Nighttime Aircraft Intercepts of Biomass Burning Plumes: Observations and Box Model Analysis

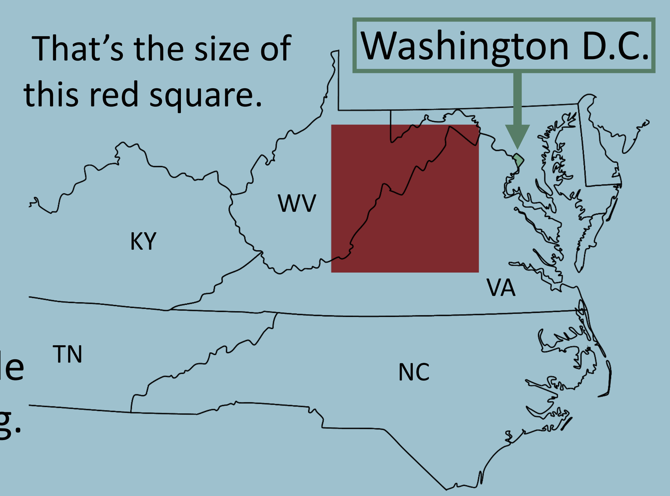
Zachary C. J. Decker[1,2,3], Kyle J. Zarzana[1,2,3], Matthew Coggon[1,3], Kyung-Eun Min[1,3,‡], Ilana Pollack[1,γ], Thomas B. Ryerson[3], Jeff Peischl[1,3], Pete Edwards[4], William P. Dubé[1,3], Milos Z. Markovic[1,Ω], James M. Roberts[1,3], Patrick R. Veres[3], Martin Graus[1,§], Carsten Warneke[1,3], Joost de Gouw[1,2], Lindsay E. Hatch[5], Kelley C. Barsanti[5], Steven S. Brown[2,3,*]

[1]Cooperative Institute for Research in Environmental Sciences, University of Colorado Boulder, Boulder, Colorado, USA. [2]Department of Chemistry, University of Colorado Boulder, Boulder, Colorado, USA. [3]NOAA Earth System Research Laboratory (ESRL), Chemical Sciences Division, Boulder, Colorado, USA. [4]Wolfson Atmospheric Chemistry Laboratories, Department of Chemistry, University of York, York, United Kingdom. [5]Department of Chemical and Environmental Engineering and College of Engineering – Center for Environmental Research and Technology (CE-CERT), University of California, Riverside, Riverside, CA, USA. [‡]Gwangju Institute of Science and Technology, School of Earth Sciences and Environmental Engineering, Gwangju, South Korea. [γ]Colorado State University, Atmospheric Science Department, Ft. Collins, CO, USA. [Ω]Picarro Inc., Toronto, Canada. [§]Department of Atmospheric and Cryospheric Sciences, University of Innsbruck, Austria.

Wildfire size and frequency are increasing[1]

Last year 16.4 million acres burned in the U.S.[2]

That's the size of this red square.



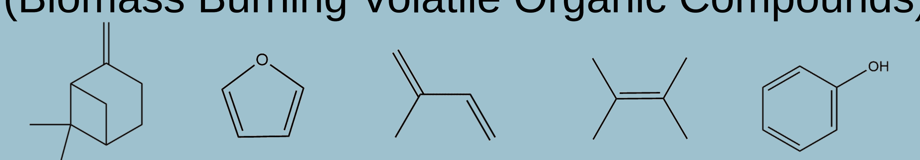
That doesn't include agricultural burning.

Smoke Plumes Produce NO_3 (R1) from $NO_2 + O_3$

NO_3 is a nighttime oxidant (it's destroyed in sunlight)

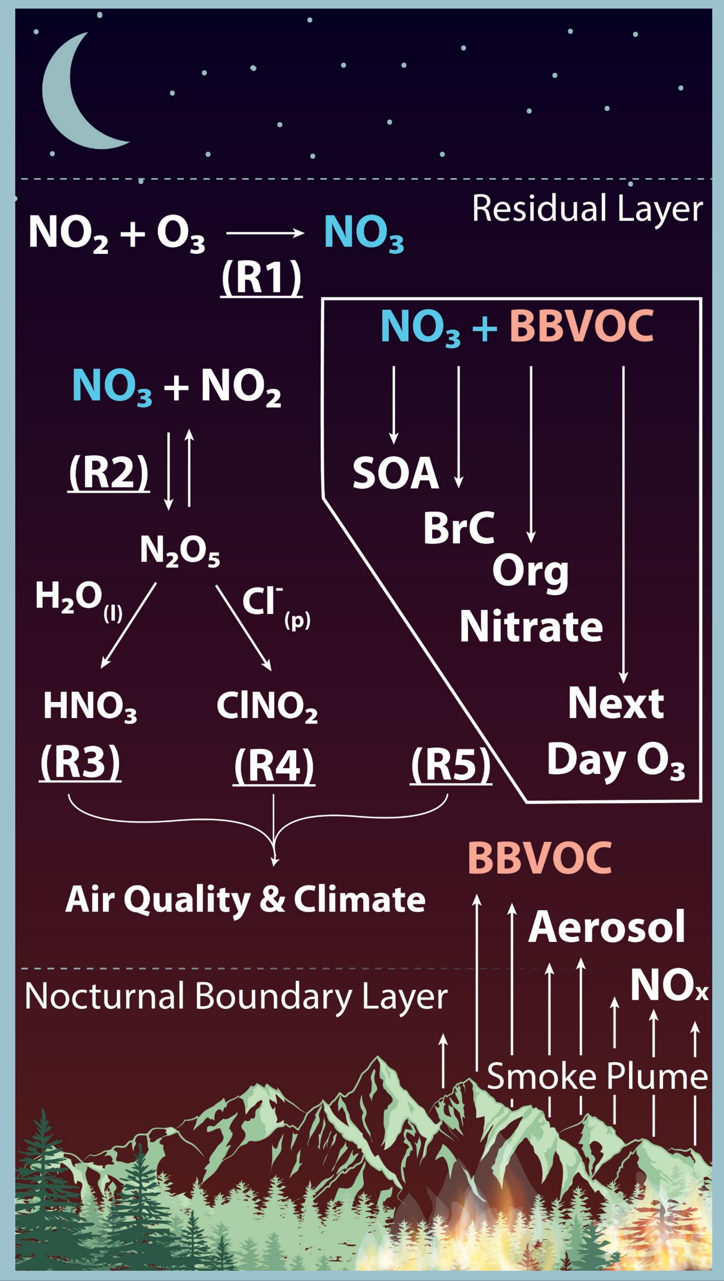
Fires emit BBVOCs

(Biomass Burning Volatile Organic Compounds)



NO_3 + BBVOCs is an open science question

What we know →



NO_3 is Produced Within Smoke & Lost (>99%) to BBVOCs – Not Aerosol

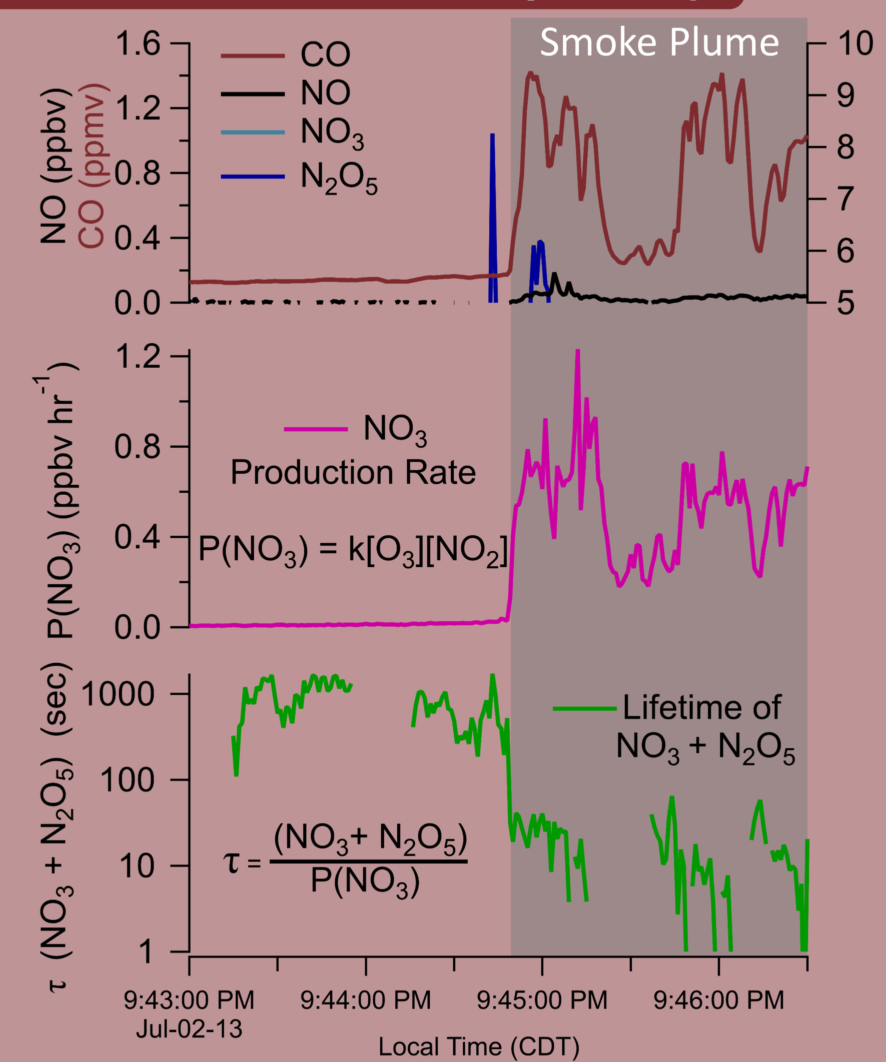
The South East Nexus (SENEX 2013) campaign intercepted a nighttime agricultural burning plume. This smoke plume intercept is the only known nighttime aircraft smoke sampling with NO_3, N_2O_5, NO_x, and NO_y measurements.

NO_3 is produced, but reacts quickly

Both NO_3 and N_2O_5 are at or below the detection limit within the smoke plume (≤~5 pptv).

Yet, NO_3 is being produced within the smoke plume.

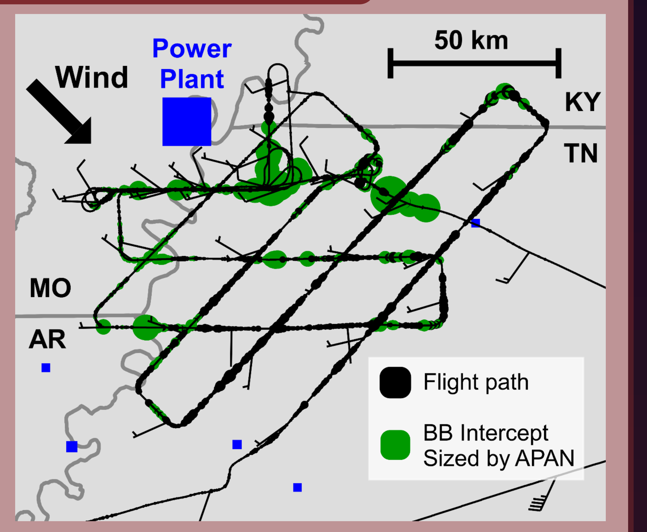
This suggests NO_3 & N_2O_5 are reacting quickly within the plume.



NO_3 loss is due to BBVOCs

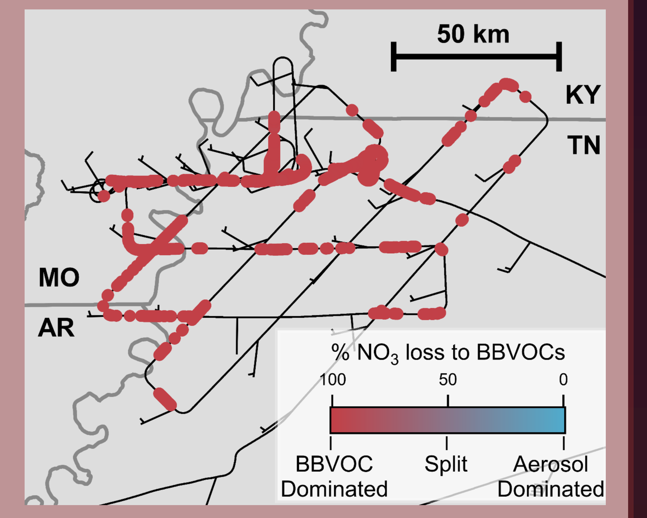
These maps show the SENEX 2013 night flight.

Multiple smoke plumes were intercepted and are shown in green.



We compared both NO_3 & N_2O_5 aerosol uptake rates (R2-R4) to NO_3 + BBVOC rates (R5).

The rate of NO_3 + BBVOCs is a factor of $10^2 – 10^3$ greater than aerosol uptake. The median $\%NO_3$ loss to BBVOCs is >99%.



We initialized a model with these observations to understand nighttime plume chemistry:

What makes a nighttime smoke plume reactive?

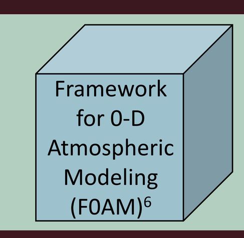
We considered two fuels: **western wildfire** (ponderosa pine fuel); **agricultural burning** (rice straw fuel)

We gathered rates and BBVOC emissions[3,4] ($Reactivity_x = k_x\,[BBVOC]_x$)

We calculated reactivity for **303 compounds**

How does NO_3 oxidation compare to O_3 or OH in a nighttime smoke plume?

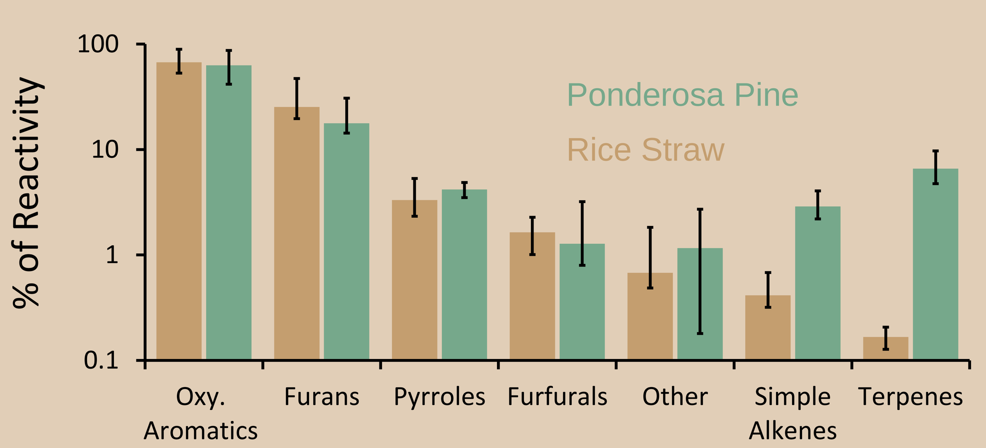
Master Chemical Mechanism[5] + Over 150 new BBVOCs →



0-D Box Model

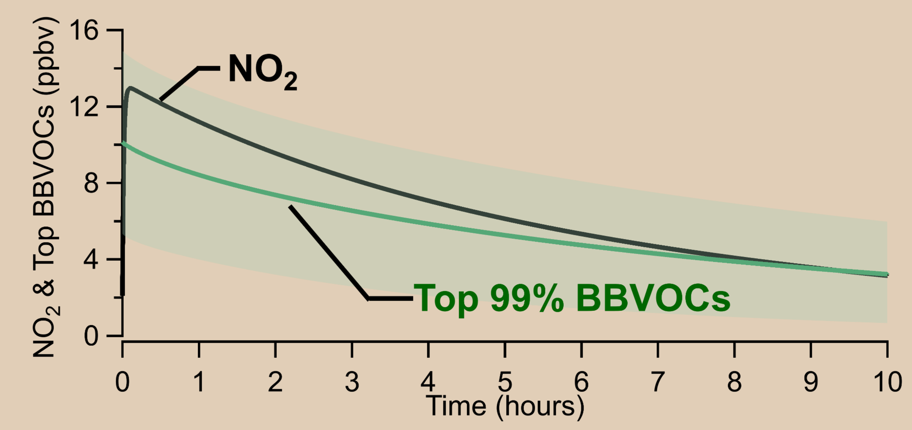
We modeled a **10 hour summer night**

Oxygenated and hetero-aromatics are most reactive



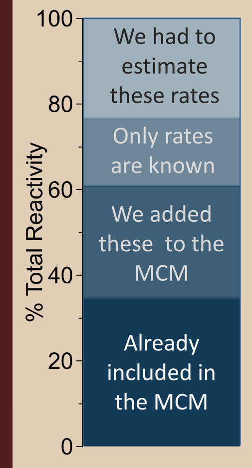
Ponderosa pine fires emit more terpenes relative to rice straw fires and therefore will have a higher fraction of terpene oxidation products.

Roughly 60% of NO_2 & reactive BBVOC mass is lost overnight



In both fuels there is as much NO_3 precursor (NO_2) as there is BBVOC to be oxidized. This leads to a 19% loss (out of total mass) of BBVOCs we modeled.

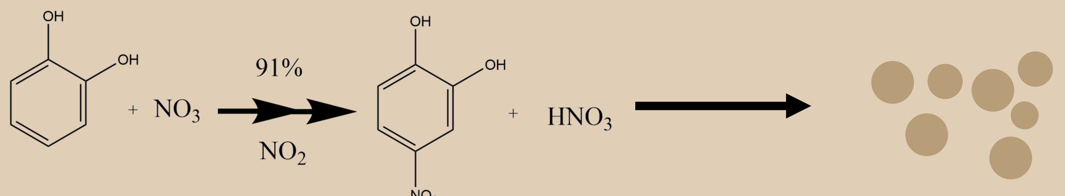
What we don't know



Nearly 23% of the reactivity was calculated with an estimated k_{NO_3}.

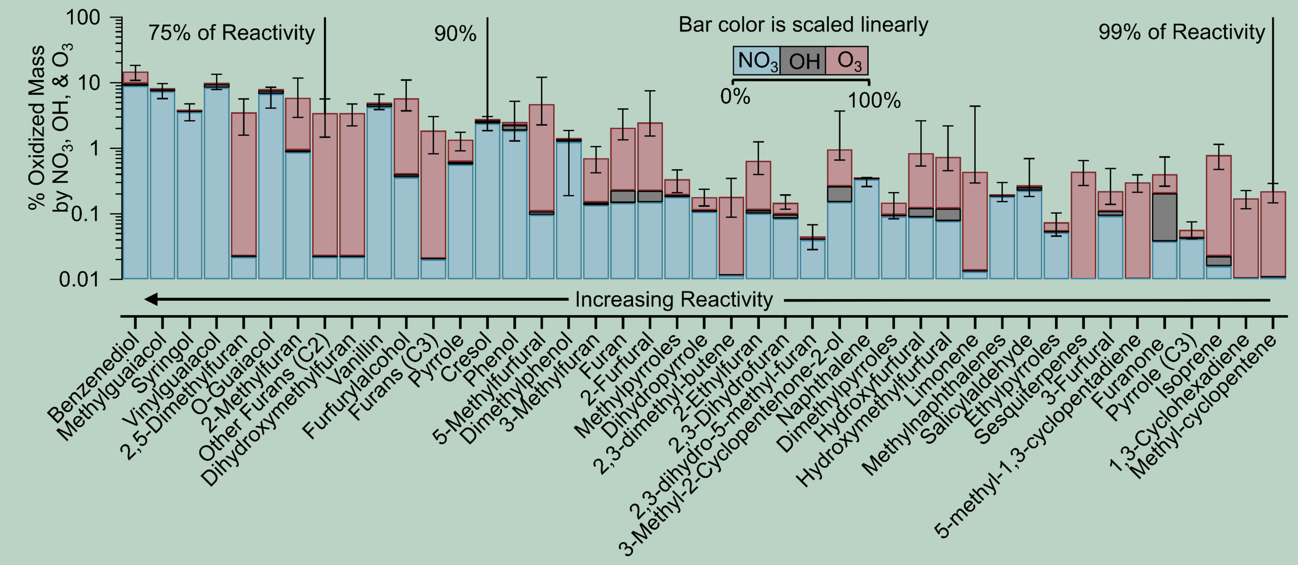
To our knowledge there are no published rate coefficients for any pyrrole derivatives in the emissions inventories.

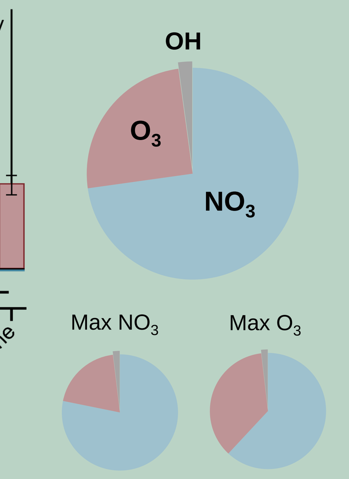
Nighttime oxidation may be a significant source of BrC



Catechol is the most reactive compound and will deplete within one night to form nitro-catechol, a brown carbon (BrC) precursor with near unity molar yield.[7]

NO_3 governs oxidation of a nighttime agricultural burn plume

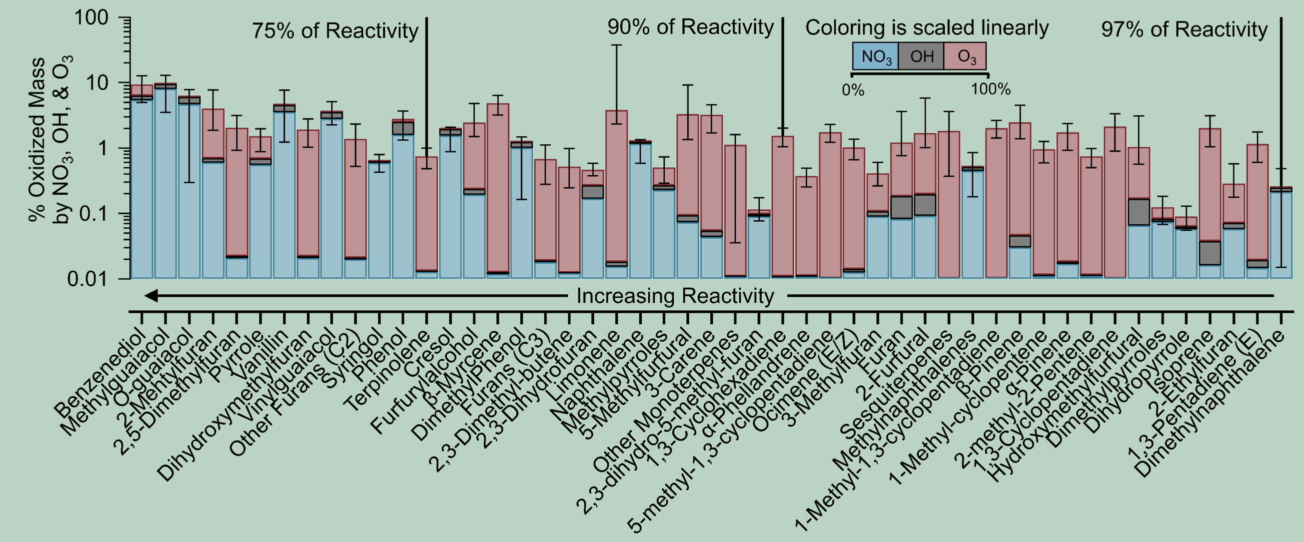


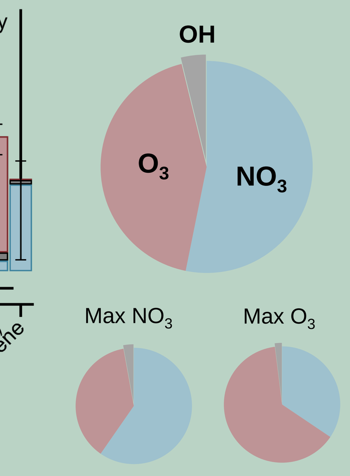


The majority of mass is oxidized by NO_3 ($72^{+6}_{-11}\%$).

Emissions are rich in oxygenated aromatics and hetero-aromatics, which are generally less reactive toward O_3.

Nighttime oxidation is split in a western wildfire plume





Almost half of the mass is oxidized by O_3 ($43^{+21}_{-6}\%$).

Increased fraction of O_3 oxidation is the result of the increased fraction of unsaturated hydrocarbons and terpenes in ponderosa pine fire emissions.

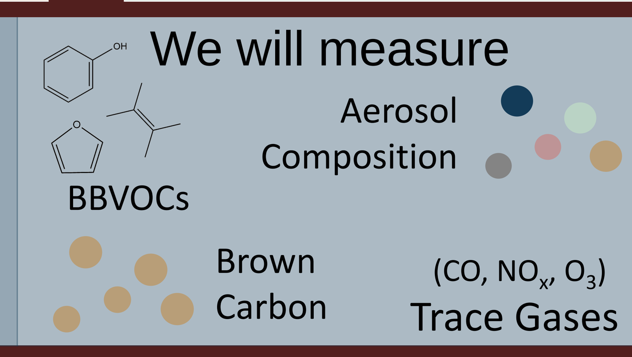
Up next is the FIREX-AQ 2019 Campaign

(Fire Influence on Regional to global Environments and Air Quality)

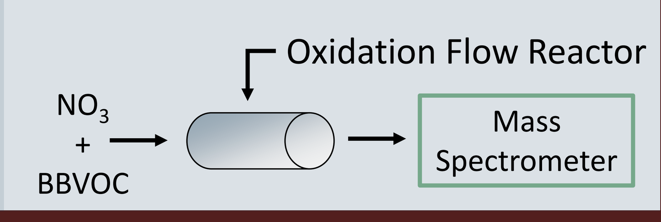
We are taking our research to the field.

Our team will be on the NOAA Twin Otter Aircraft.

We will measure



To prepare for FIREX-AQ we are identifying NO_3 + BBVOC intermediates



References

(1) Dennison et al. Geophys. Res. Lett. 2014, 2014GL059576

(2) National Interagency Fire Center

(3) Koss et al. *Atmos. Chem. Phys.* **2018**, *18*, 3299–3319.

(4) Hatch et al. *Atmos. Chem. Phys.* **2017**, *17* (2), 1471–1489.

(5) MCM v3.3.1 , via website: http://mcm.york.ac.uk

(6) Wolfe et al. *Geosci. Model Dev.* **2016**, *9* (9), 3309–3319.

(7) Finewax, et al. *Environ. Sci. Technol.* **2018**, *52* (4), 1981–1989.