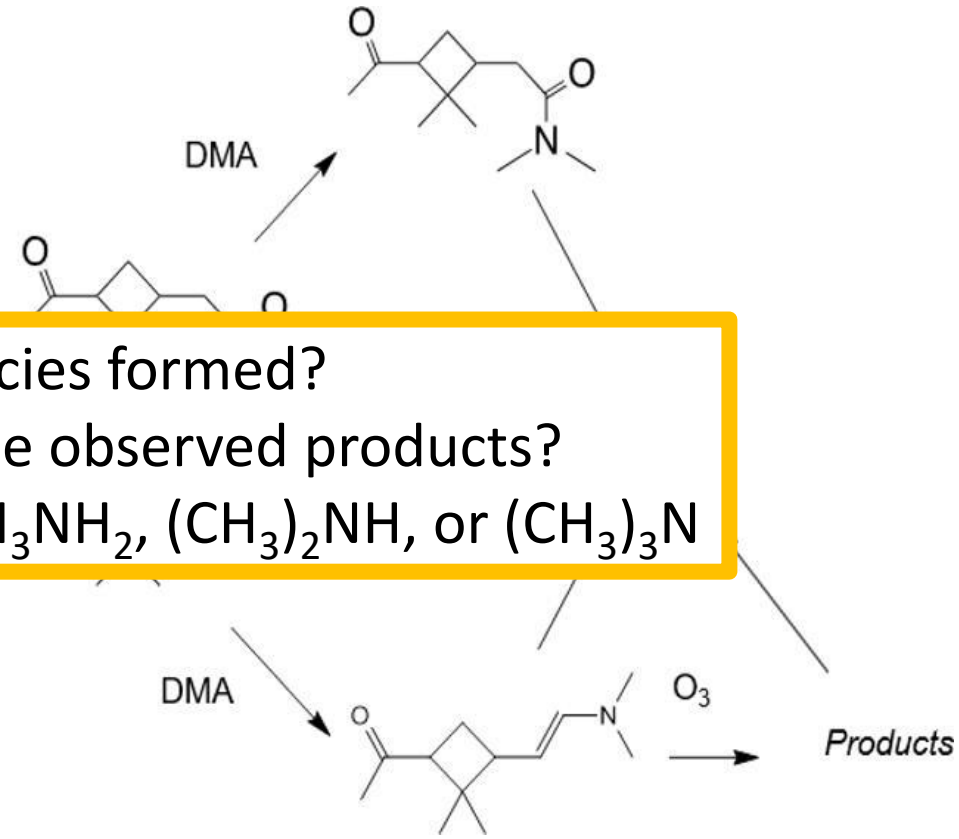
Duporté et al., *ES&T,* 2016, 2017.

Application of EtOH CIMS

N, NO, NO_2, NO_3
C17-C29
DBE of 7+

Are gas-phase organic nitrogen species formed?
Does the structure of the amine influence the observed products?
Ozonolysis of α-pinene in the presence of NH_3, CH_3NH_2, $(CH_3)_2NH$, or $(CH_3)_3N$





Duporté et al., *ES&T,* 2016, 2017.

Experimental Set-up

α-pinene
50 ppb

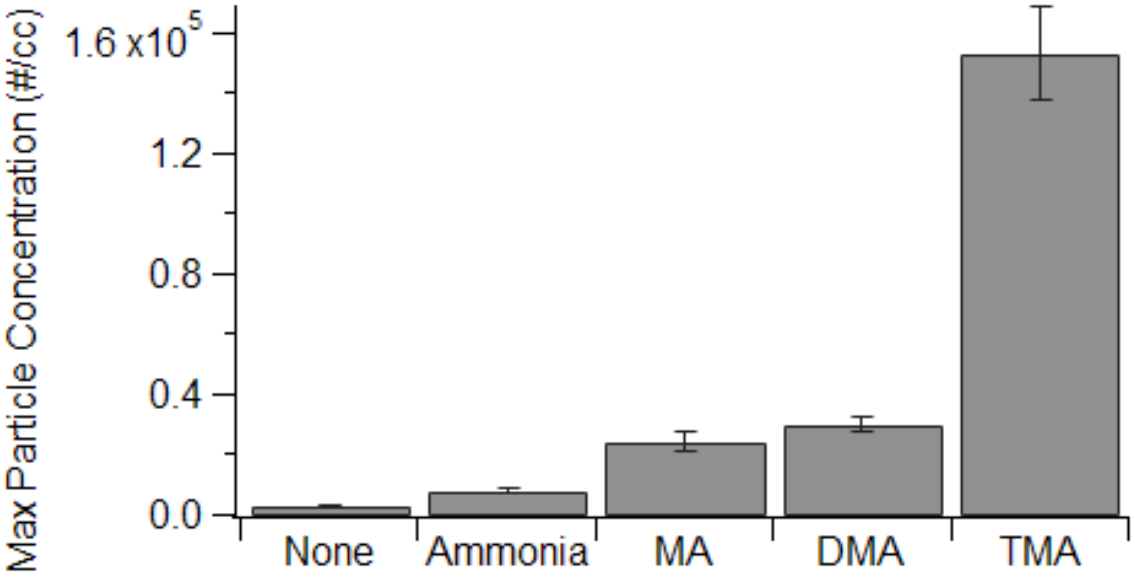
O_3
100 ppb

Amine/NH_3
5 ppb

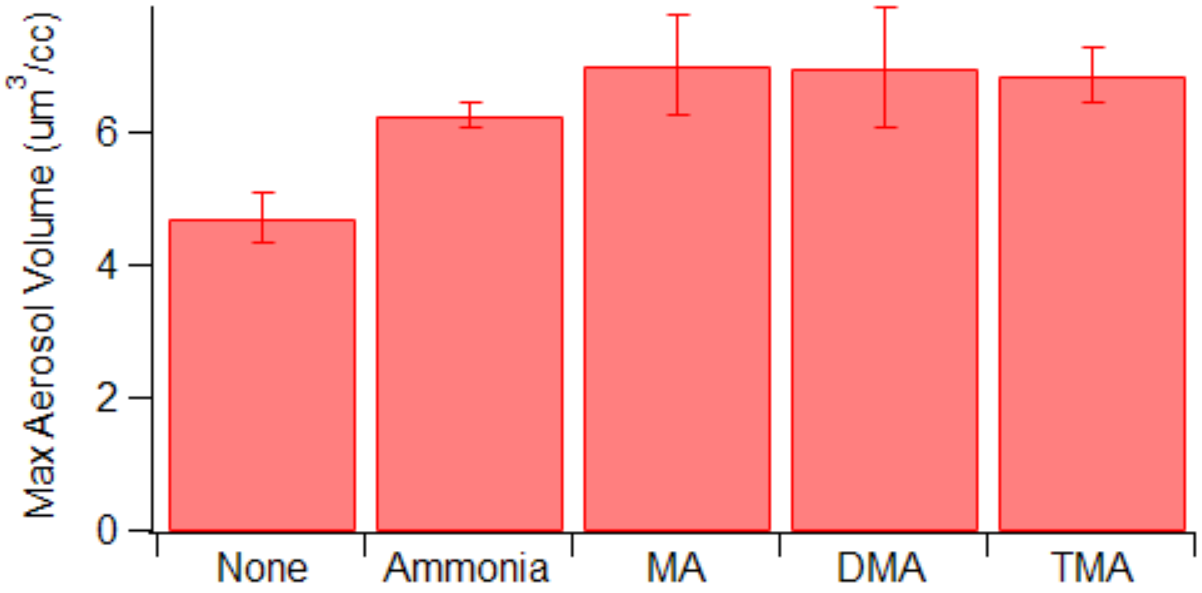
Scanning
Electrical
Mobility Sizer

EtOH-CIMS

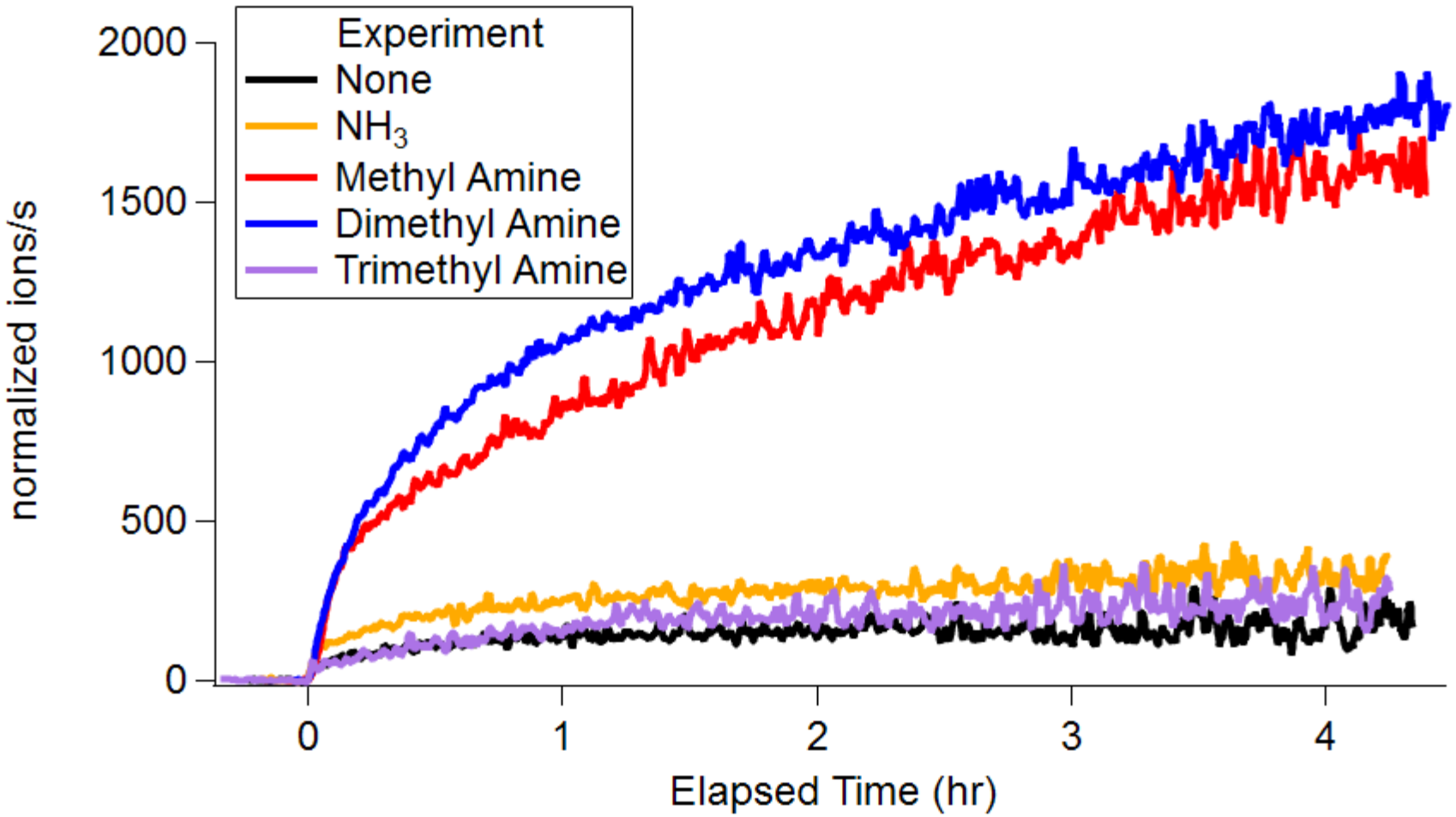
New particle formation is enhanced in the presence of bases.



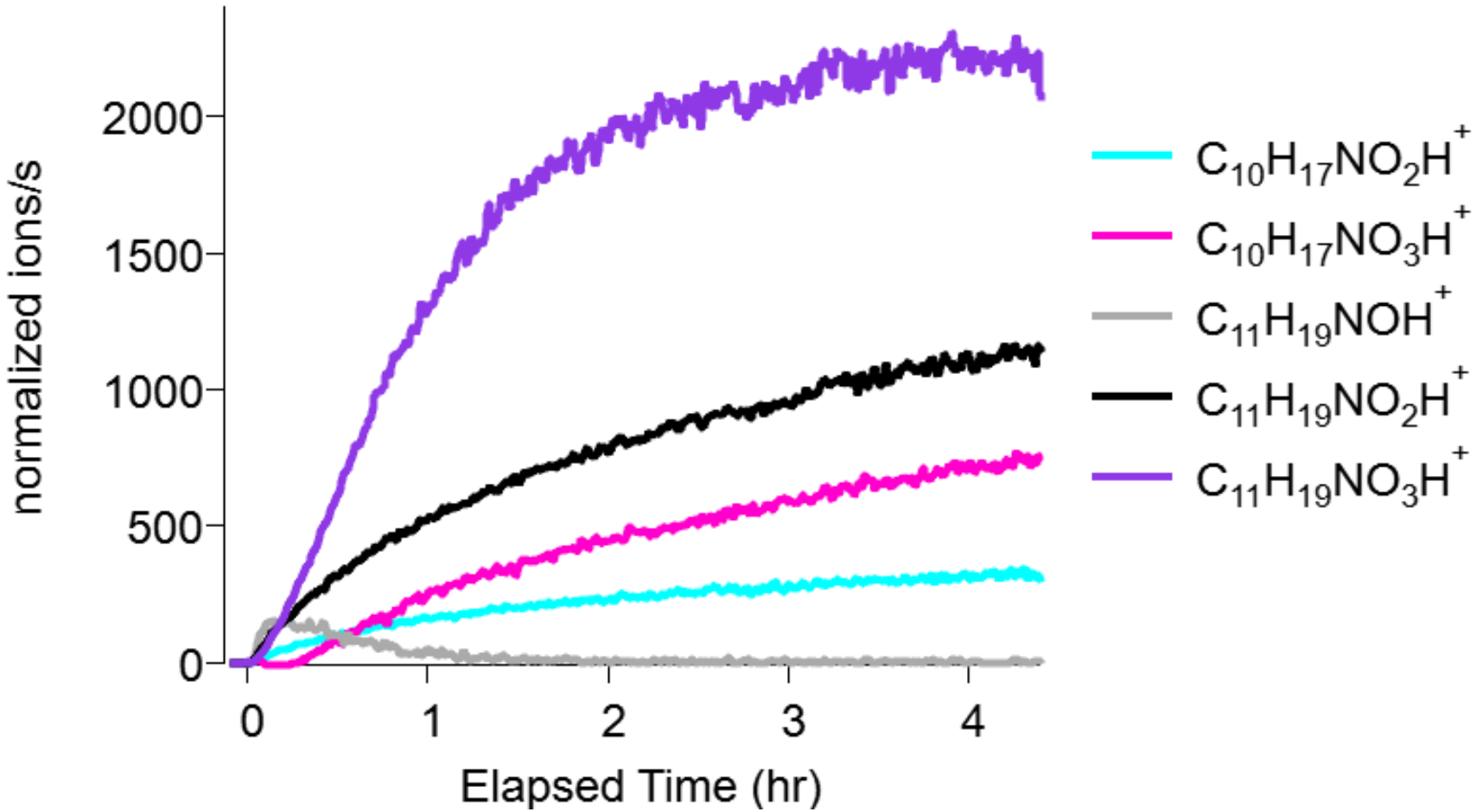
Proton Affinity (kJ/mol)	853.6	899	929.5	948.9



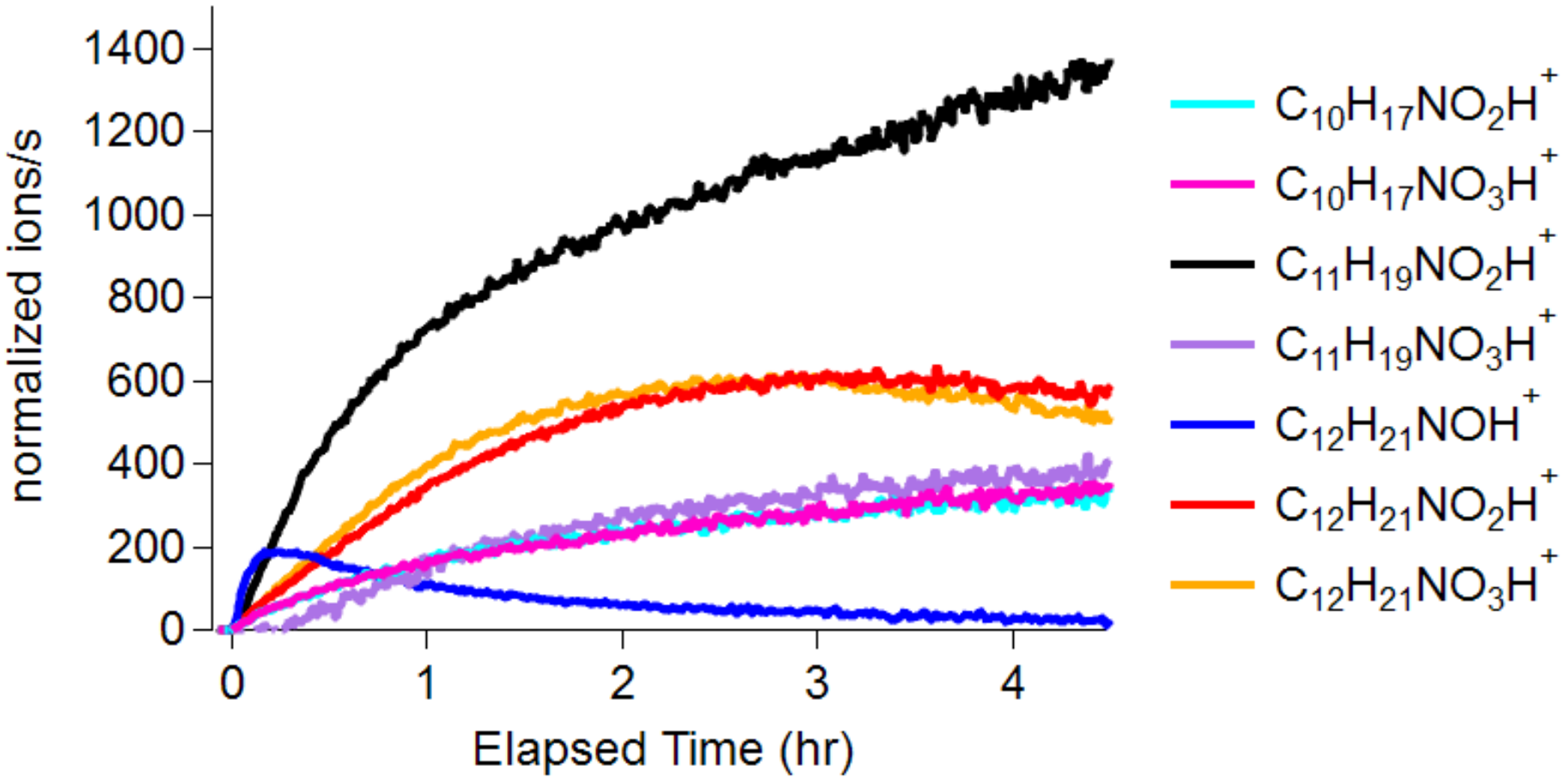
Σhigh intensity N ions is much larger for MA and DMA experiments.



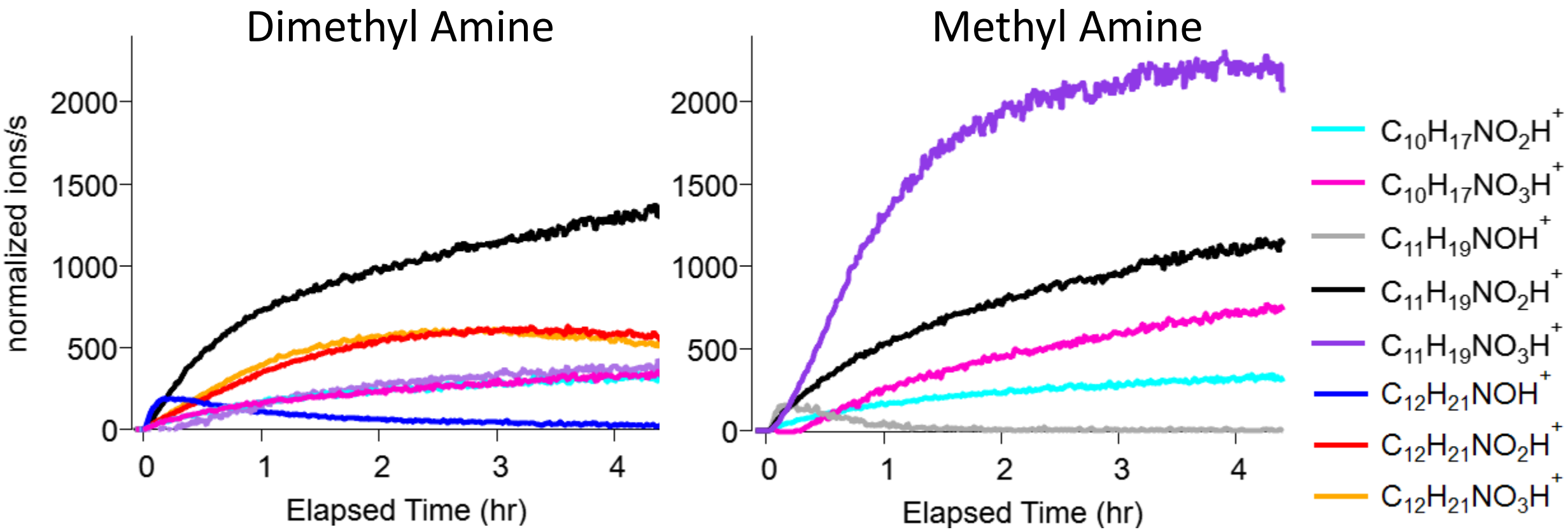
Methyl amine + α-pinene



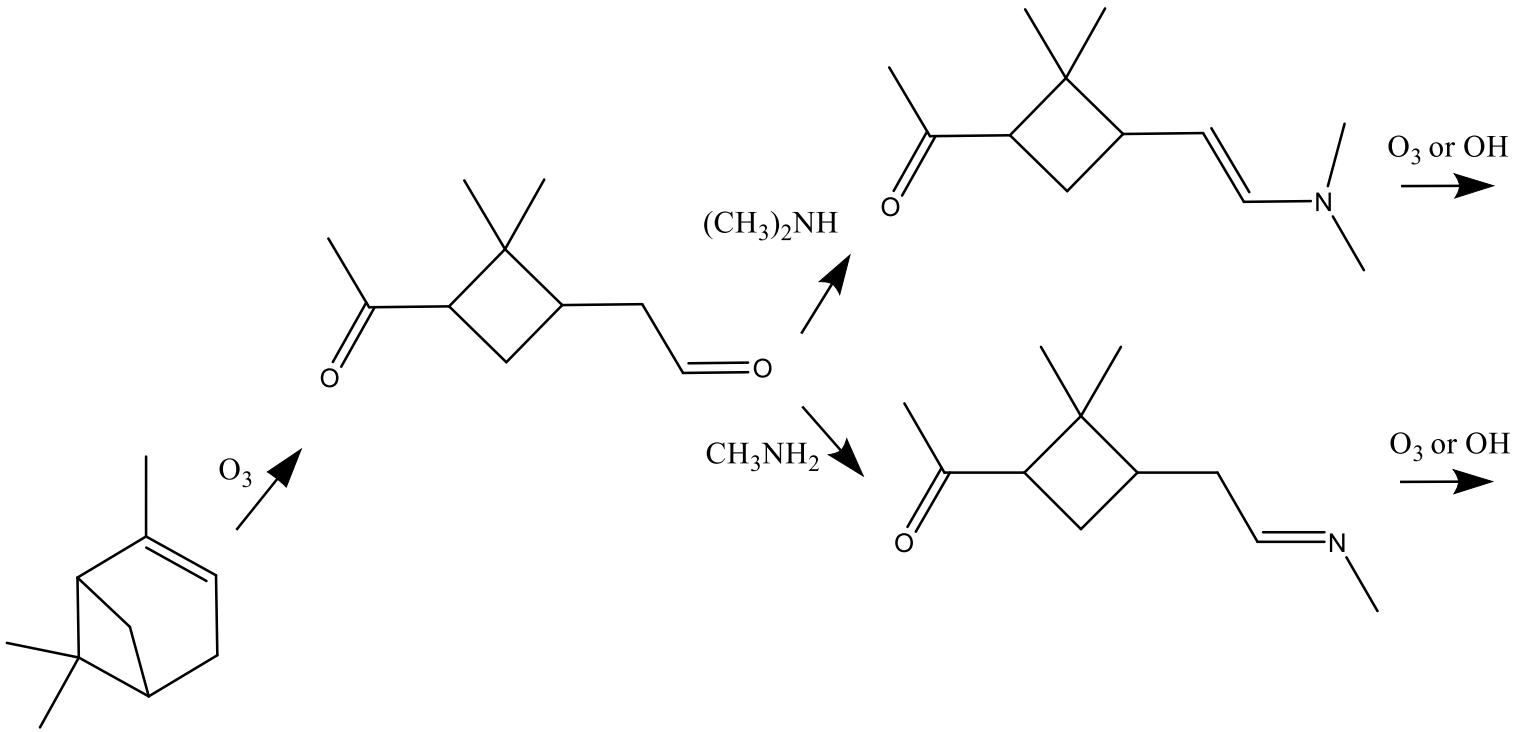
Dimethyl amine + α-pinene



Products of α-pinene ozonolysis in the presence of amines



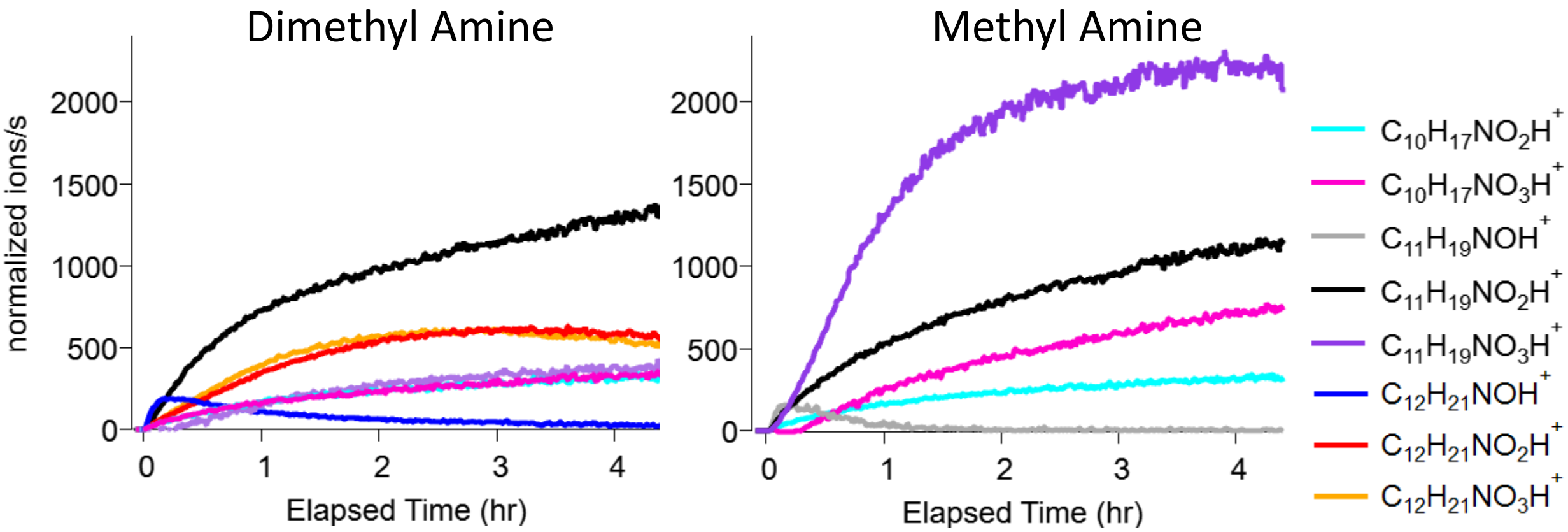
Proposed Pathways



Rapid oxidation of imines/enamines

Formation of stable amides

Products of α-pinene ozonolysis in the presence of amines



Summary

- EtOH-CIMS
  - Sensitive
  - Measure multiple classes of organic N compounds
- Multiphase chemical reaction of amines results in the formation of gas-phase organic N
  - Imines/enamines
  - Amides