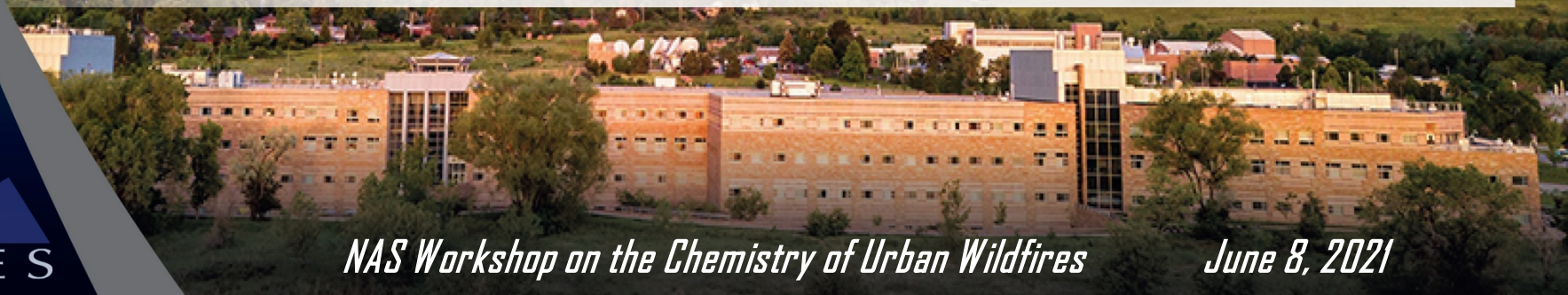
Regional Chemistry in Urban Wildfire Plumes

Halogens, Plastics and Other Unknowns

Dr. Steven S. Brown

Tropospheric Chemistry Program Leader
NOAA Chemical Sciences Laboratory
Boulder, Colorado, USA

Adjoint Professor of Chemistry
University of Colorado
Boulder, Colorado, USA

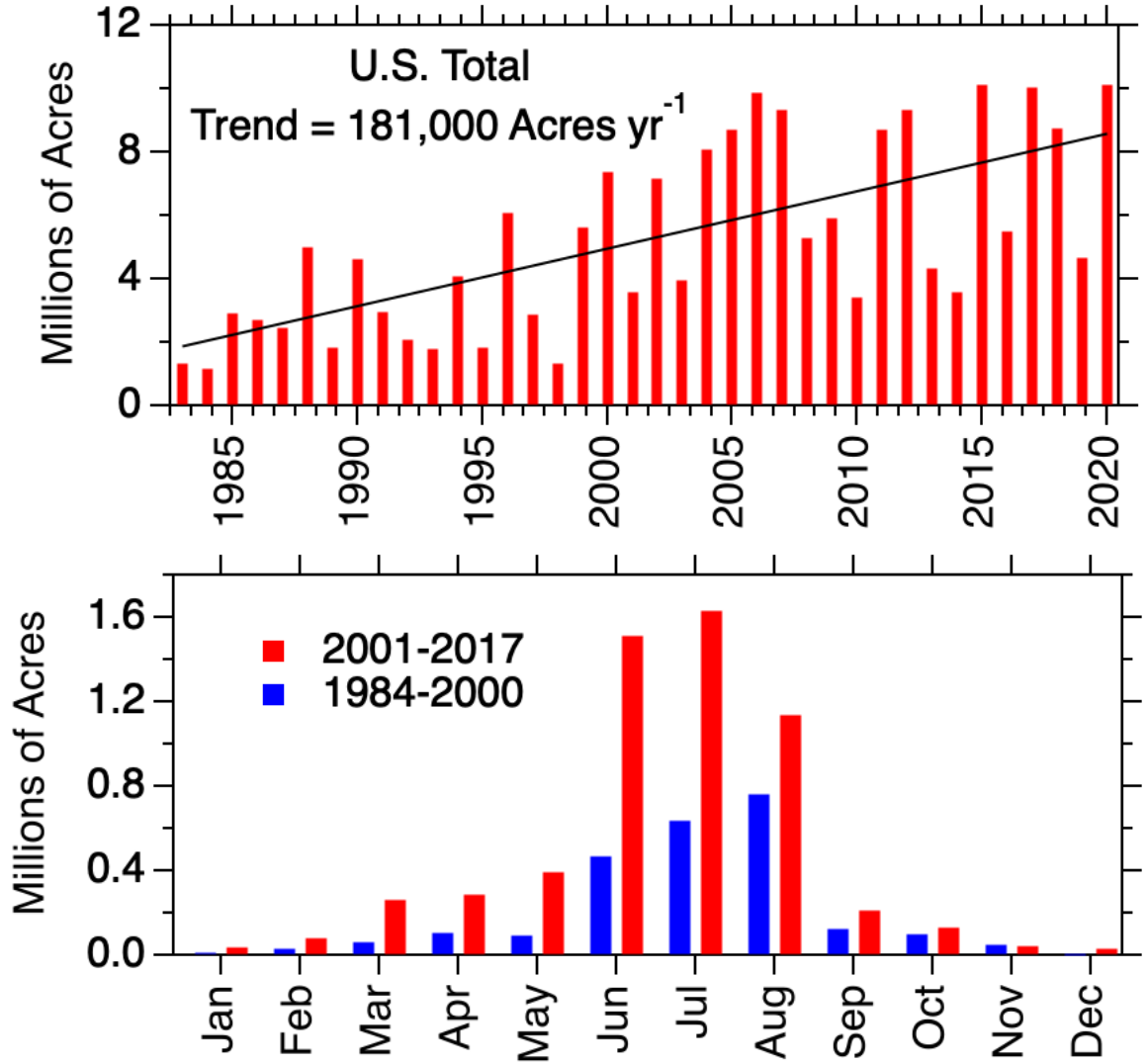


Outline

- Introduction – Wildland Fires, Air Quality and the Wildland Urban Interface (WUI)
- Recent Advances in Understanding Chemical Transformations in Wildfires
- Halogens in Wildland Fires – Sources and Chemical Transformations
- Structures - Knowledge Gaps in Emissions and Chemistry
- Toward a Study Design of Chemical Transformations in Fires at the WUI

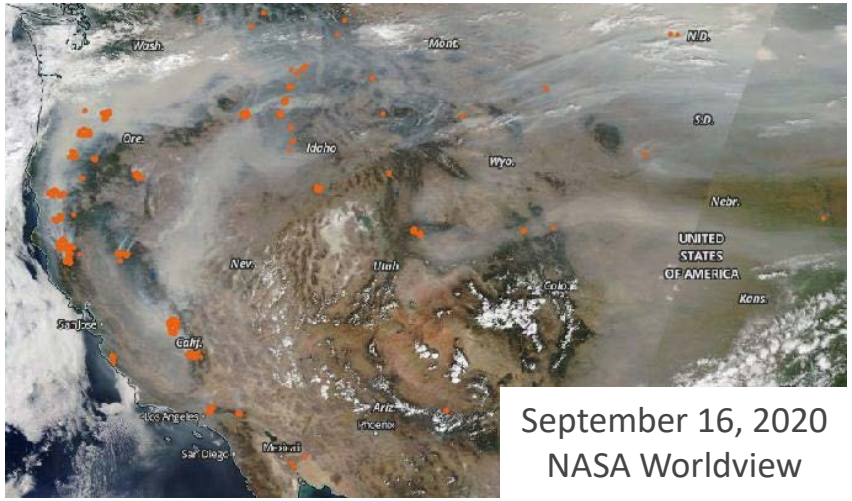
Photo: Dan Lack

Increasing Trends in Wildland Fires



Wildfire area and biomass burning emissions are increasing in the U.S. as a result of climate change and past fire suppression (e.g., Dennison et al., Geophys. Res. Lett. 2014)

Seasonal cycle shows large increases in summer, dominated by fires in the Western U.S. & Alaska

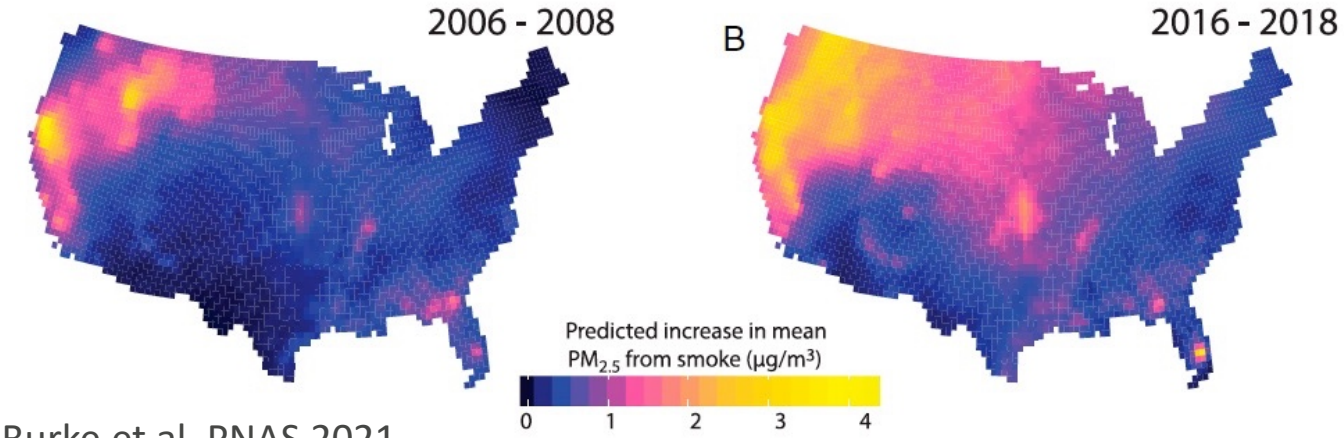


September 16, 2020
NASA Worldview

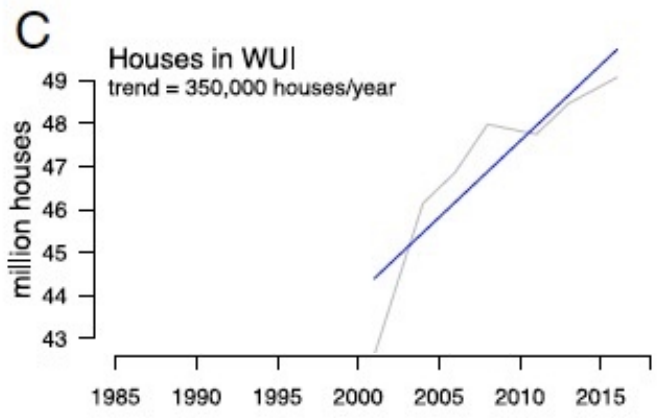
Data: National Interagency Fire Center, U.S. EPA

Air Quality Impacts of Wildland Fires

$PM_{2.5}$ = Particulate Matter smaller than 2.5 microns
Regulated pollutant, negative human health impacts



Burke et al. PNAS 2021

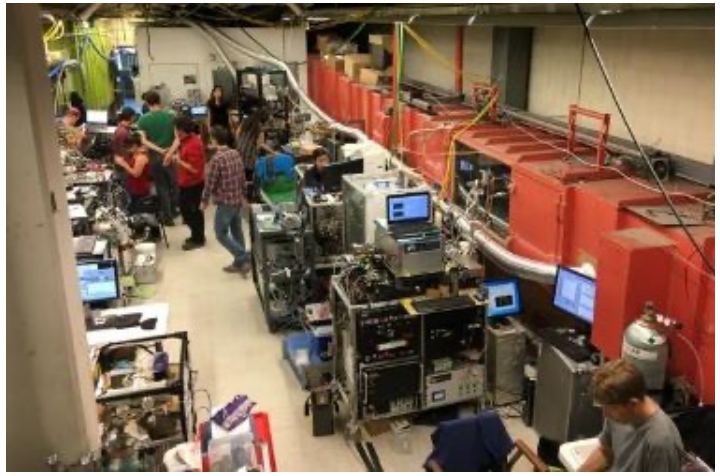


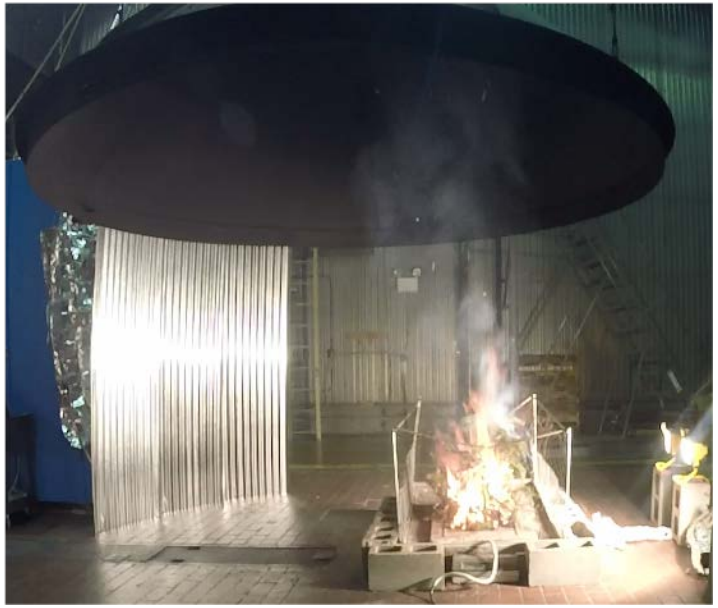
Homes in the Wildland Urban Interface have undergone concurrent increase

Ozone = O_3 Secondary pollutant from NO_x, VOC emitted from fires and urban sources

Brey et al., Environ. Sci. Tech. 2016: Clear increase in maximum daily average ozone (MDA8) at sites across the U.S. on smoke impacted days

Understanding Emissions – The Fire Lab





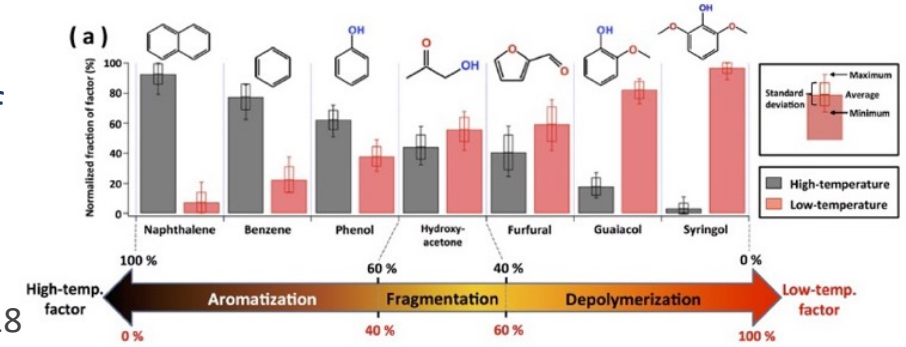
Fire Lab 2016 Campaign: USFS Missoula, MT Fire Sciences Laboratory

6 weeks, > 15 research groups, 50 instruments, 27 publications so far

Large scale campaign, suite of ***new instruments*** for updated emissions, chemistry

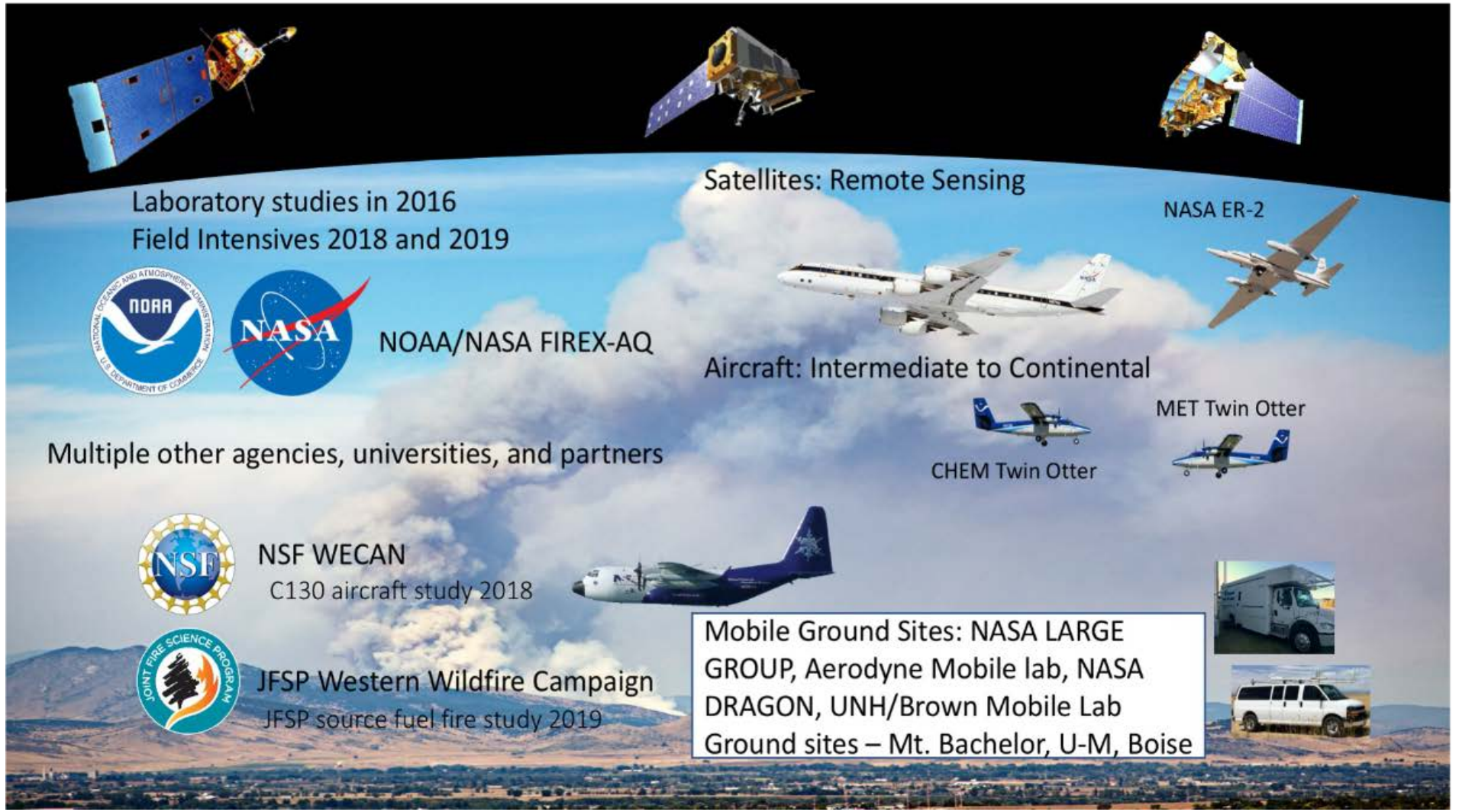
Five major intensives through 2016 to characterize detailed emissions of carbon, nitrogen, particulates, etc. from a wide range of wildland and agricultural fuels

Seikimoto ACP 2018



Extensive characterization of wildland and agricultural fuels; no structural materials

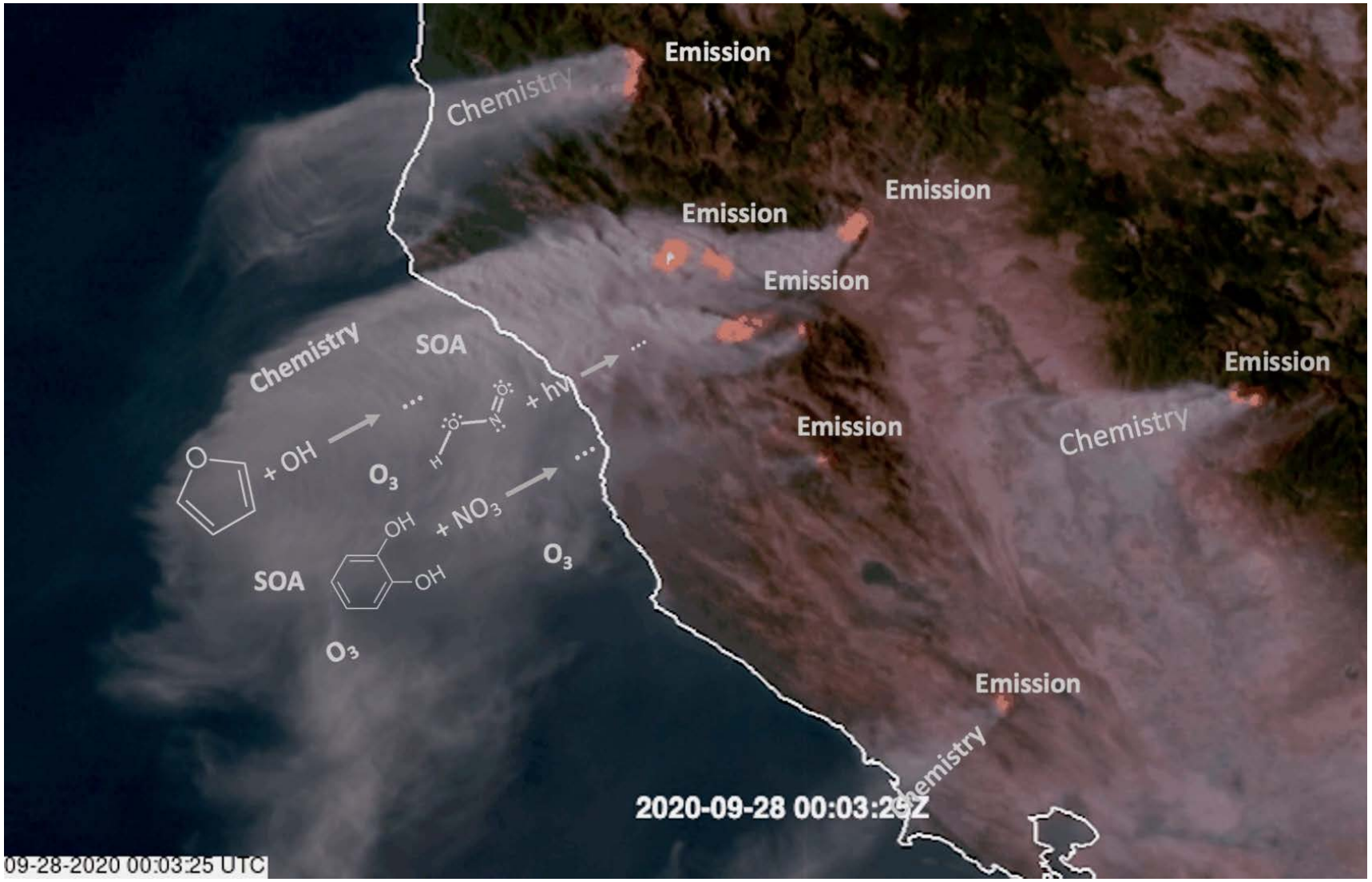
Wildland Fires – The Field Work



FIREX-AQ 2019

- 4 Aircraft (NASA DC-8, 2 NOAA Twin Otters, NASA ER-2)
- Mobile laboratories & ground sites (NASA LARGE, Aerodyne, DRAGON)
- Coordination with satellite remote sensing
- Partnership with wildland fire and fuels community
- NOAA & NASA together with other federal & state agencies (EPA, NSF, USDA, JFSP, CARB)

Wildland Fires – Chemical Transformation



Fire plume chemistry takes place over broad spatial and time scales – from the source to 100's of km downwind, and from seconds to weeks

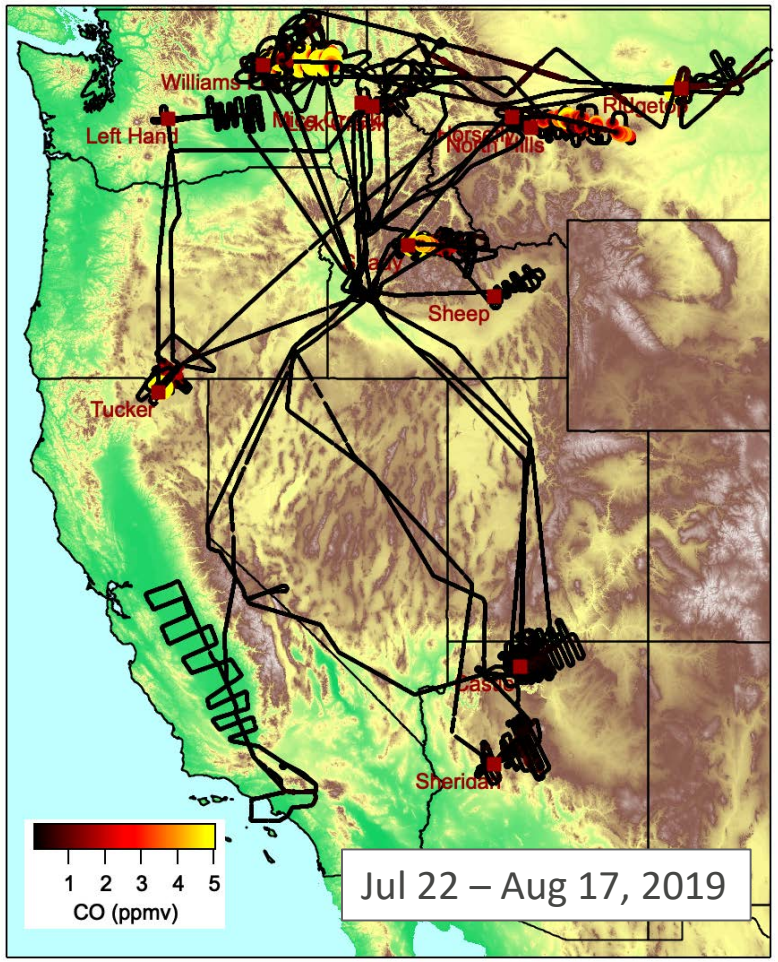
Emissions are *complex* and undergo rapid atmospheric chemistry driven by sunlight during the daytime and by "dark" reactions during day and night

O_3 is produced through chemical transformations in fire plumes

$PM_{2.5}$ is both directly emitted and produced through atmospheric reactions

Studying Chemical Transformation from Aircraft

NASA DC-8: Western wildfires and eastern agricultural fires, focus on emissions and photochemistry



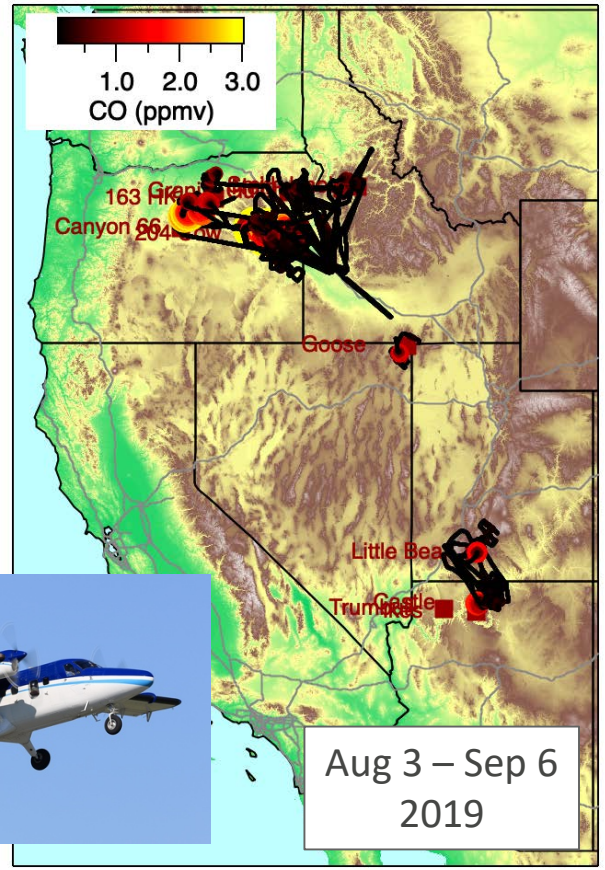
14 research flights in the western U.S., 8 in the east
14 western fires or fire complexes

NOAA Twin Otter: Western wildfires, focus on emissions, photochemistry and nighttime chemistry

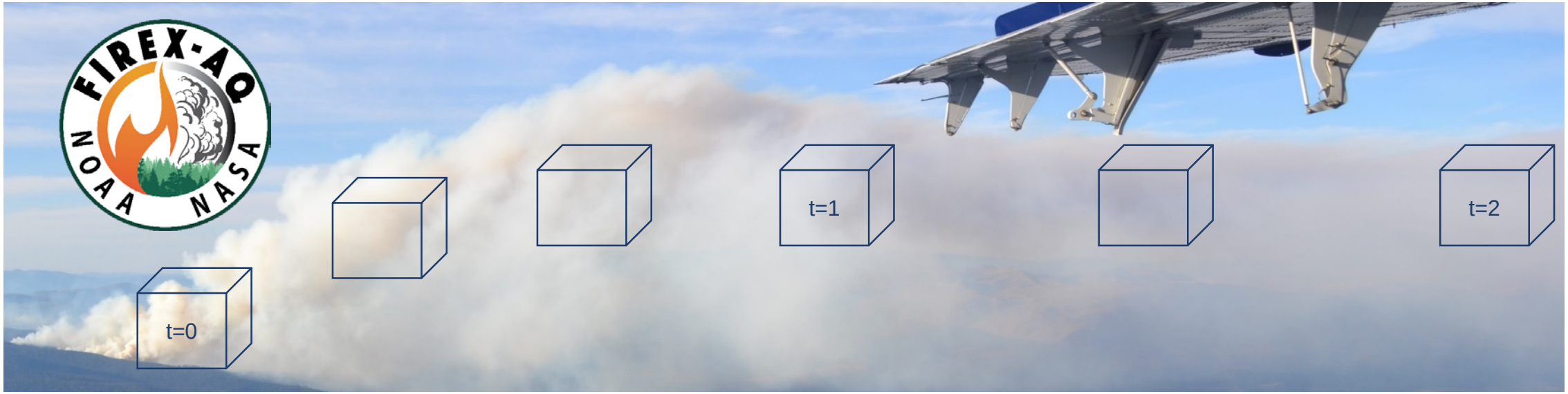
16 flight days

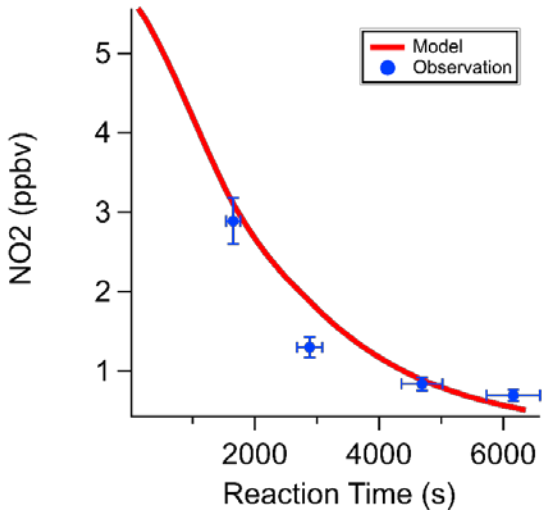
39 research flights

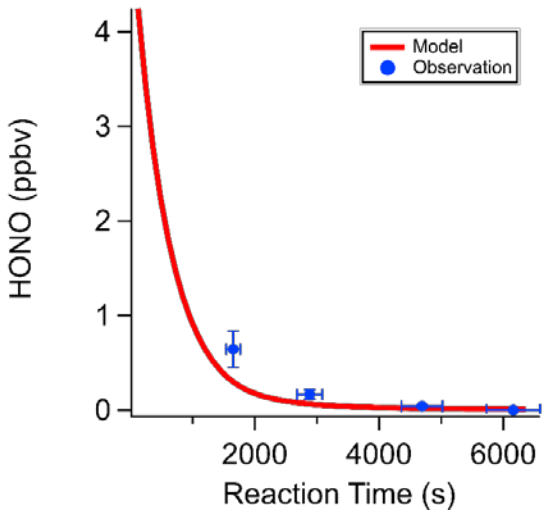
10 fires or complexes

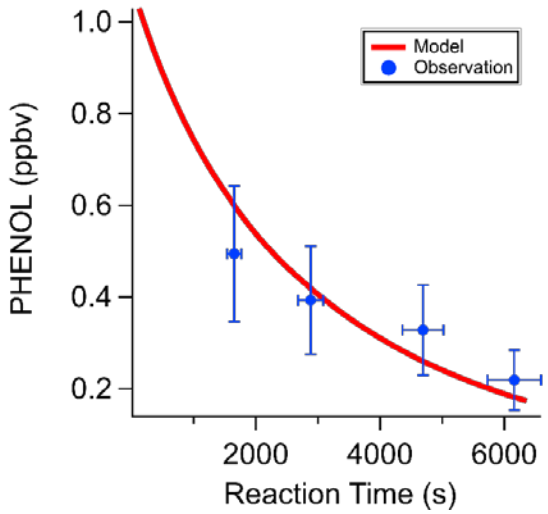


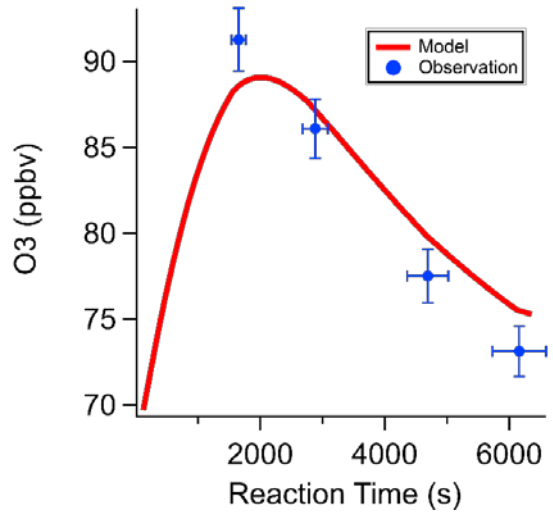
Ozone Production in Wildfire Plumes





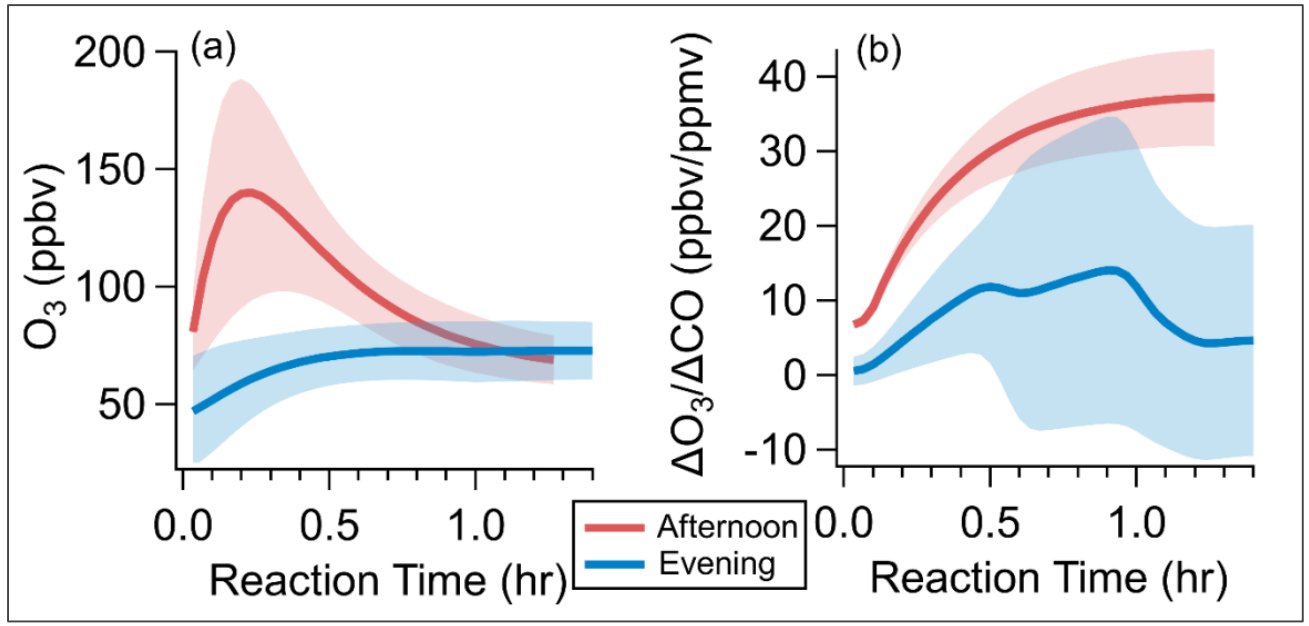




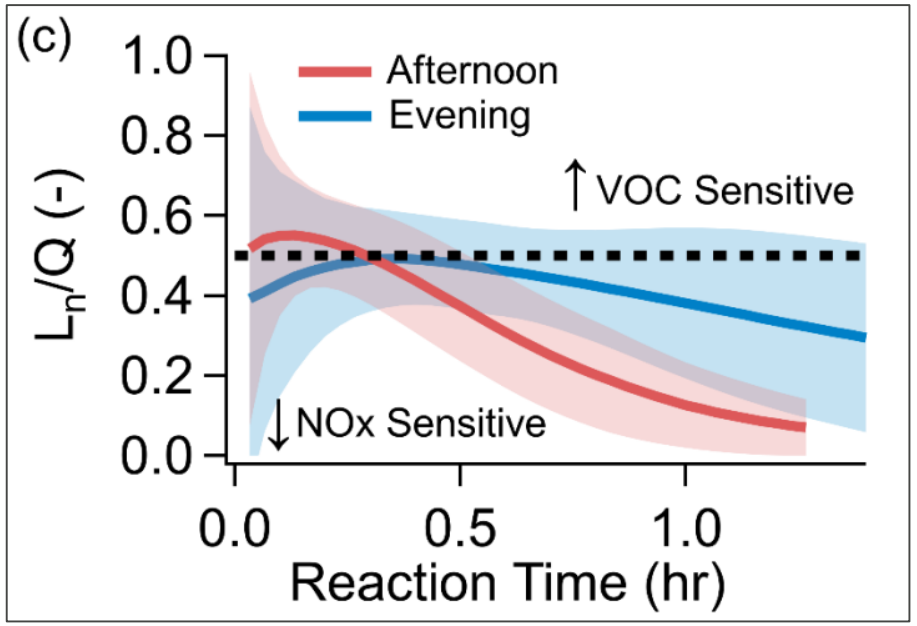


Ozone Production in Wildfire Plumes

Modeled Ozone Production



Sensitivity to Fire Emissions (NO_x & VOC)



- Max O_3 produced within *30 minutes* on average
- Diel cycle strongly influences rates of O_3 production and other chemical cycles

Robinson et al., Environ. Sci. & Tech., submitted 2021

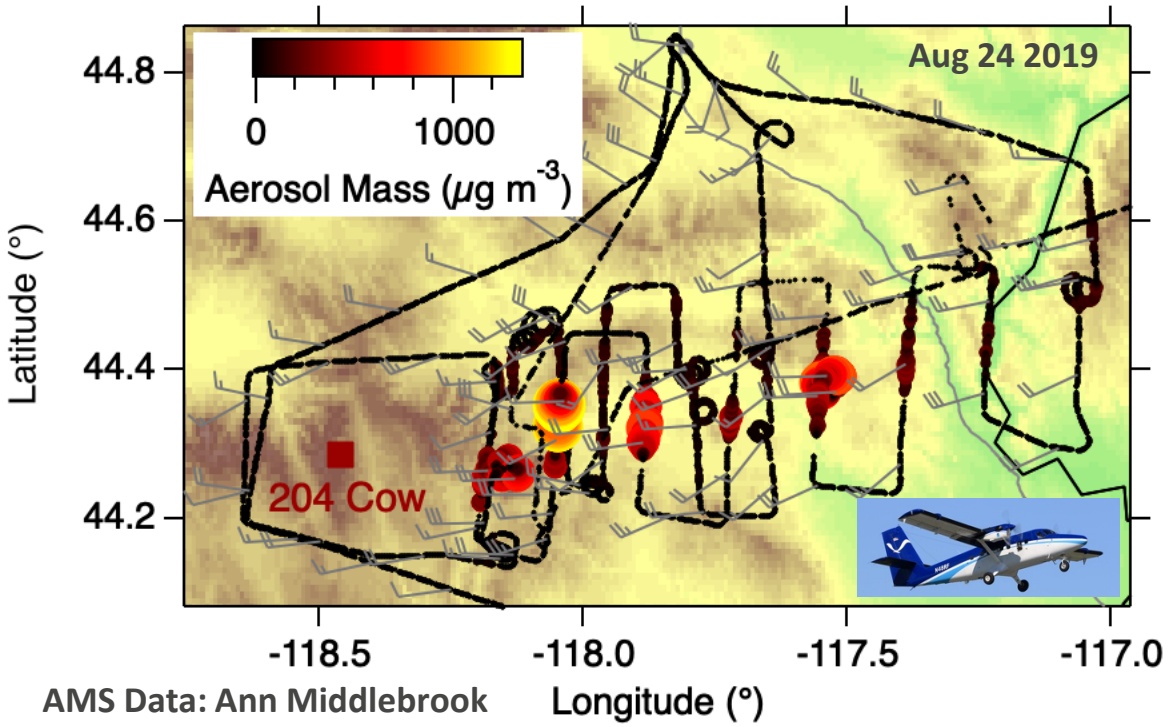
- Nitrogen oxides (NO_x) react away quickly - O_3 production becomes rapidly NO_x limited

Fires in the WUI in proximity to urban areas: addition of urban NO_x to wildland emissions may dramatically increase wildland fire O_3

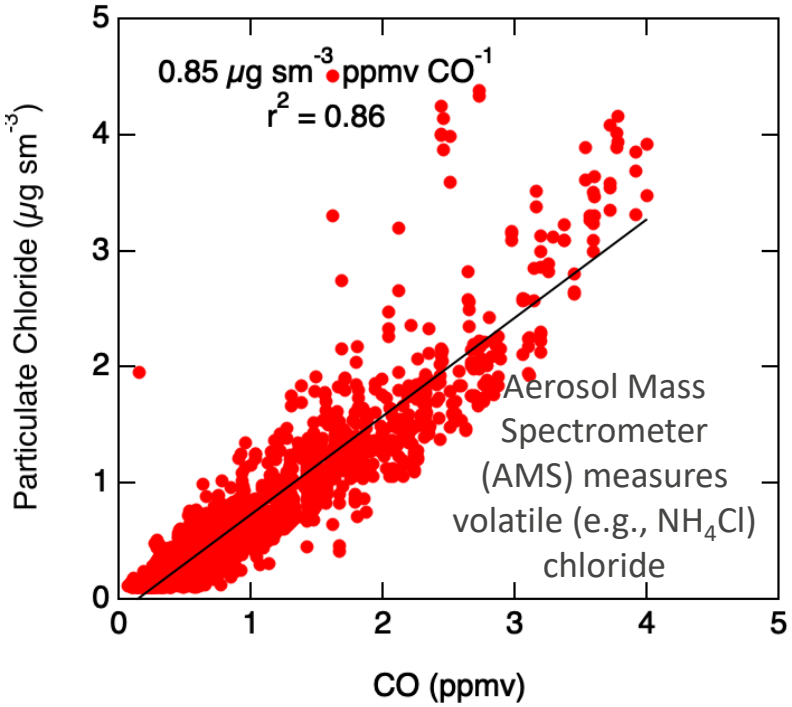
Halogen Emissions & Chemistry from Wildland Fires

- Wildland Fires are known to emit chlorine in the form of particulate chloride (Cl^-) and hydrogen chloride (HCl)
- Fires also emit potassium (K^+) and ammonia (NH_3) → expect potassium & ammonium chloride (KCl, NH_4Cl)
- Emission factors vary by fuel: e.g., 0.1 – 1.3 g Cl^- / kg fuel (McMeeking, J. Geophys. Res. 2009), although chlorine content of the biomass has been reported to be larger (Lobert, J. Geophys. Res. 1999)

Wildland fire sampled by Twin Otter in Oregon



AMS Data: Ann Middlebrook



- Particulate chloride often (not always) correlated with CO
- Slopes vary by day, 0.6 ± 0.4 μg sm^{-3} / ppmv CO
- Expected for montane fuel 0.4 μg sm^{-3} / ppmv CO (50% fuel C content, MCE = 0.9)

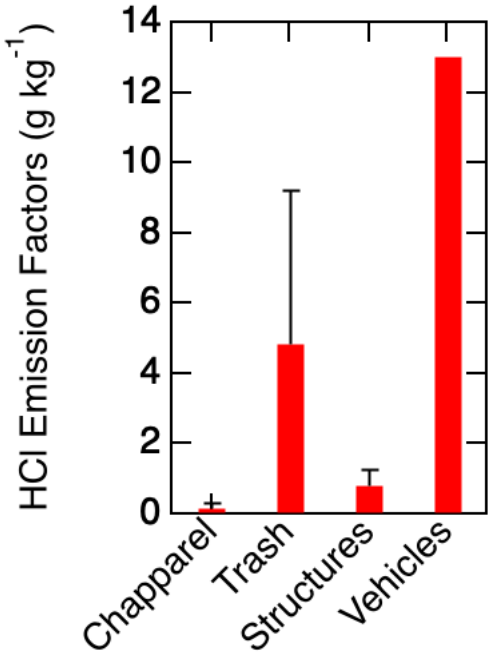
Halogen Emissions – Trash, Structures & Vehicles

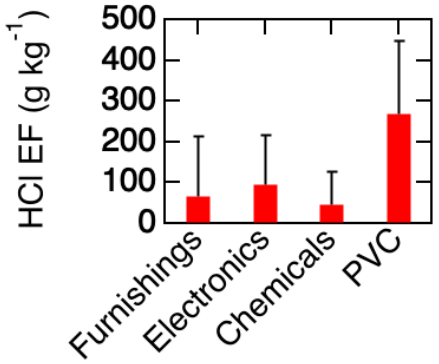
Hydrogen Chloride, HCl

- Few reported emission factors for gas phase HCl from wildland or agricultural fuels
- Trash, structures and vehicles have large emission factors compared to wildland fires
- But … large emissions of ammonia, NH_3, likely partition chloride to particulate phase

$$HCl(g) + NH_3(g) \leftrightarrows NH_4Cl(p)$$

- Emission factors for plastics burning *much* larger than any categories above



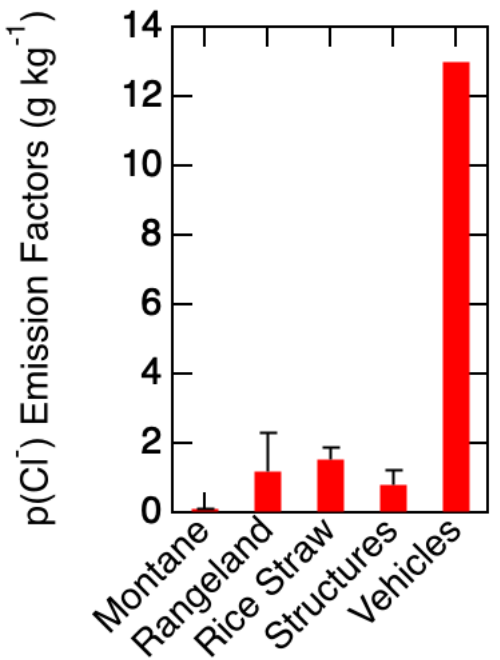


Trash, Chaparral EFs: Akagi, ACP 2011
Structures, Vehicle, Material EFs: EPA
Database courtesy of Amara Holder

Particulate Chloride, p(Cl$^-$)

- Larger number of pCl$^-$ emission factors from biomass fuels
- pCl$^-$ may be NH_4Cl or KCl
- Grasses and agricultural fuels >> forests (~10x)
- pCl- emission factors from structures comparable to agricultural fuels, but trash & vehicles are still larger

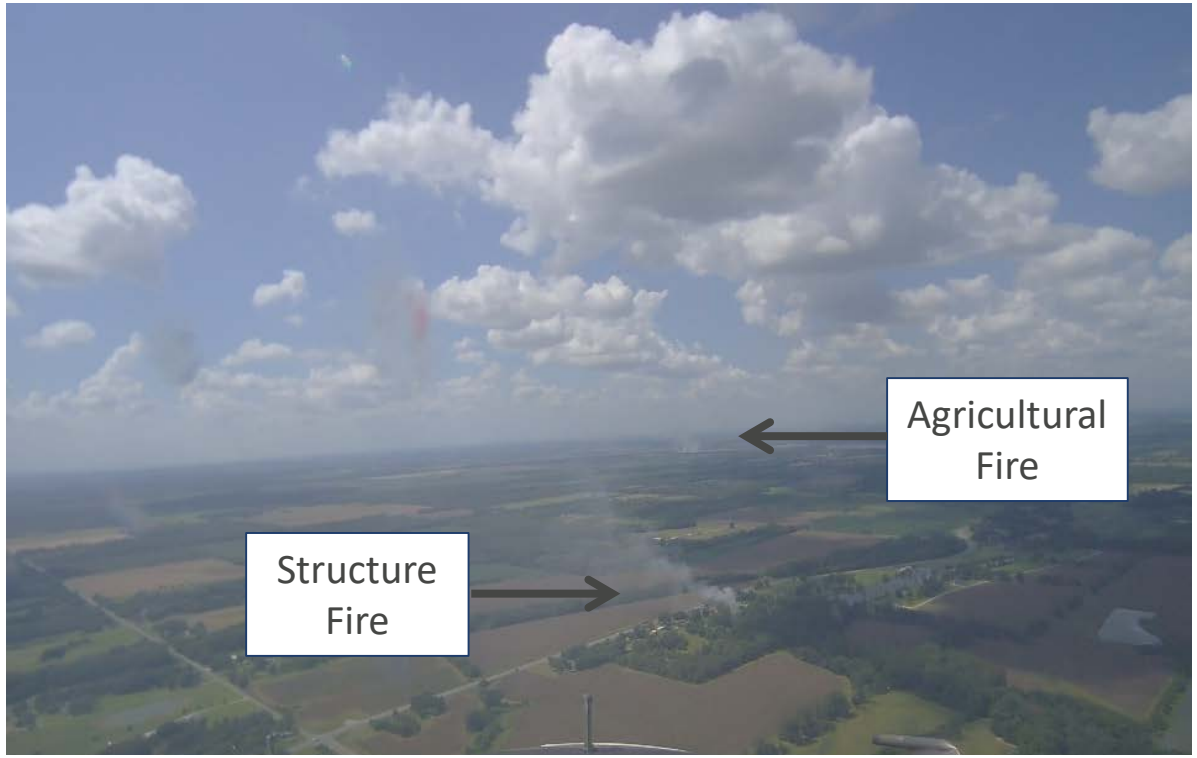
pCl- EFs: McMeeking, JGR 2009

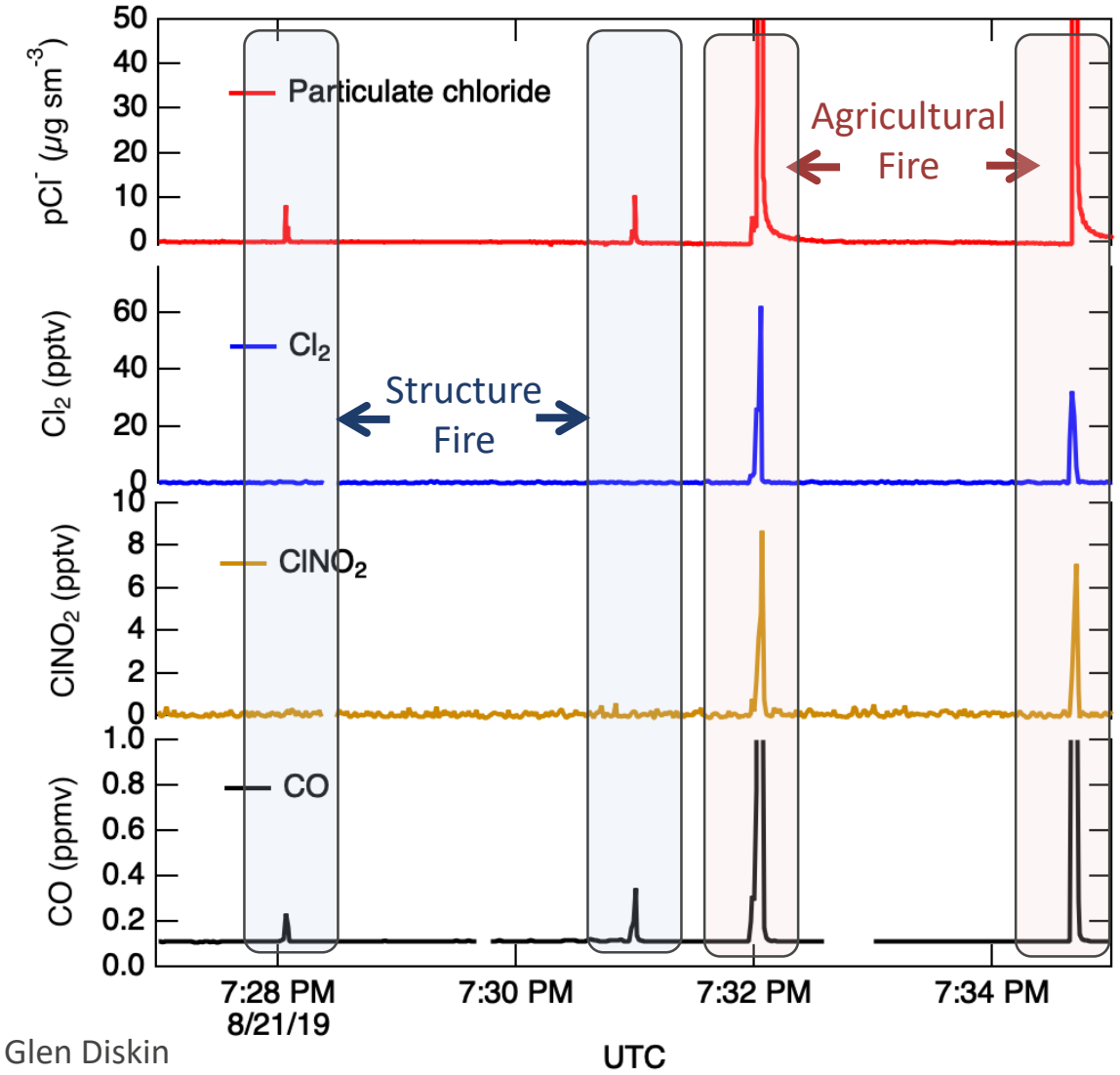


- Heterogeneous chemistry that activates chloride out of the particulate phase may enable halogen chemistry from biomass, trash or structures
- Christian et al. (Atmos Chem Phys 2010) estimate global HCl source from trash burning = 6-9 Tg yr^{-1}

Structure Fire Sampled by NASA DC-8

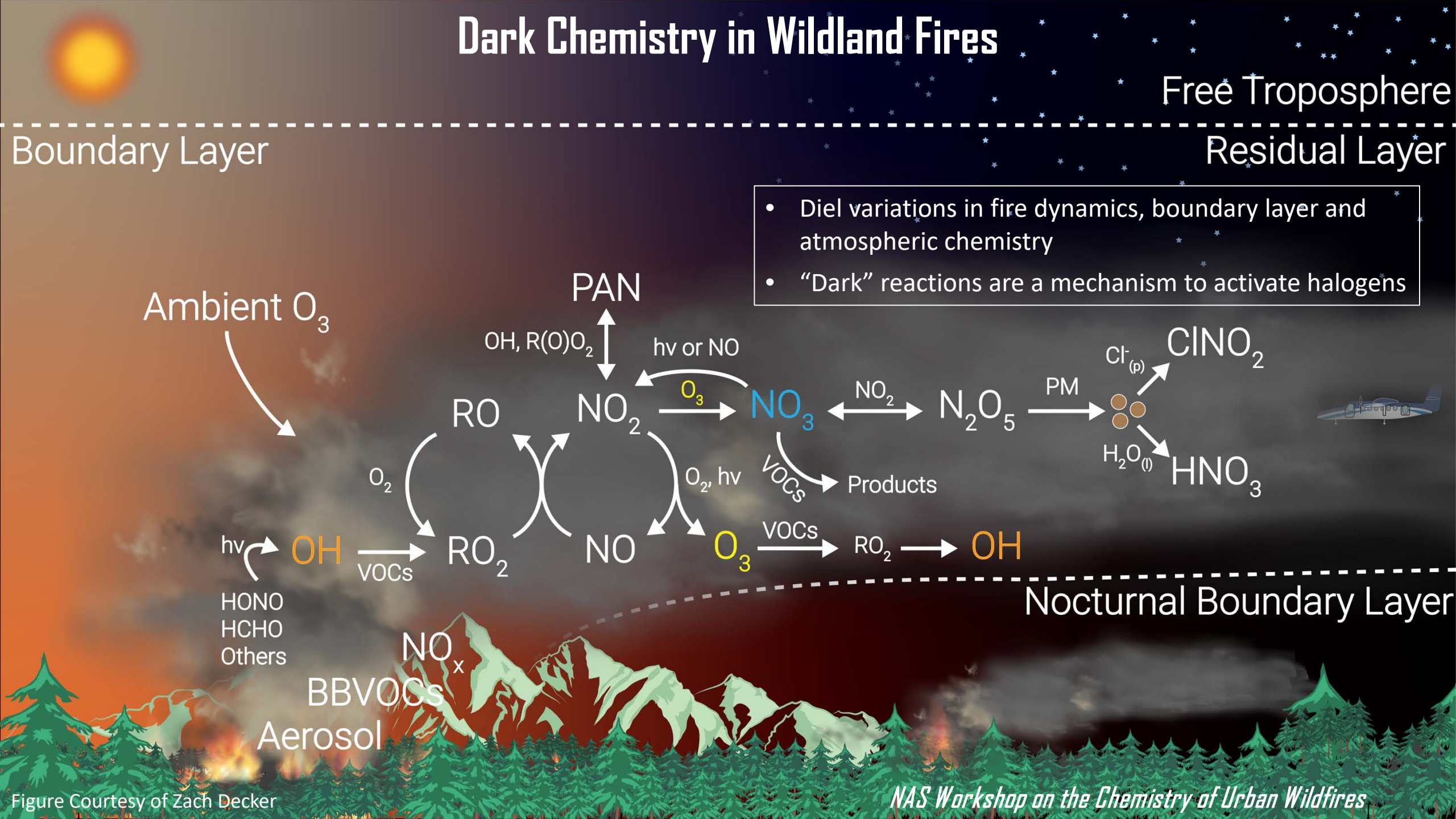
- NASA DC-8 sampled structure fire during agricultural burn flight
- Chloride emission factors large relative to CO, but not larger than adjacent agricultural fires
- Other halogen species absent in structure fire





I⁻ CIMS Data: Patrick Veres, Andy Neuman; AMS Data: Jimenez Group, CU; CO Data: Glen Diskin

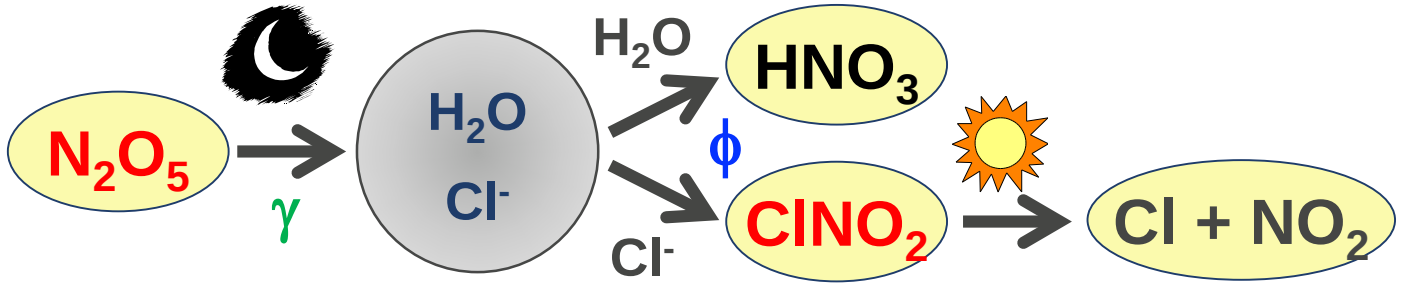
Dark Chemistry in Wildland Fires



- Diel variations in fire dynamics, boundary layer and atmospheric chemistry
- "Dark" reactions are a mechanism to activate halogens

Figure Courtesy of Zach Decker

Halogen Activation in Biomass Burning – Lab Studies



- Halogen activation process typically takes place in the dark
- Next day photochemistry produces Cl atoms and halogen cycles

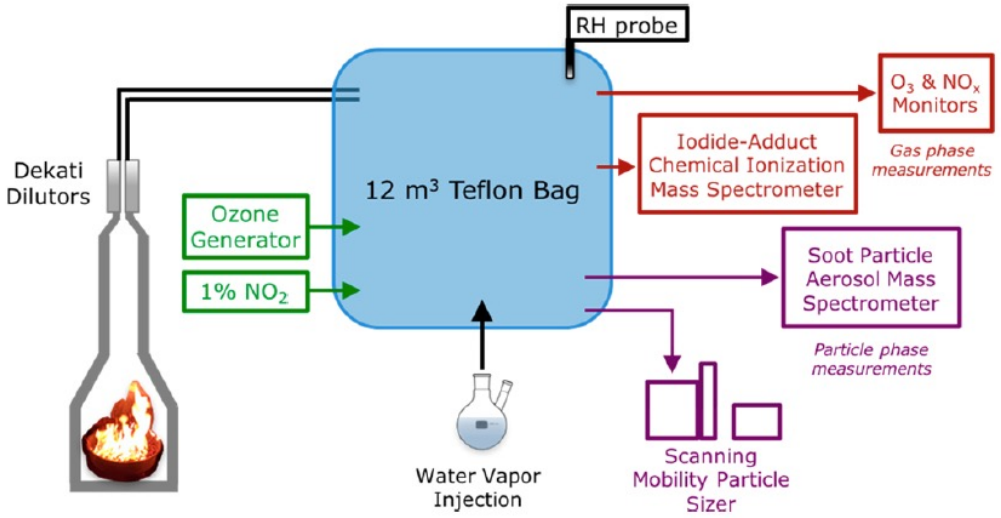
γ = Heterogeneous uptake coefficient for N_2O_5

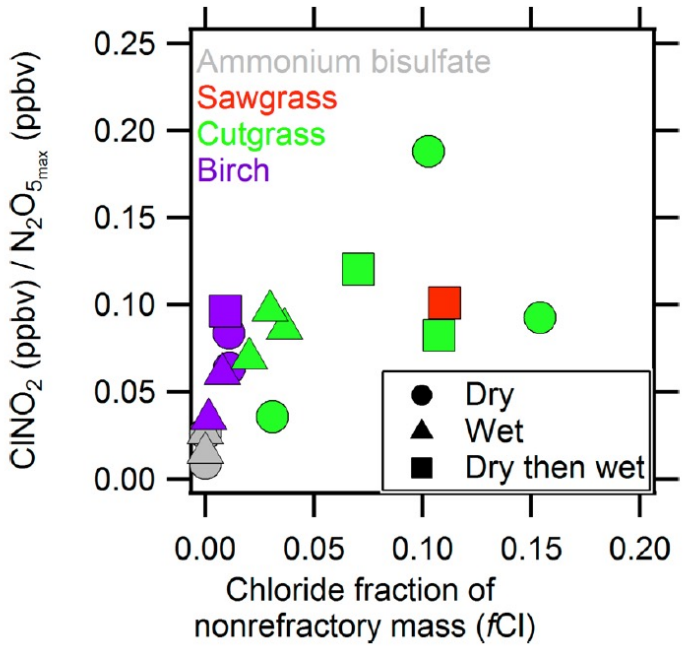
ϕ = Yield of $ClNO_2$ ($ClNO_2$ produced per N_2O_5 lost)

- Large body of literature parameterizing γ and ϕ as a function of $p(Cl^-)$ and $p(H_2O)$
- Recent lab studies: $\phi(ClNO_2)$ of ~10% on authentic biomass burning samples

Ahern et al., Environ. Sci. & Tech. (2018)

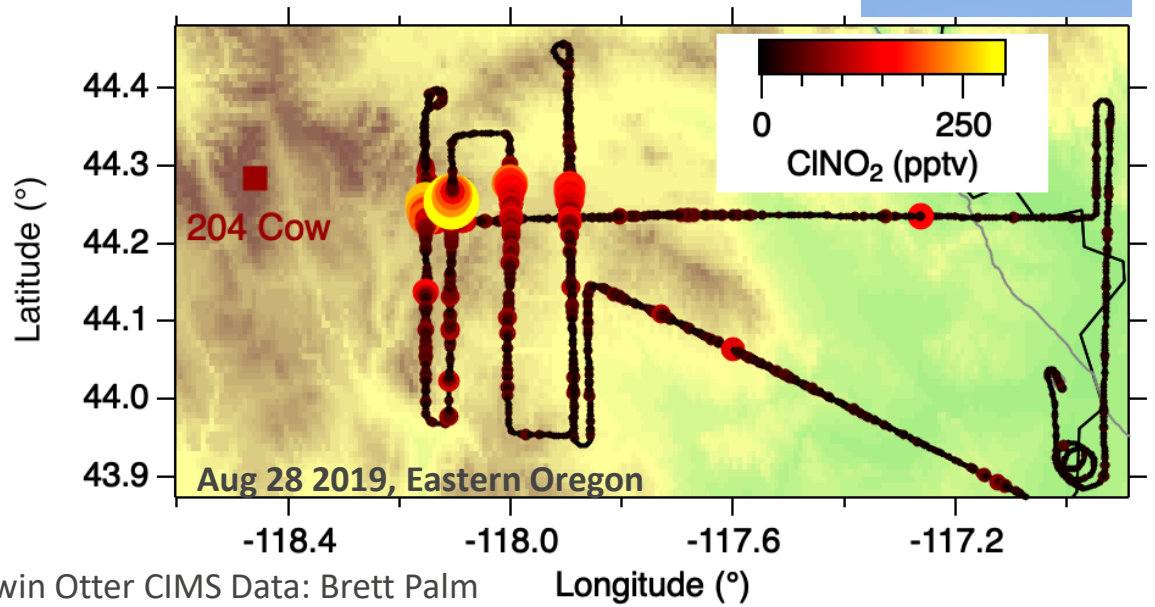
Goldberger et al., Environ. Sci. Proc. Impacts (2019)





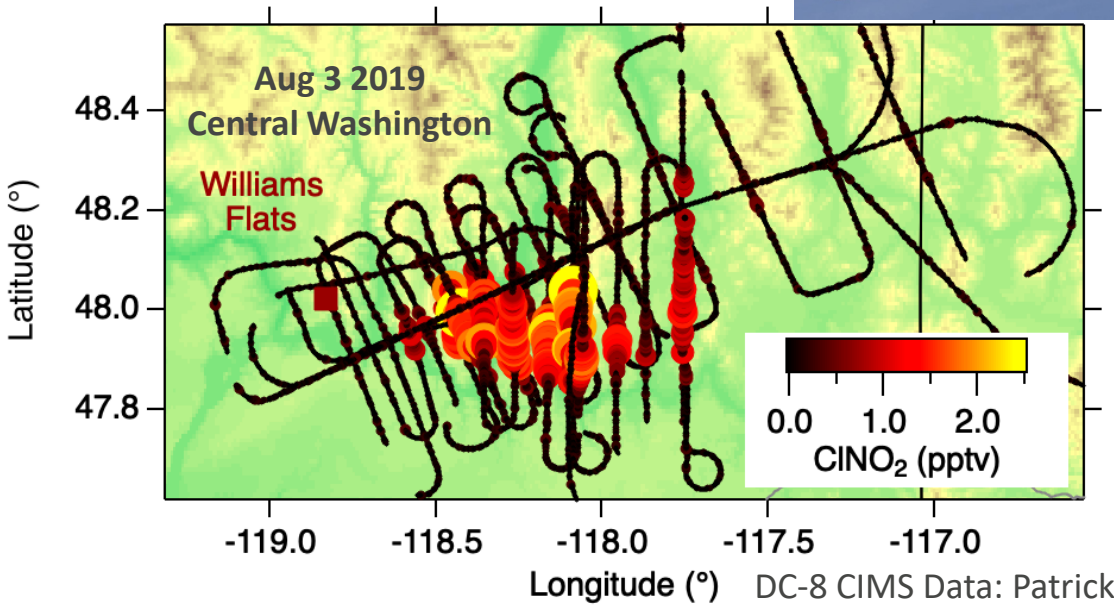
Halogen Activation in Biomass Burning – Field Studies

$ClNO_2$ sampled on night flight from NOAA Twin Otter



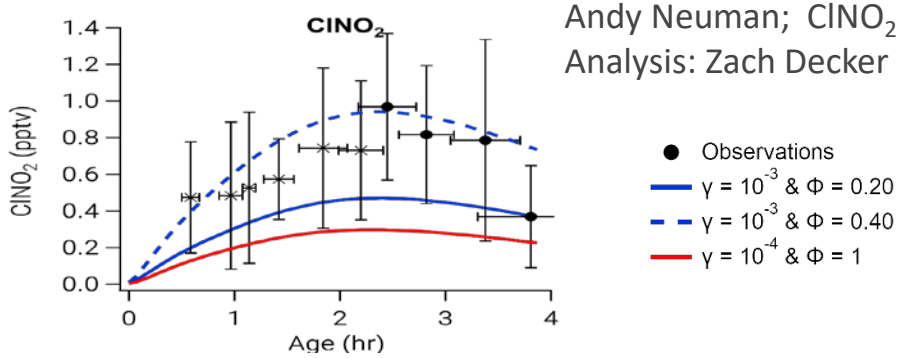
Twin Otter CIMS Data: Brett Palm

$ClNO_2$ sampled during daytime flight from NASA DC-8



DC-8 CIMS Data: Patrick Veres, Andy Neuman; $ClNO_2$ Analysis: Zach Decker

- Analysis ongoing to quantify $ClNO_2$ yields (ϕ) from these observations
- Notable presence of measurable $ClNO_2$ even during daytime
- Limitation to BB halogen activation from competing chemistry
- No analysis of this chemistry from structure fires in current literature

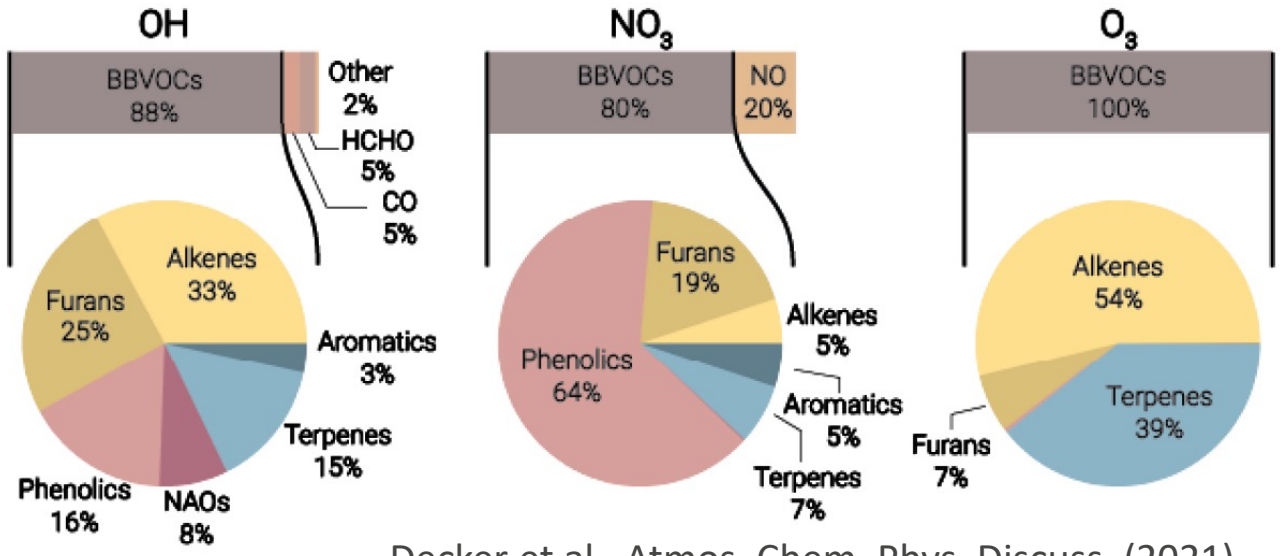


Fire Plume Oxidant Reactivity – Knowledge Gap for Cl

- Chemical transformations in biomass burning smoke (and other emission sources) considered in terms of the three major atmospheric oxidants

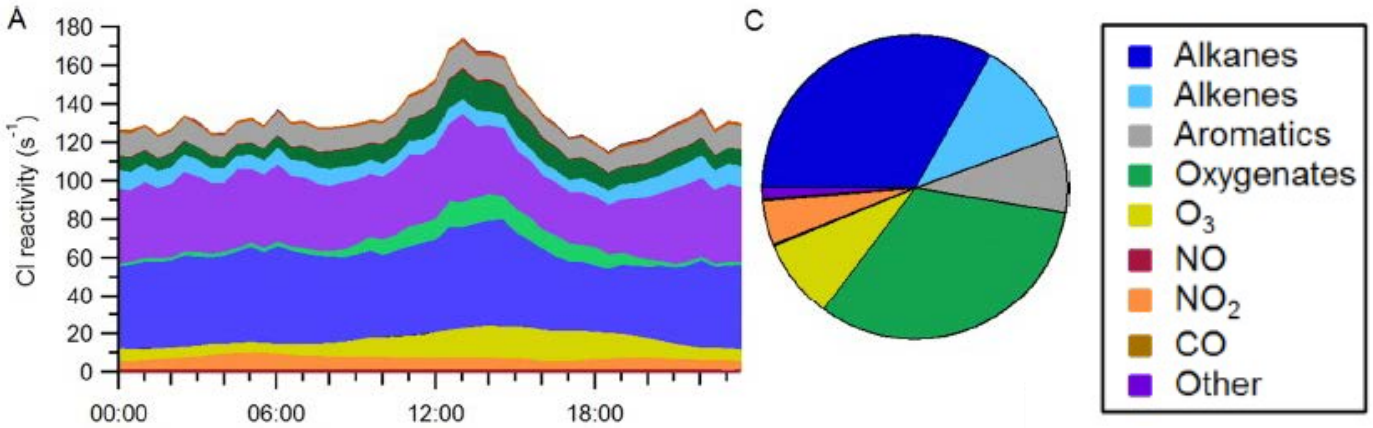
  Hydroxyl Radical (OH)
  Ozone (O_3)
  Nitrate Radical (NO_3)

- Biomass burning is unusual for its high reactivity toward O_3 and NO_3 and the role of oxygenated aromatics (phenols, furans)



Decker et al., Atmos. Chem. Phys. Discuss. (2021)

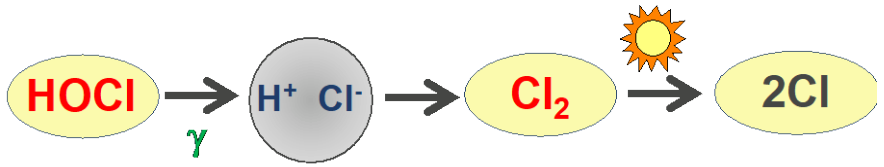
- Young et al., Atmos. Chem. Phys. (2014): Chlorine Radical (Cl•) reactivity budget for urban air in Pasadena, CA
- Similar analysis required for biomass burning, possibly to include structure / WUI emissions



Fate of chlorine radicals (Cl•), if produced in burning plumes, is unknown

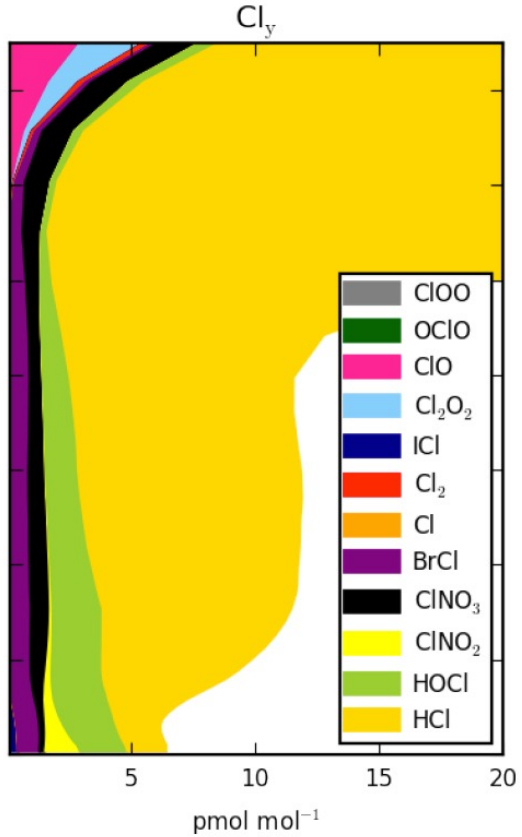
Other Potential Halogen Cycles in Fires

Chlorine activation through hypochlorous acid (HOCl)



HOCl produced from ClO + HO_2 reaction not likely significant in fires

Sherwen et al., Atmos. Chem. Phys. (2016): Major Cl tropospheric cycles involve HCl, $ClNO_2$ and HOCl



Reaction of gas phase HCl with hydroxyl radical (OH)

$$OH + HCl \rightarrow H_2O + Cl$$

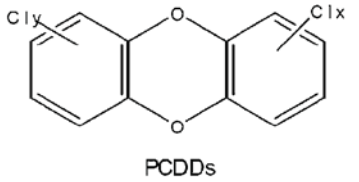
Large OH reactivity, aerosol partitioning of chloride make this unlikely in fires

Bromine chemistry

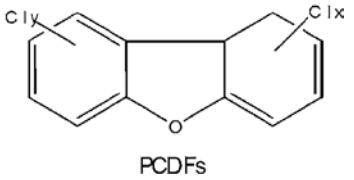
- Bromide emission factors sparse or non-existent for wildland and agricultural fuels
- Non-negligible HBr emission factors from structure fires (0.24 ± 0.21 g kg^{-1}) could make this an interesting topic
- Little known about chemical transformations in fires

Chlorinated Dioxins and Dibenzofurans

Polychlorinated dibenzo-p-dioxins (PCDD) and polychlorinated dibenzofurans (PCDF)



PCDDs



PCDFs

Well known toxins emitted from combustion of chlorine containing substances

PCDD emission factors: 0.2 – 2 mg kg-1
PCDF emission factors: 2– 56 mg kg-1

Structures, vehicles & trash combustion

These emissions are absent or not reported in wildland & agricultural fuel inventories

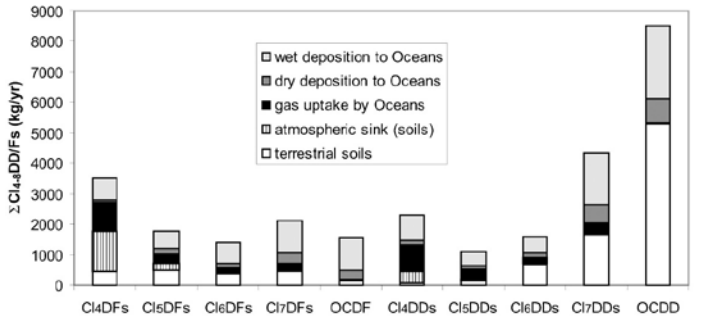
Gas phase lifetime determined by OH radical reaction

Kwok et al., Environ. Sci. & Tech. (1995):
PCDD & PCDF lifetimes of order 1-30 days

no. of chlorine atoms	tropospheric lifetime (days)[a]		
	PCDD	PCDF	PCB
0	1.0[b]	3.7[b]	2.0[b]
1	3.0[b]	2.9	2.7–5.1[b]
2	2.0–2.4	4.0–5.5	3.4–7.2[b]
3	2.5–3.3	5.5–9.5	6.9–15
4	2.8–7.2	7.7–18	8.5–40
5	4.0–8.5	15–29	16–48
6			29–90

Fate of PCDDs, PCDFs

Lohmann et al., J. Geophys. Res. (2006): Competition between gas phase oxidation and deposition



No field study of atmospheric chemical transformation of PCDDs or PCDFs in wildland fire plumes

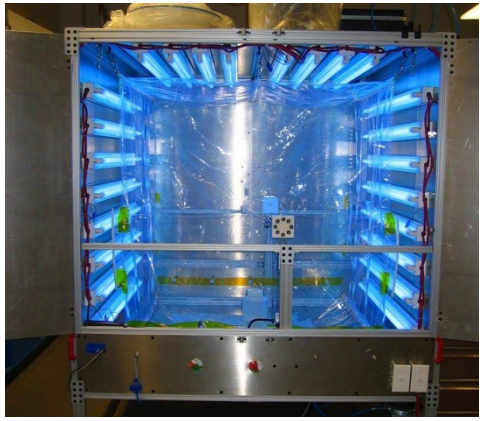
Study Design for WUI

Emissions

e.g.: NIST National Fire Research Lab

- Expand existing database for structures, vehicles, etc.
- State of the art instruments now available to characterize detailed gas and particle phase emissions

Lab Studies - Chemistry



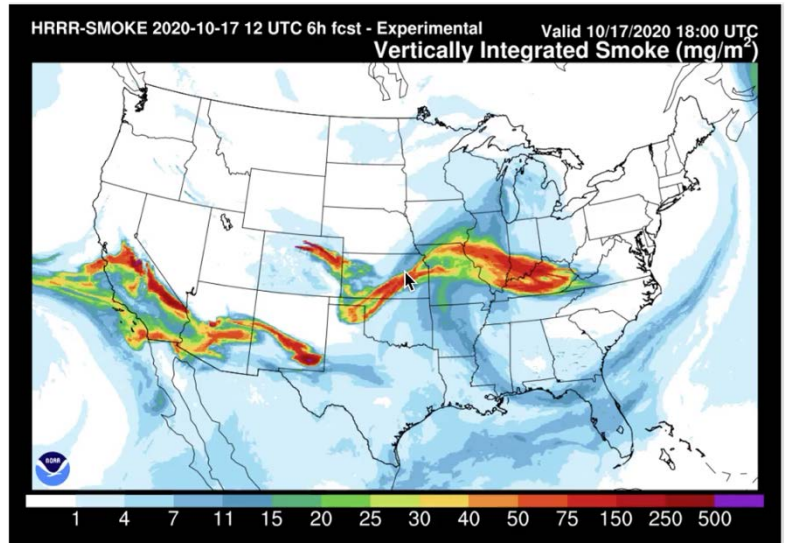
- Gas phase reactions involving all oxidants (OH, O_3, NO_3, Cl)
- Identify chemistry that is unique to emissions from structures and vehicles
- Heterogeneous and particulate phase chemistry

Field Studies – Emissions & Chemistry

- Logistically difficult – fires affecting structures / WUI not necessarily easy to find
- Heavy aircraft may be too large for more local scale measurements
- Mobile laboratories or possibly light aircraft may provide data on chemical transformations

Models - Impacts

- Incorporate chemistry into current smoke forecast models



Concluding Remarks

- Extensive recent studies have elucidated key aspects of emissions and chemistry from wildland and agricultural burning in North America and elsewhere
- Structure and / or vehicle combustion from WUI fires is a potentially large halogen source. Halogen cycles are active in wildland fires, but are uncertain and a topic of current research
- There are few, if any, field studies targeting chemical transformations characteristic of structure fire emissions or other sources that may be important in the WUI
- A study design could include 1) updated emissions; 2) targeted laboratory studies; 3) field studies at the scale of the WUI; and 4) incorporation of key findings into predictive models

Photo: Dan Lack