Exploring the complexity of gas- and particle-phase organic chemistry, and indoor infiltration rates, when wildfire smoke arrives in highly populated regions of California

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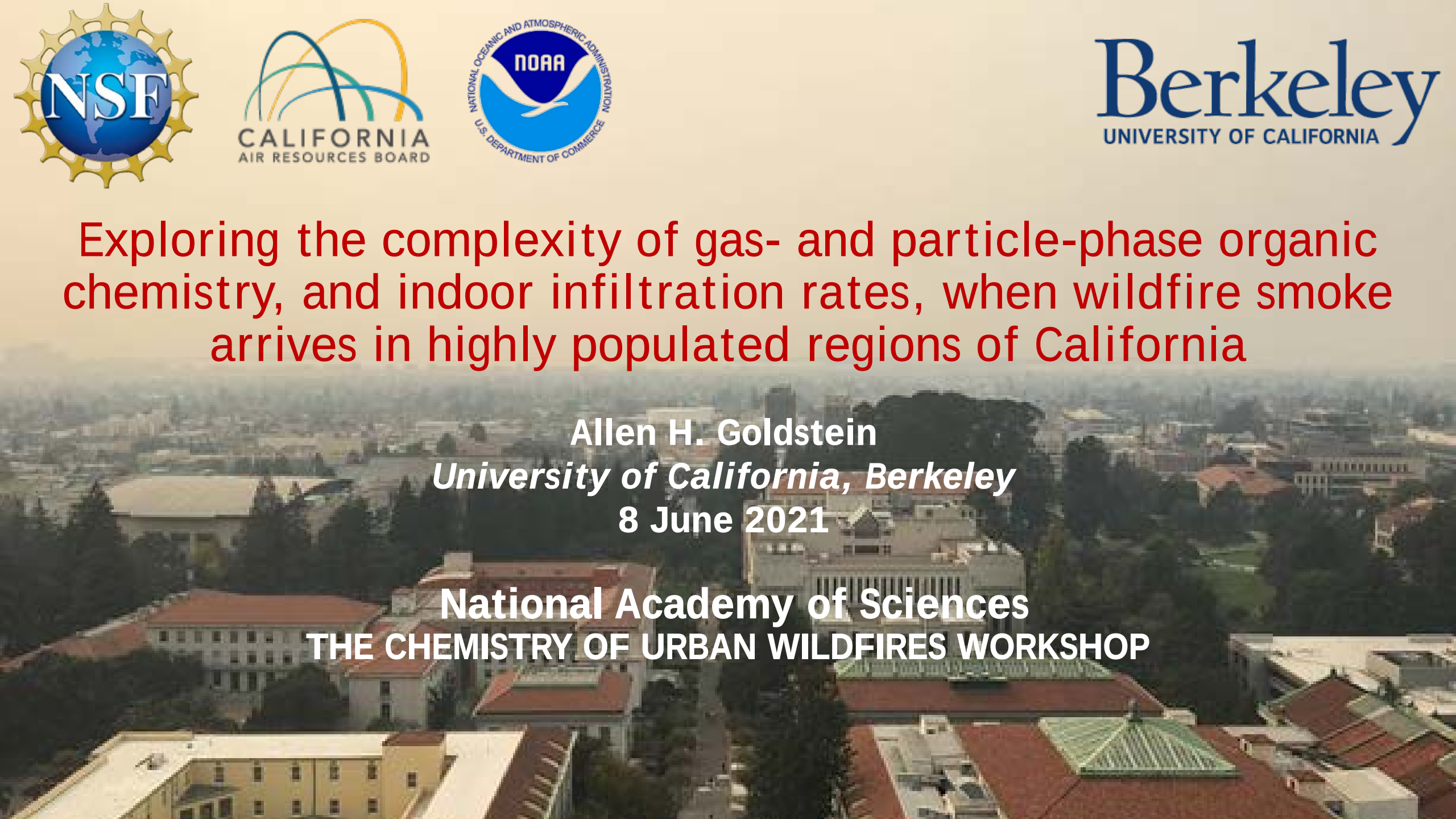
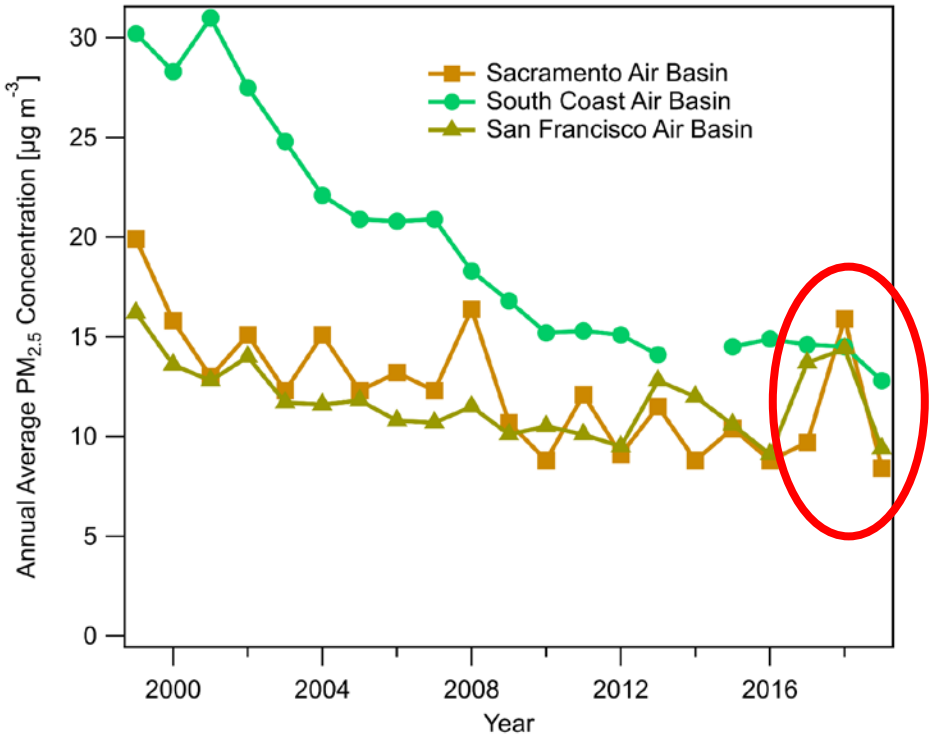
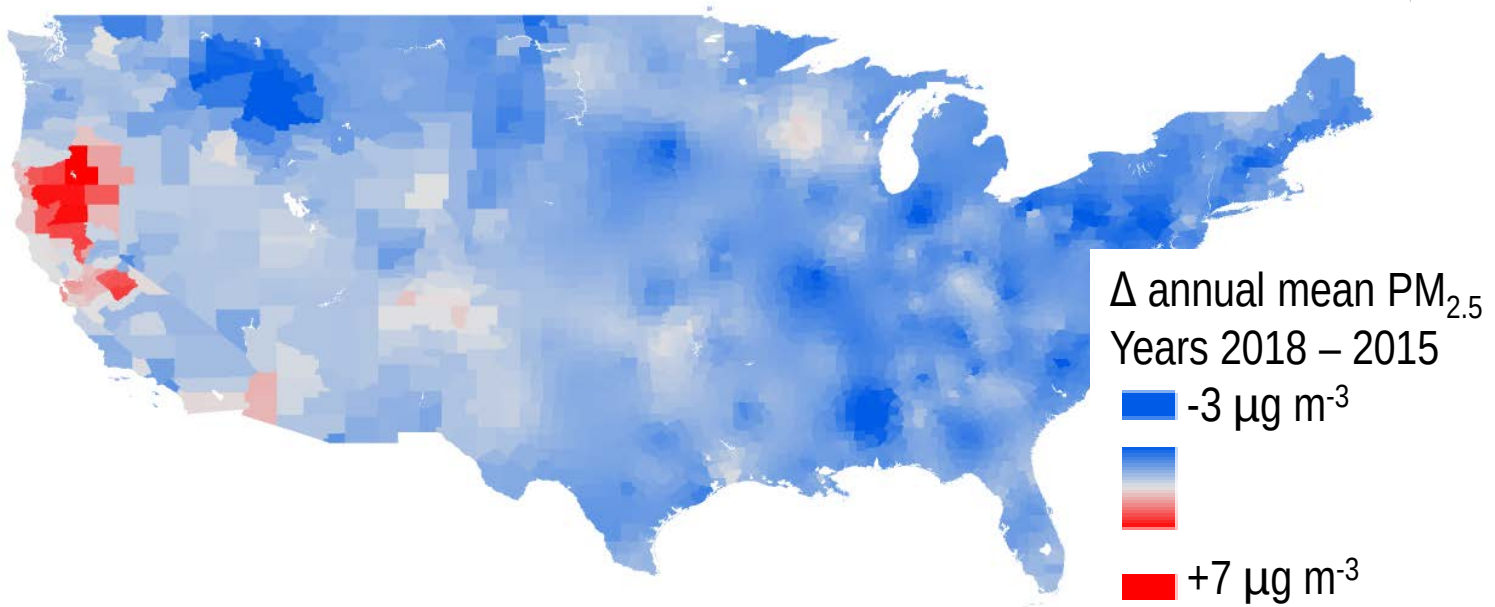
National Academy of Sciences
THE CHEMISTRY OF URBAN WILDFIRES WORKSHOP



Frequency and severity of smoke episodes with $PM_{2.5}$ exceedances has increased sharply in California





$PM_{2.5}$ in California and across the US has been declining for several decades

$PM_{2.5}$ in many regions of California is no longer declining after 2015 due to wildfires

Figures by Y. Liang, Data from CARB and EPA via O'Dell et al. *ES&T* 2019

Wildfire smoke is harmful to people's health

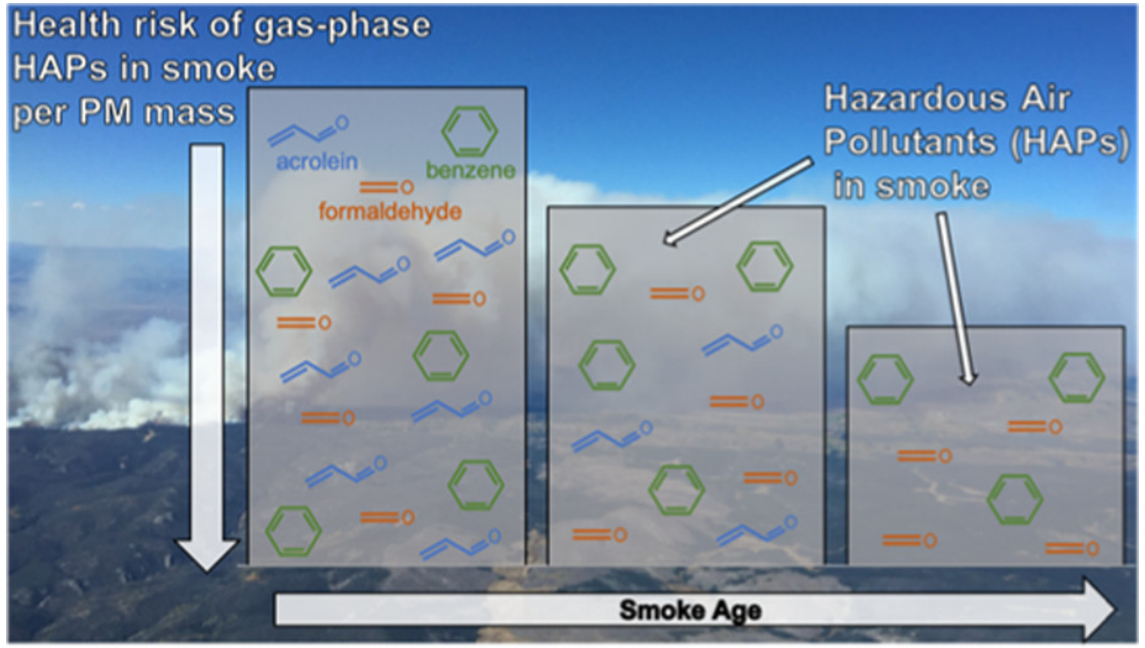
- **Main Wildfire Pollutants:** Organic gases & particles
- **Effects of exposure:** Adverse respiratory outcomes (exacerbation of asthma and chronic obstructive pulmonary disease, see Reid et al. *EHP* 2016)
- **Enhanced toxicity:** $PM_{2.5}$ from wildfires is more harmful than equal doses of non-wildfire $PM_{2.5}$. (Wesgesser et al. *EHP* 2009, Aguilera et al. *Nat. Comm.* 2021)
- **Airborne chemistry:** Some wildfire VOCs are hazardous air pollutants, VOCs in smoke may undergo photooxidation, producing harmful oxygenated VOCs, O_3 and PM

ORIGINAL RESEARCH

American Heart Association.

Out-of-Hospital Cardiac Arrests and Wildfire-Related Particulate Matter During 2015–2017 California Wildfires

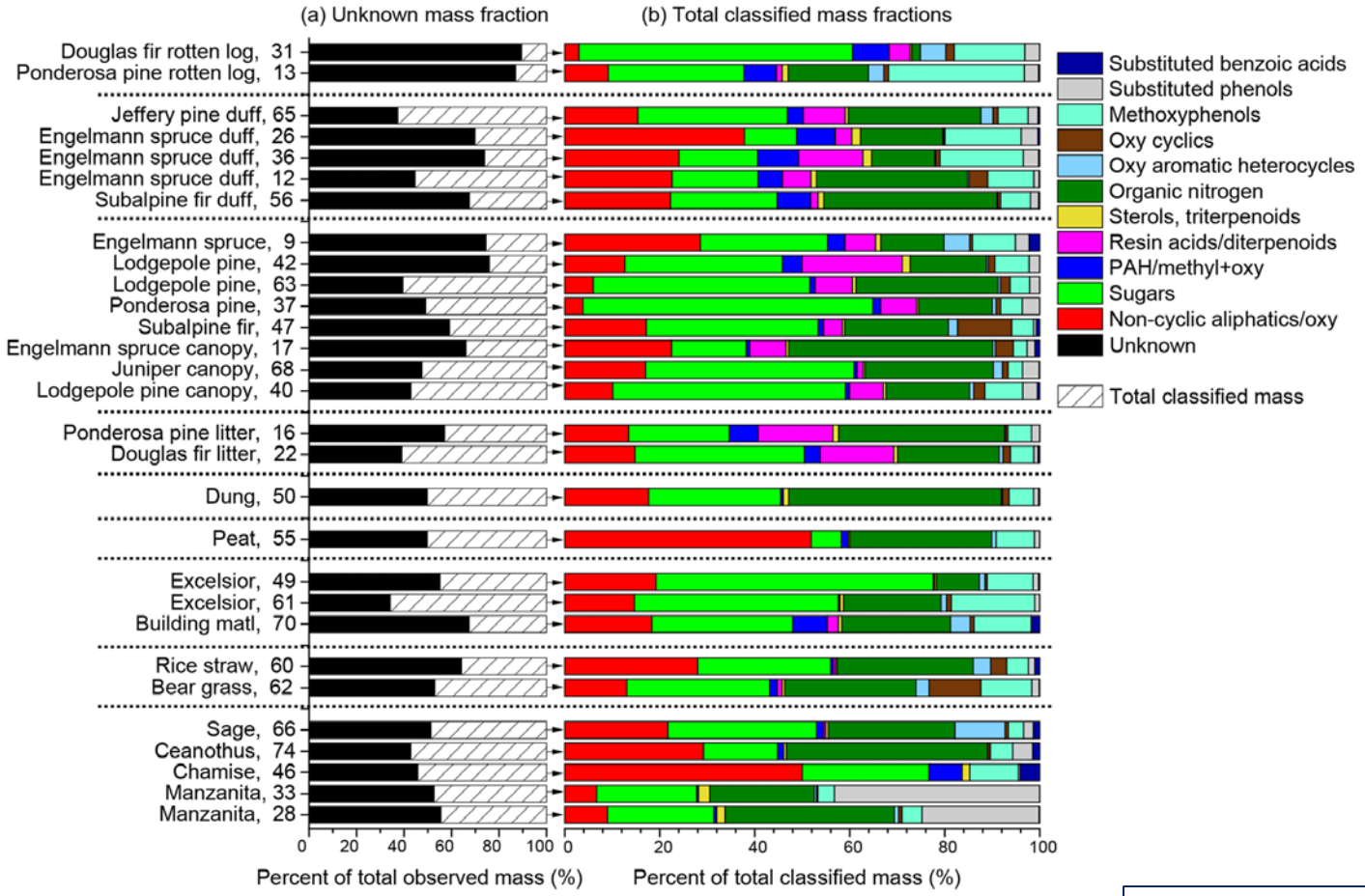
Caitlin G. Jones, MS; Ana G. Rappold, PhD; Jason Vargo, PhD; Wayne E. Cascio, MD; Martin Kharrazi, PhD; Bryan McNally, MD; Sumi Hoshiko, MPH; with the CARES Surveillance Group



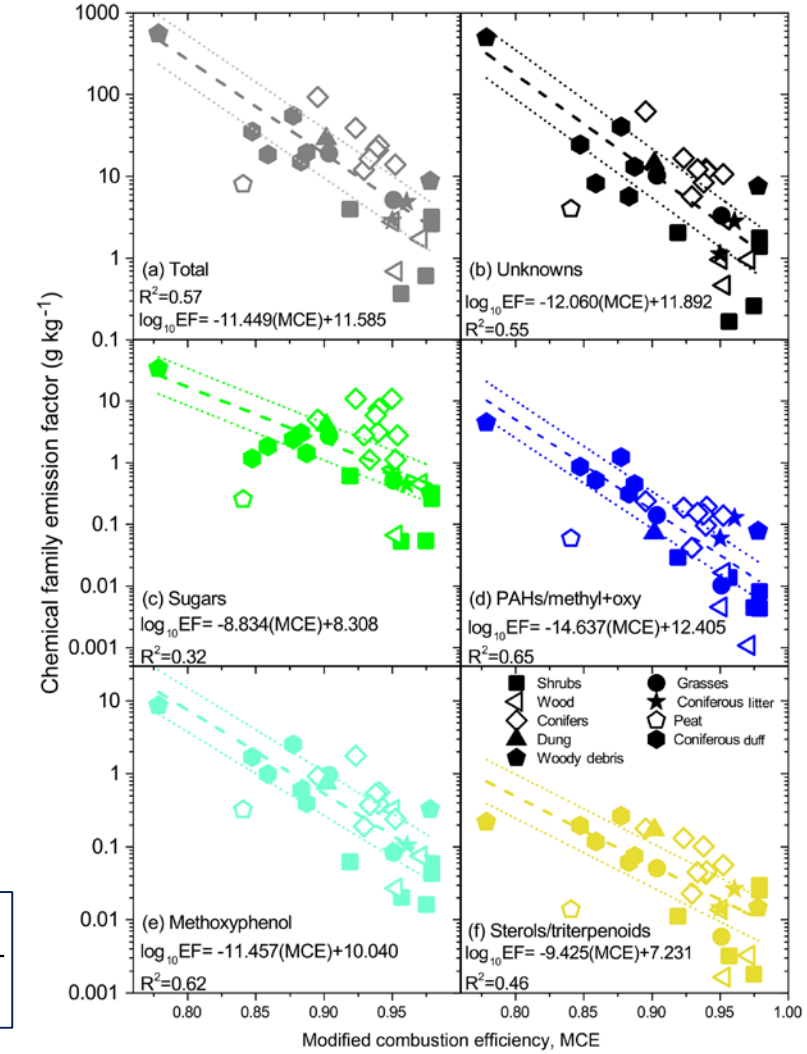
O'Dell et al. *ES&T* 2020

Biomass burning emissions are chemically complex!

>3000 organic chemicals observed in PM, Fire Lab study



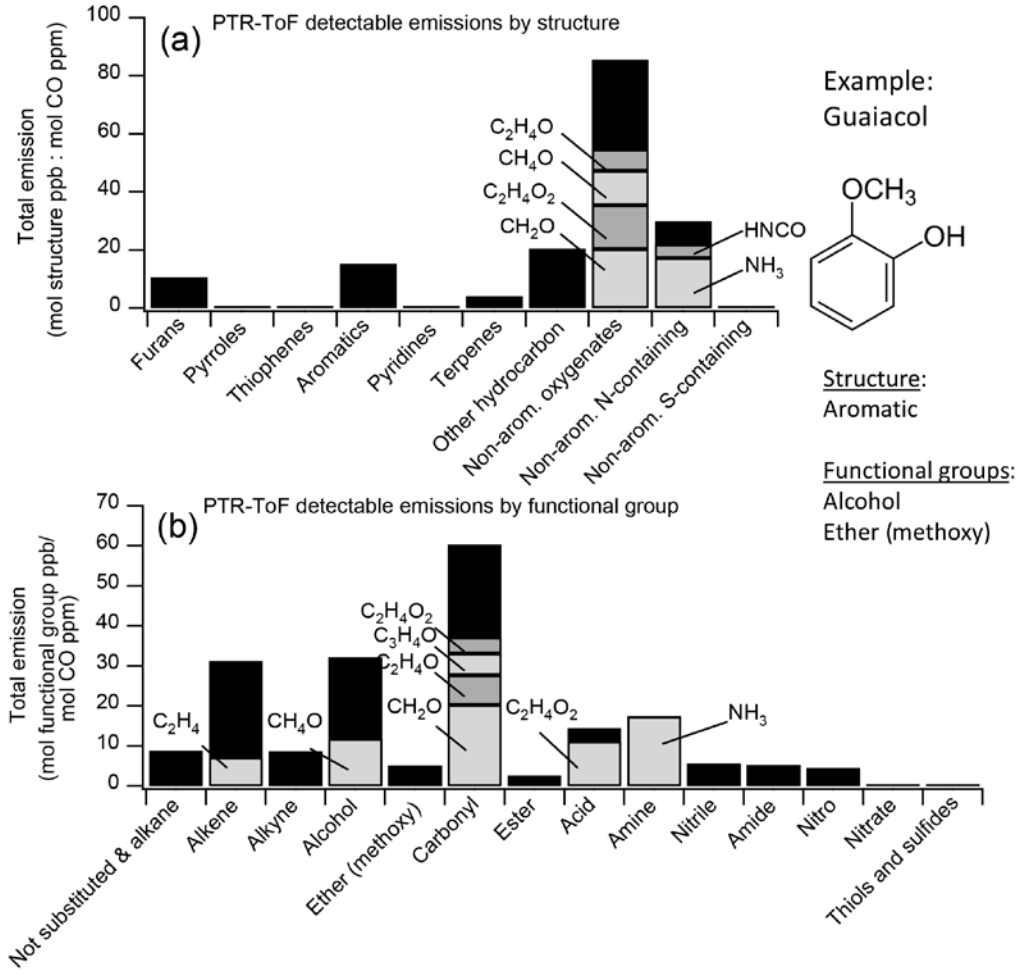
Emission Factors span 3+ orders of magnitude
smoldering emissions >> flaming emissions



$$MCE = \frac{\Delta CO_2}{\Delta CO_2 + \Delta CO}$$

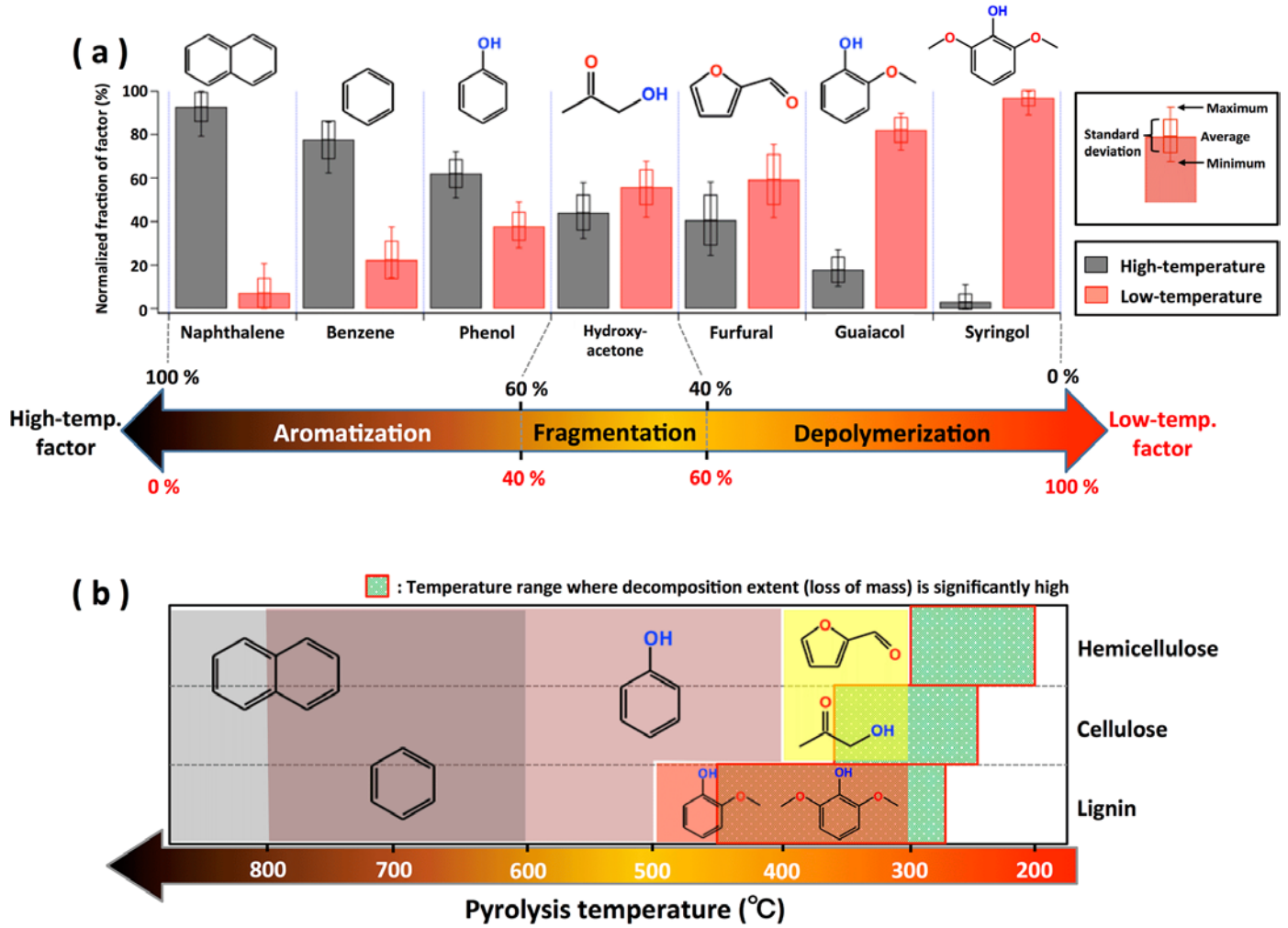
Jen et al. *ACP* 2019

100's of VOCs emitted with wide range of structures & functional groups



Koss et al. *ACP* 2018

VOC emission composition changes with pyrolysis temperature

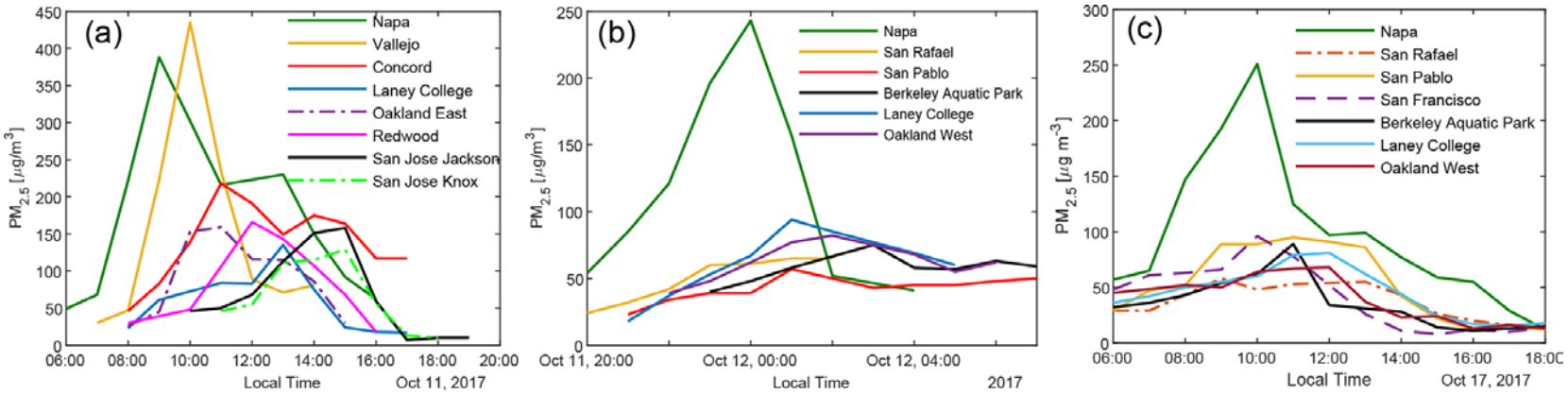


Sekimoto et al. *ACP* 2018

Oct 2017 Northern California Wildfires

- Fires at Wildland Urban Interface (WUI) triggered by power line/electrical failures, resulting from strong “Diablo” winds
- On the “deadliest & most destructive California wildfires” list
- When fires began we turned on all the instruments in my lab

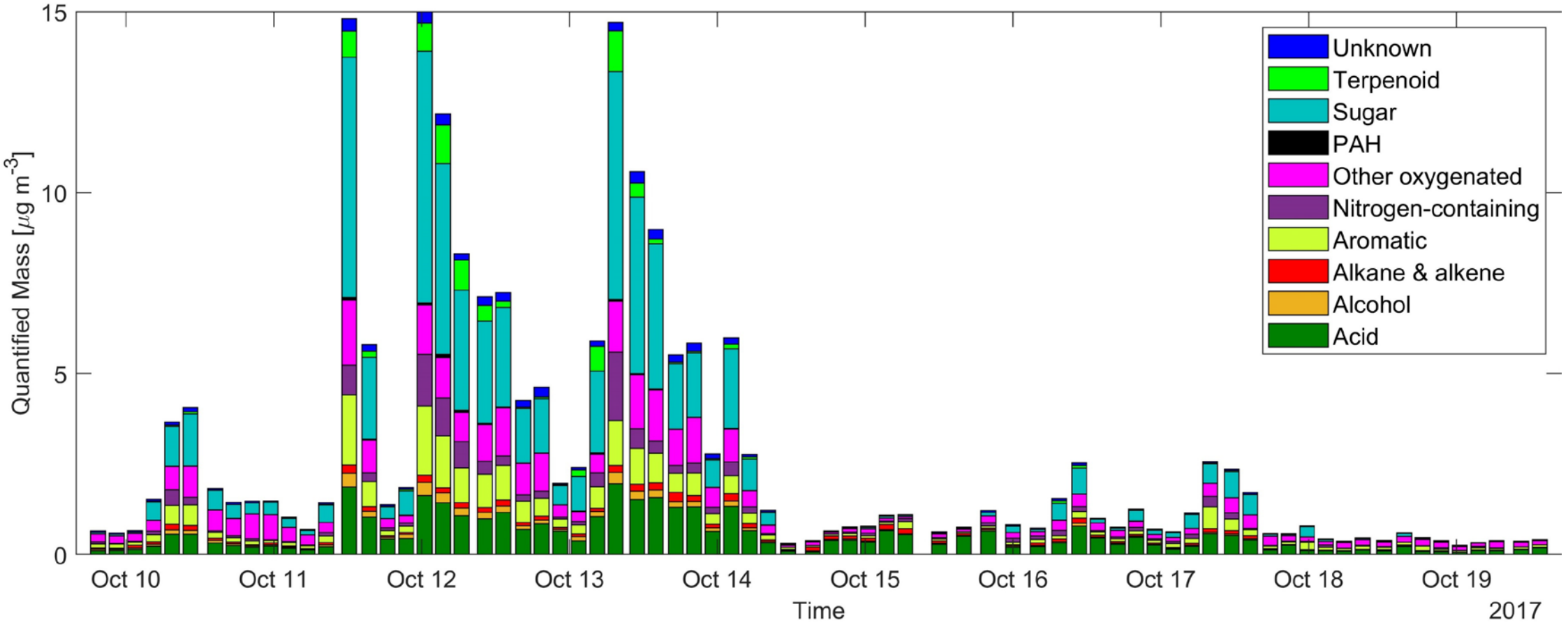
Fire	Size (hectares)	Structures destructed	Deaths
Tubbs	14,895	5,643	22
Redwood Valley	14,780	544	9
Atlas	20,891	781	6
Nuns	22,008	1,355	3



Fire points from MODIS; Photo credit: UC Berkeley’s Twitter Account

Liang et al. *ACP* 2021

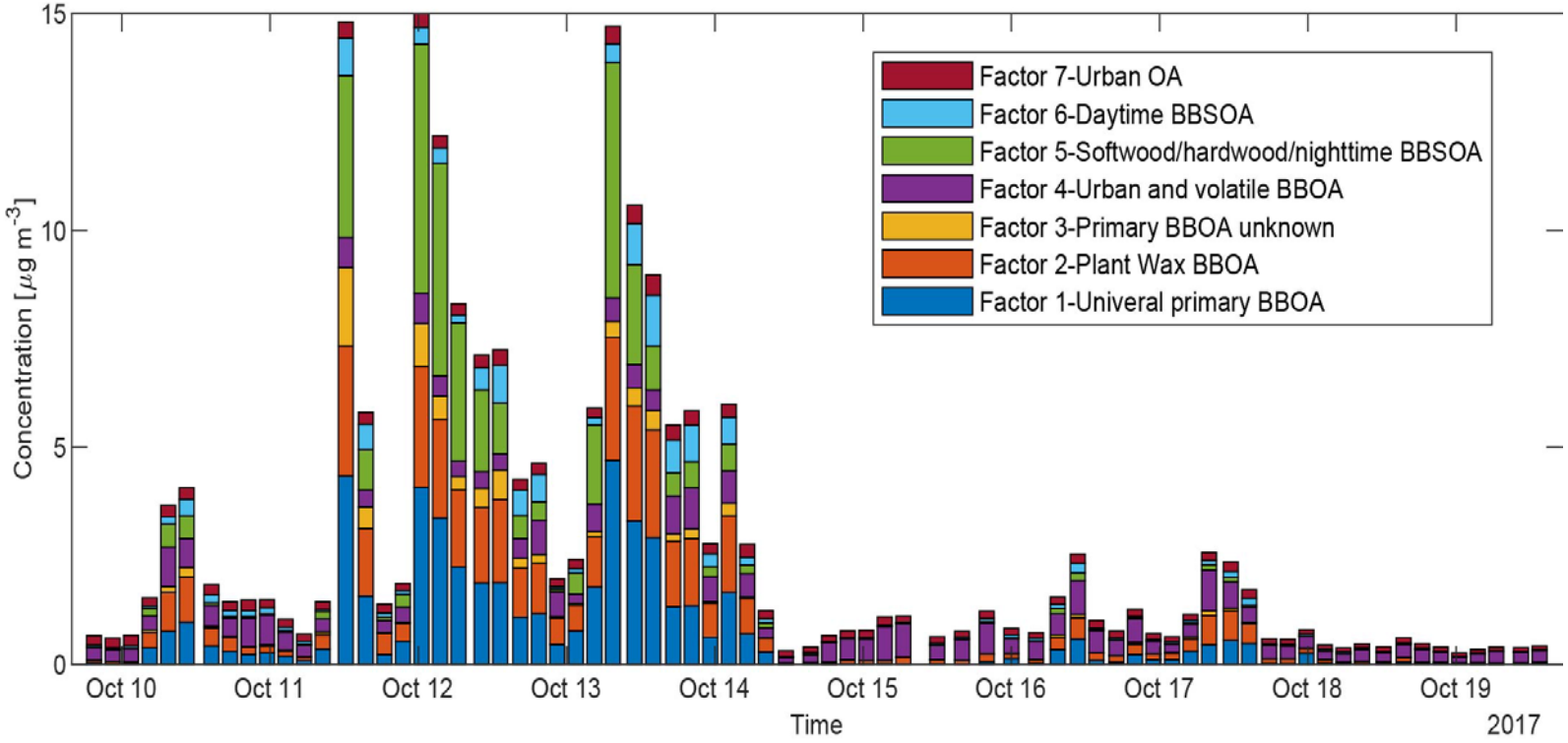
Most organic chemicals in biomass burning $PM_{2.5}$ arriving in Berkeley are "novel" and not identified by traditional methods



- Quantified 570+ organic compounds accounting for ~20% of OC (4 hr filter samples)
- Sugars & sugar derivatives are the dominant identified groups of compounds
- Level of PAHs is below 0.3% of total quantified organic $PM_{2.5}$ (up to 5% in fresh smoke)

Liang et al. *ACP* 2021

Source apportionment using measured markers can differentiate types of fuels burned and other contributing $PM_{2.5}$ sources



Comparison of average emission factors (EFs) from non-biomass fuels (e.g. structures, furnishings, vehicles) versus natural fuels

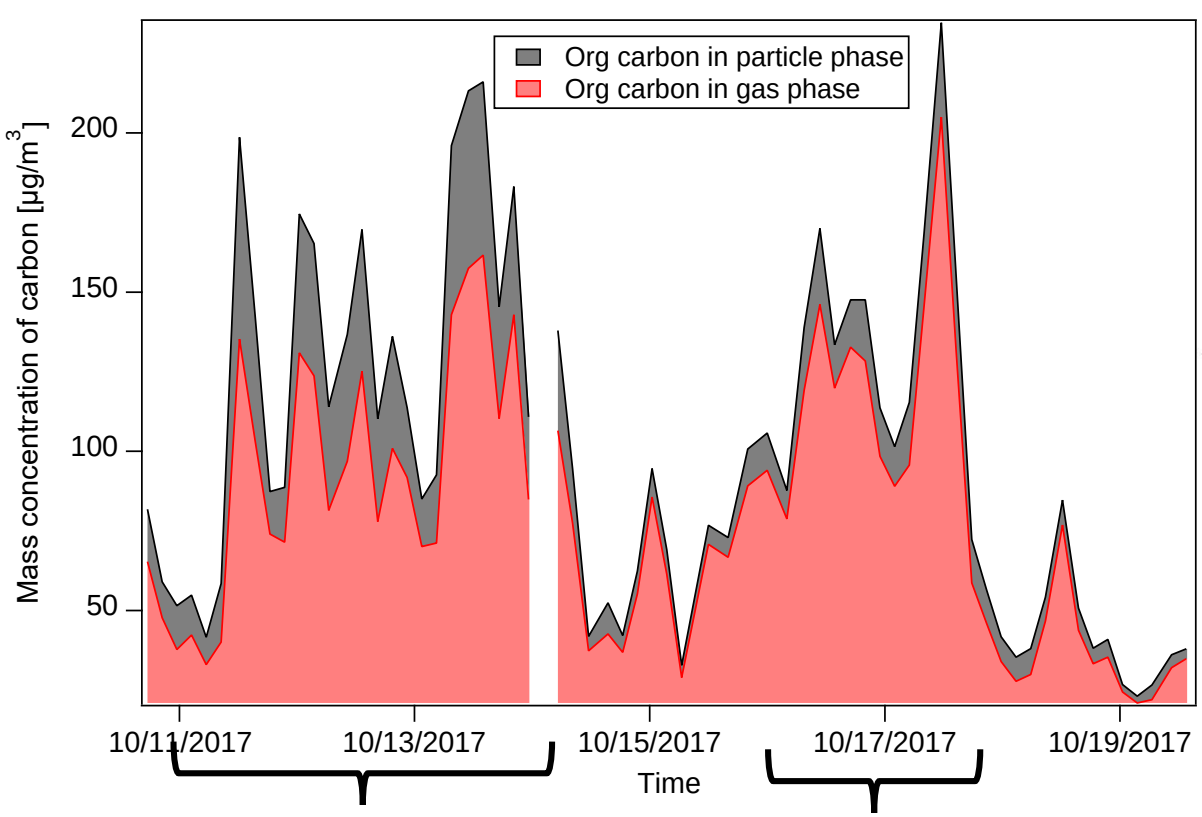
Reported WUI/wildland fire EF ratios	
Benzene	85
Benzo(a)pyrene	366
Polychlorinated dibenzofurans	667

Although fires were at WUI, we were not able to find a factor or representative compounds indicative of “non-biomass fuels” for smoke in Berkeley.

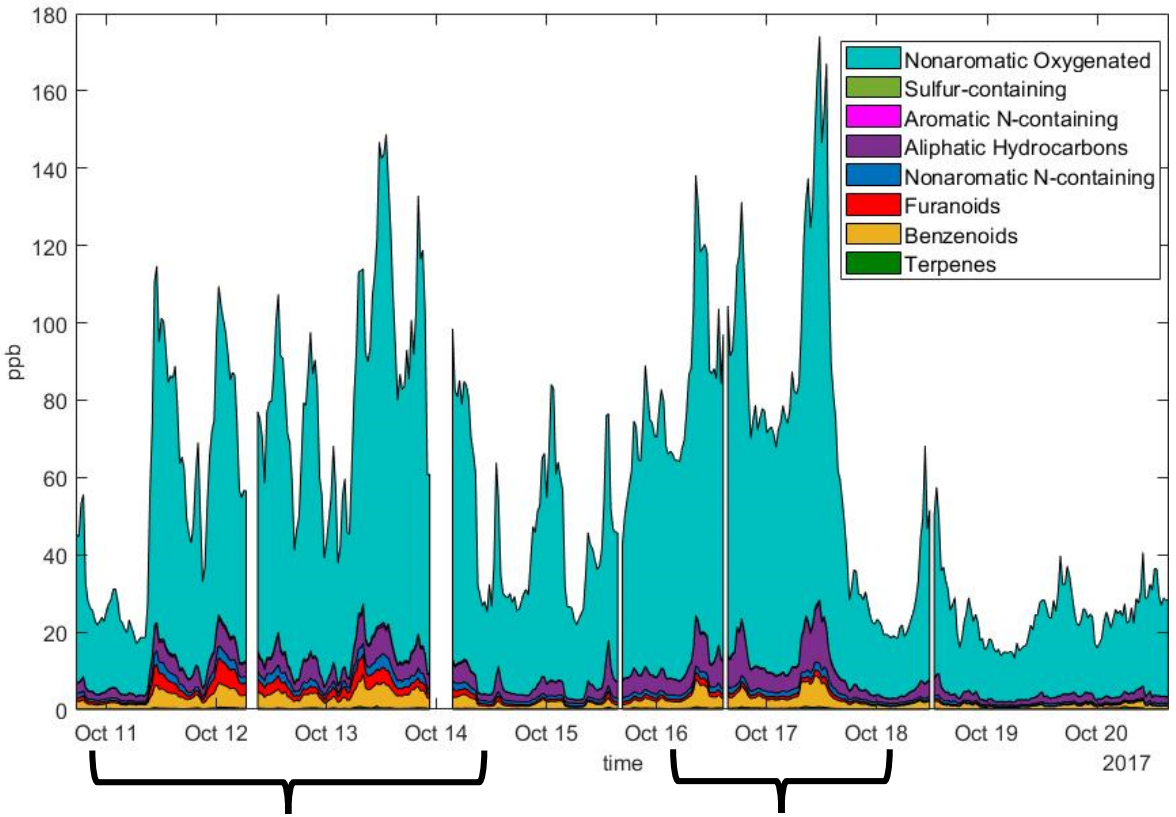
Liang et al. *ACP* 2021

Jaffe et al. *Air & Waste Mngmnt* 2020

VOCs dominate the total observed organic carbon



plume periods



plume periods

Mass of organic carbon in VOCs accounts for 70%-75% of total organic carbon in smoke plume periods (VOCs measured by PTR-TOF-MS)

VOCs were dominated by oxygenated compounds

Liang et al. in prep

Daytime oxidation produced many secondary oxygenated VOCs

$$\Delta VOC = \left(\frac{\Delta X}{\Delta CH_3CN}\right)_{day} - \left(\frac{\Delta X}{\Delta CH_3CN}\right)_{night}$$

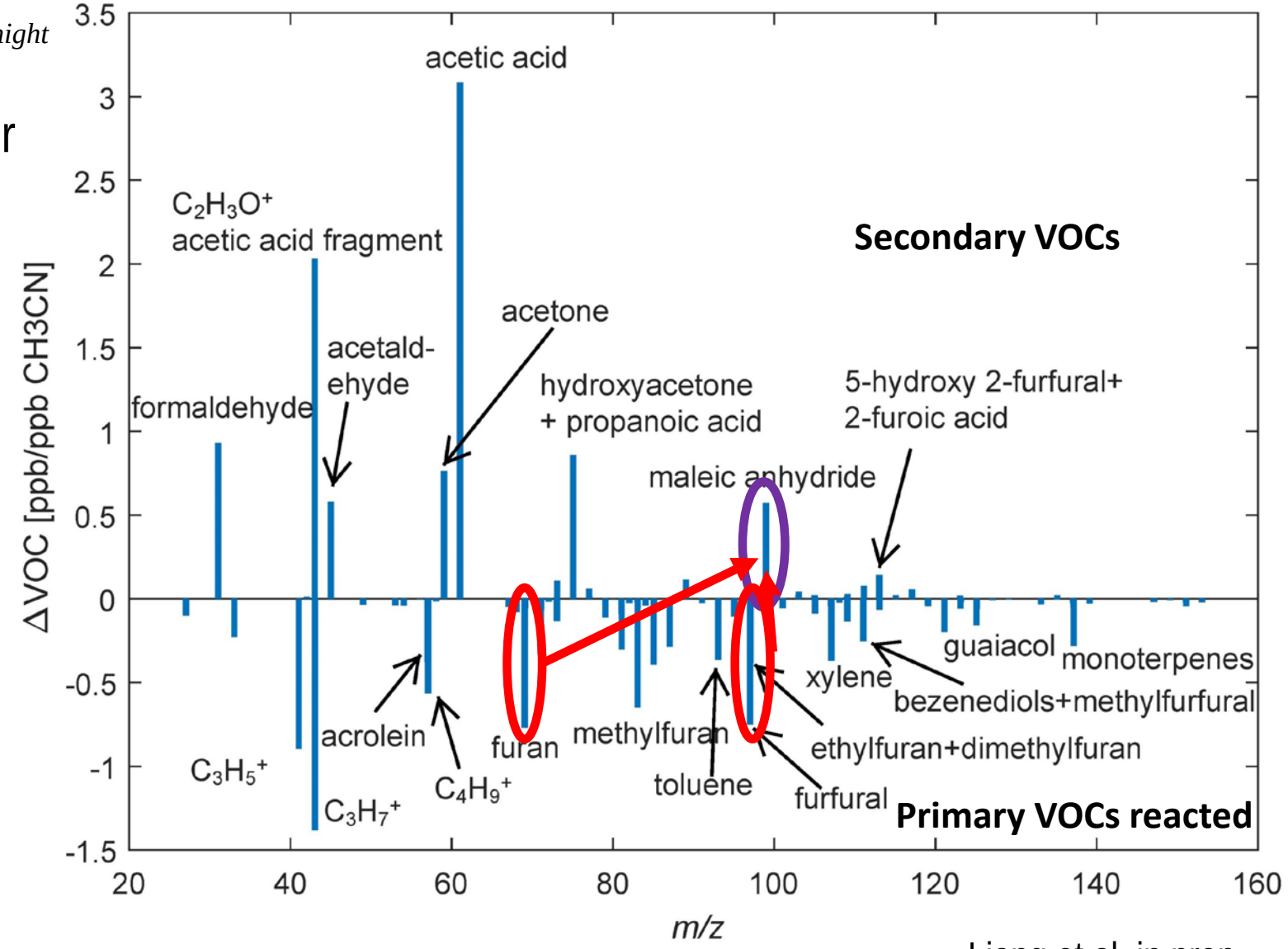
CH_3CN (acetonitrile) = stable fire tracer

furan + OH ⟶ maleic anhydride
Lifetime of furan = 4.4 hours
for [OH] = 1.5×10^6 molec cm^{-3}

Maleic anhydride provides a clear tracer for secondary VOCs from oxidation of wildfire emissions

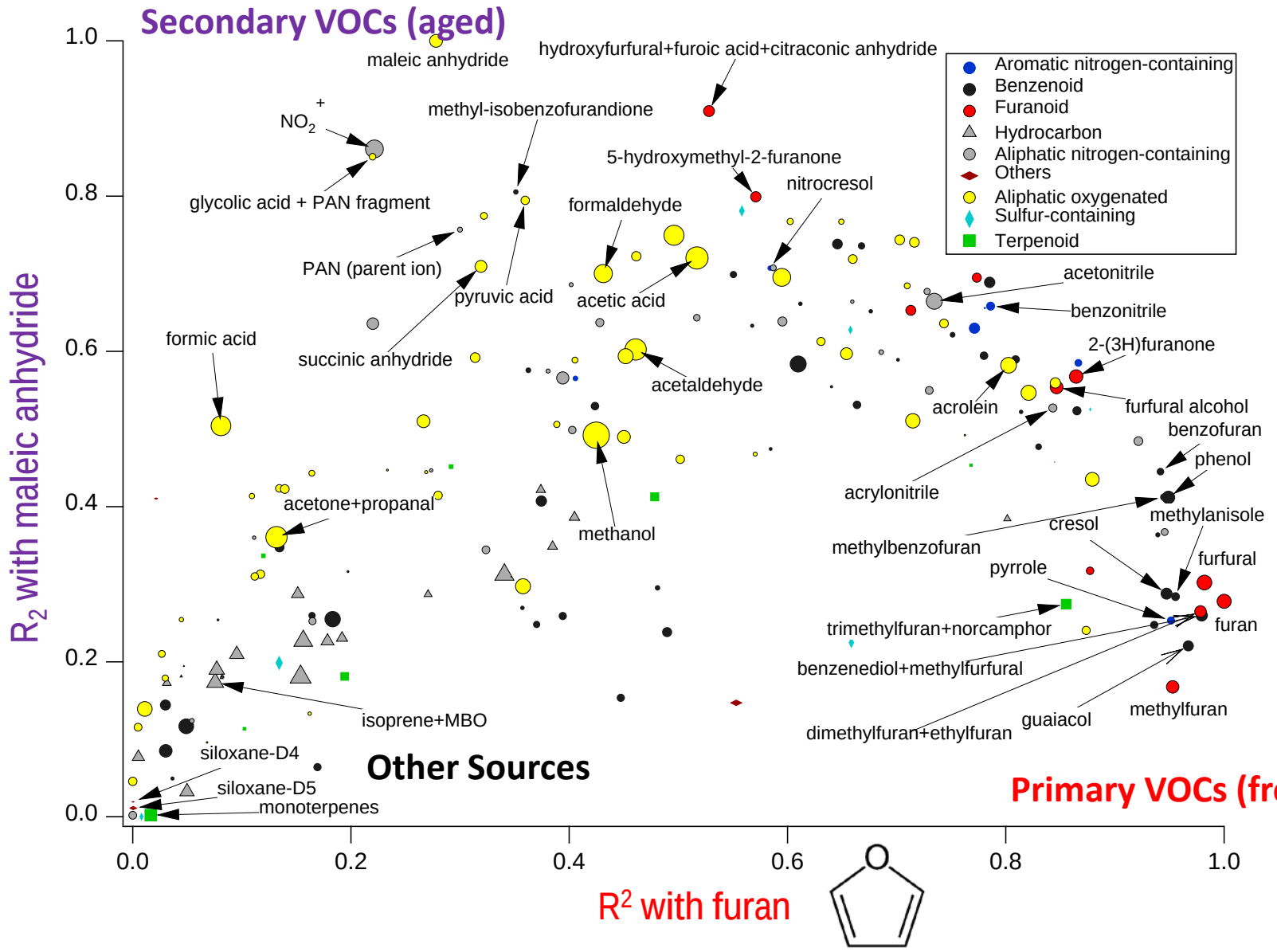
Plume transport time to Berkeley
Daytime ~ 7-8 hours
Nighttime ~ 2-3 hours

Mechanism from Coggon *et al. ACP* (2019)



Liang et al. in prep

Primary VOCs can be differentiated from secondary VOCs by correlation with furan (primary) and maleic anhydride (secondary)



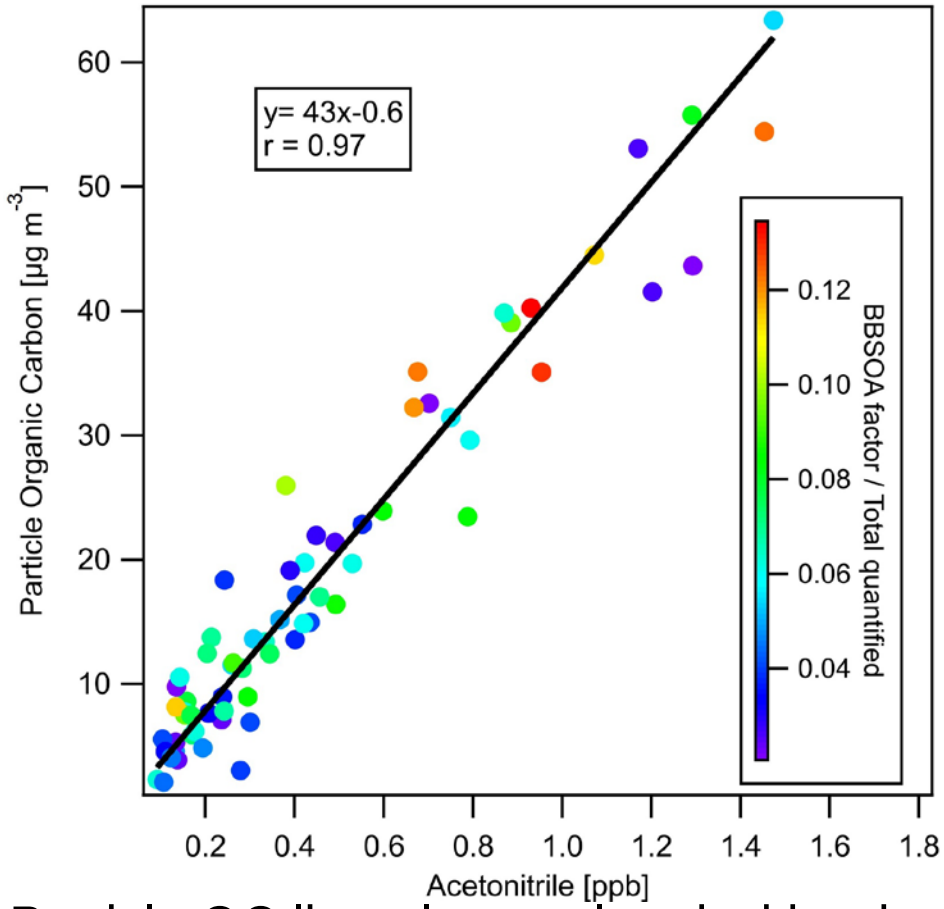
Mixture of VOCs arriving in Berkeley has very different composition than fresh emissions

Chemicals with lifetimes < a few hours have been transformed

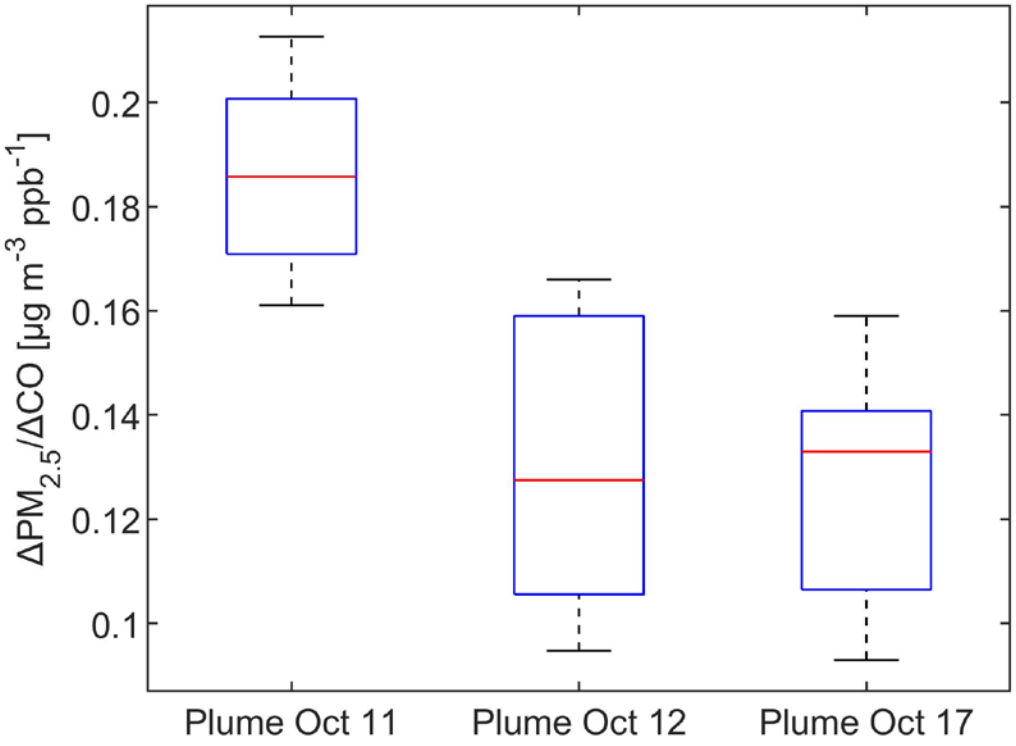
Liang et al. in prep

PM OC **evaporation ≈ Secondary** PM OC formation

No net growth of PM OC as smoke ages,
but substantial change in chemical composition does occur



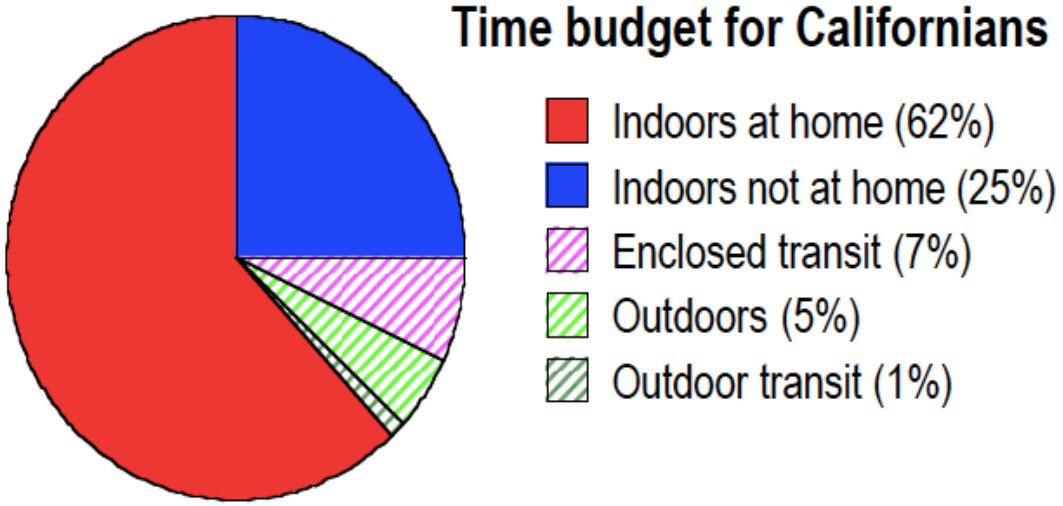
Particle OC linearly correlated with primary stable smoke tracer acetonitrile



$\Delta PM_{2.5}/\Delta CO$ ratios in fire plumes intercepted at different sites have a narrow distribution

Liang et al. *ACP* 2021

Exposure to wildfire smoke dominantly occurs indoors



- People spend ~90% of our times indoors
- EPA recommends staying indoors during wildfires
- Human behavior (e.g., window shutting, use of particle filtration devices) may be responsive to knowledge about levels of wildfire smoke PM

- Assessments of wildfire exposure typically rely on outdoor concentration measured at EPA stations
- Understanding the indoor penetration and persistence of smoke during wildfires is very important

Jenkins et al. *Atmos. Environ.* 1992
Klepeis et al. *J. Expos. Analysis Environ. Epidemiol.* 2001

What happens when outdoor smoke comes indoors?
Indoor air ≠ outdoor air

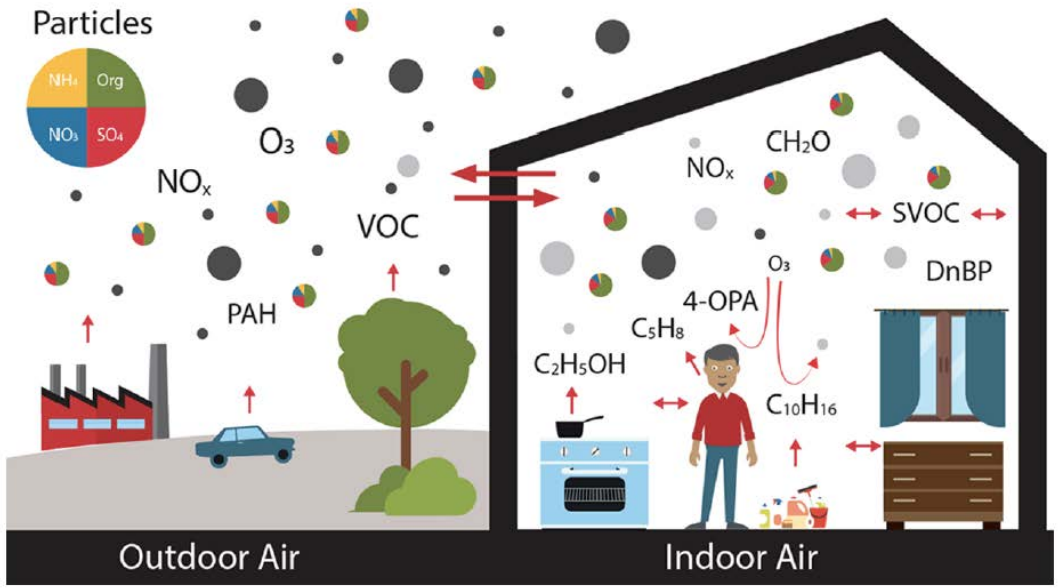
- Buildings are partially protective
(through filtration and deposition)

- PM size distribution is altered
(more efficient reduction of ultrafine and coarse particles)

- Chemical composition shifts
(changes equilibrium partitioning for semi-volatile species)

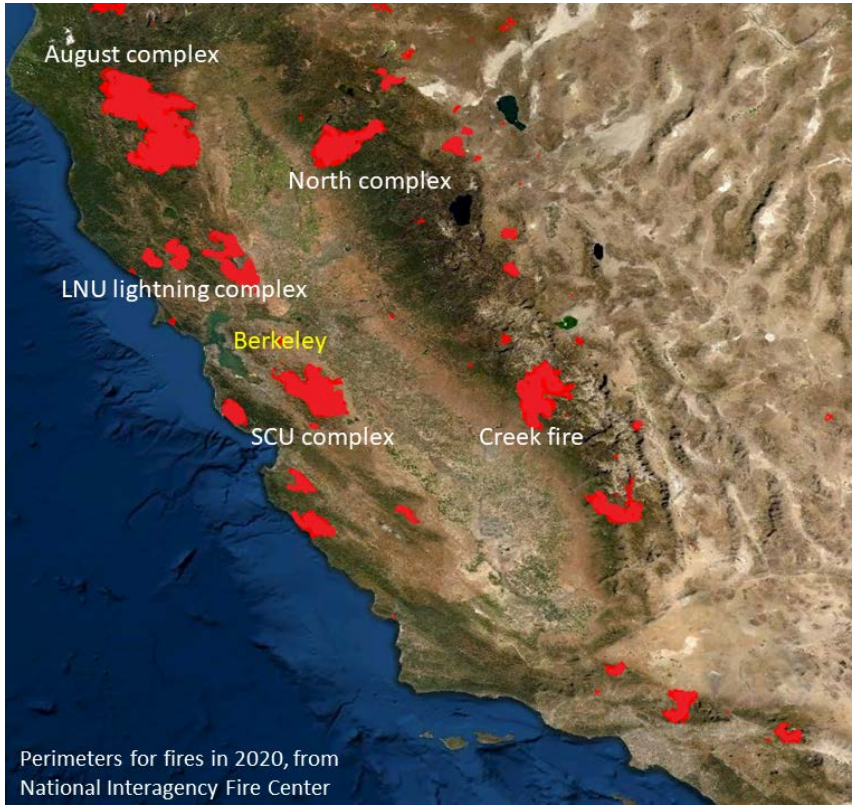
- Indoor semi-volatile organics partition to smoke particles

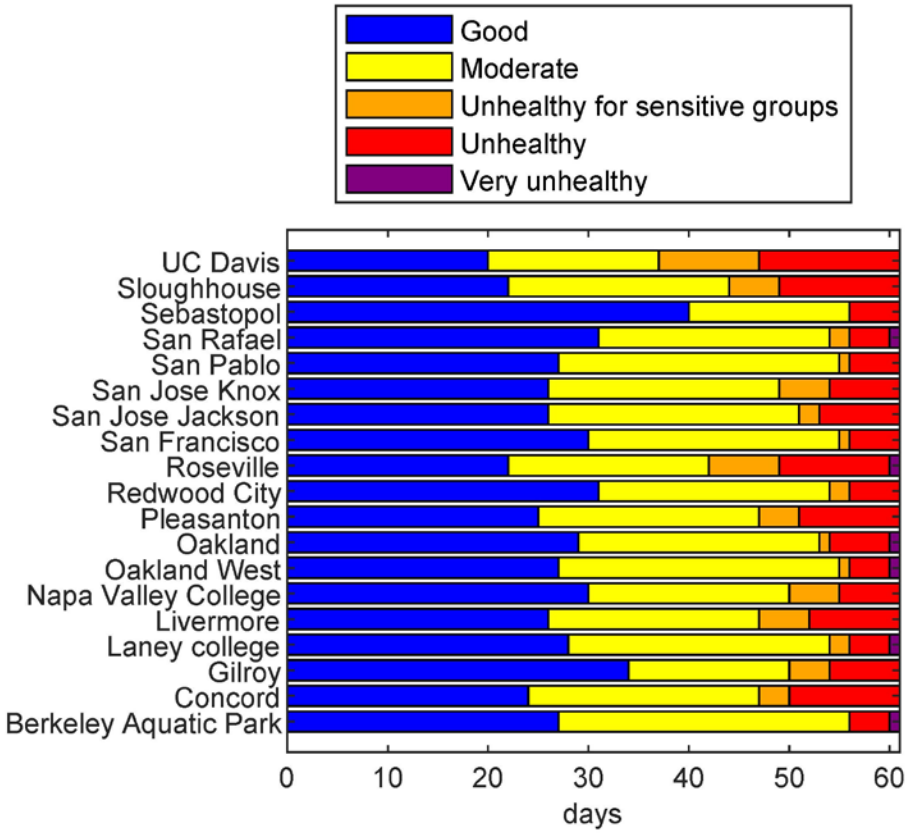
- Indoor surface uptake followed by slow release of
gaseous species may extend exposure to smoke organics



Goldstein et al. *Environmental Science & Technology* 2021

2020 Wildfires in California (many at WUI) caused poor air quality over broad regions

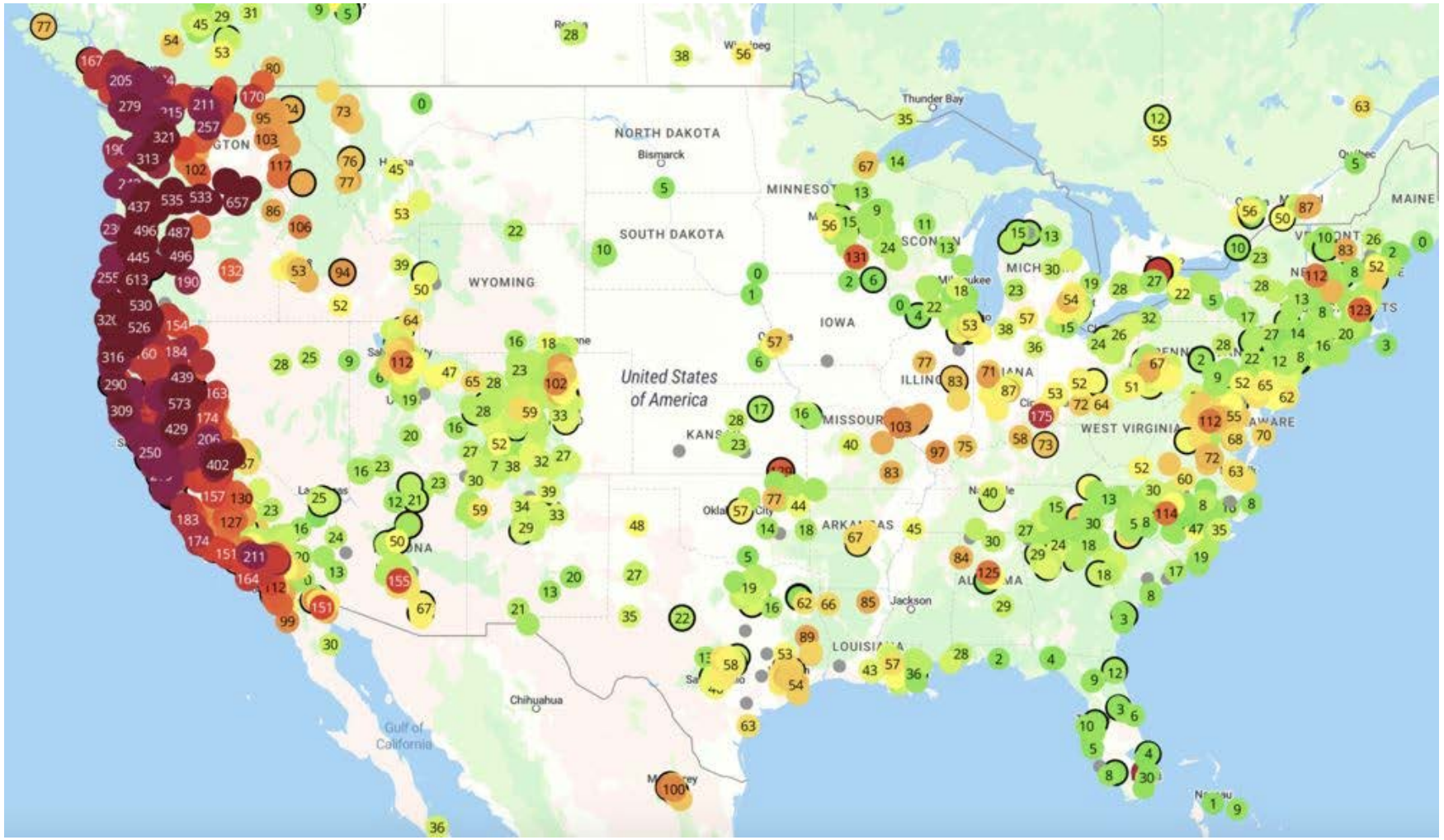




In 2020, SF Air Basin had the longest (46 days) “Spare the Air” alert in history, with 25 days of $PM_{2.5}$ exceeding national 24-hour standard (worst since 1991)

Figures by Y. Liang, Data from MODIS and EPA

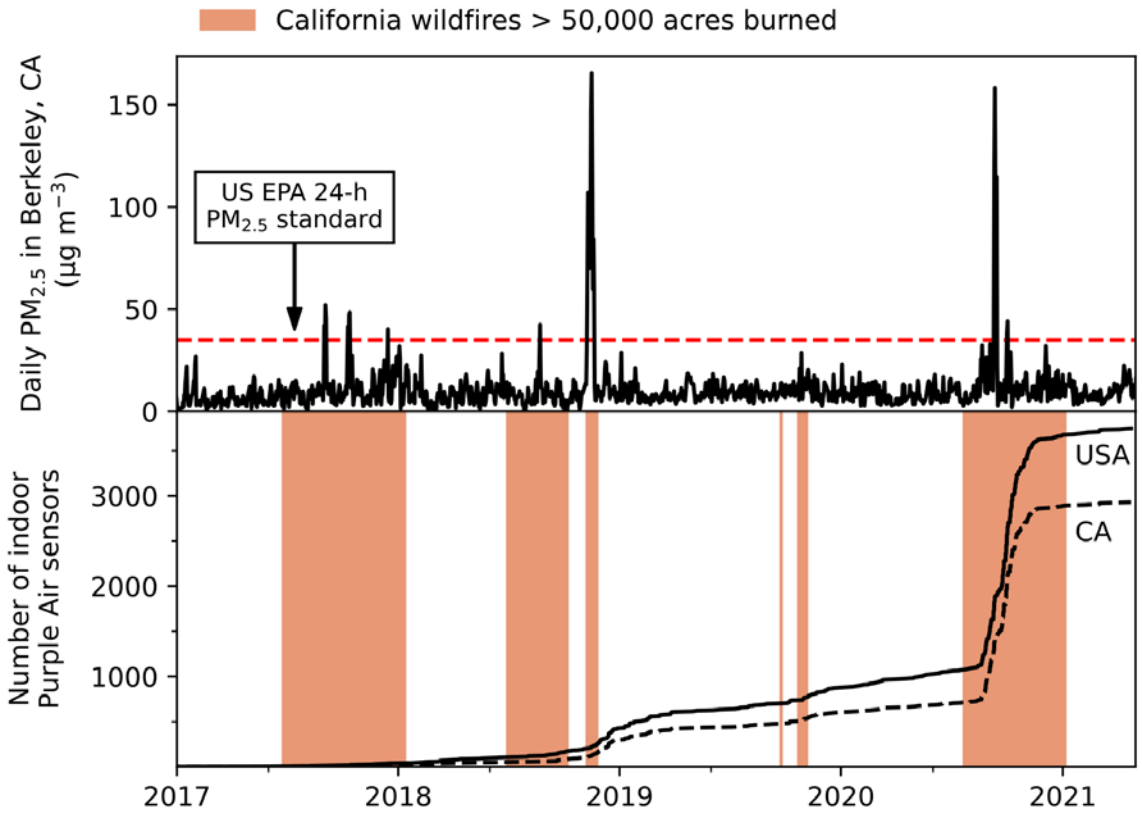
Many people view PurpleAir (PA) data to assess air quality during fires

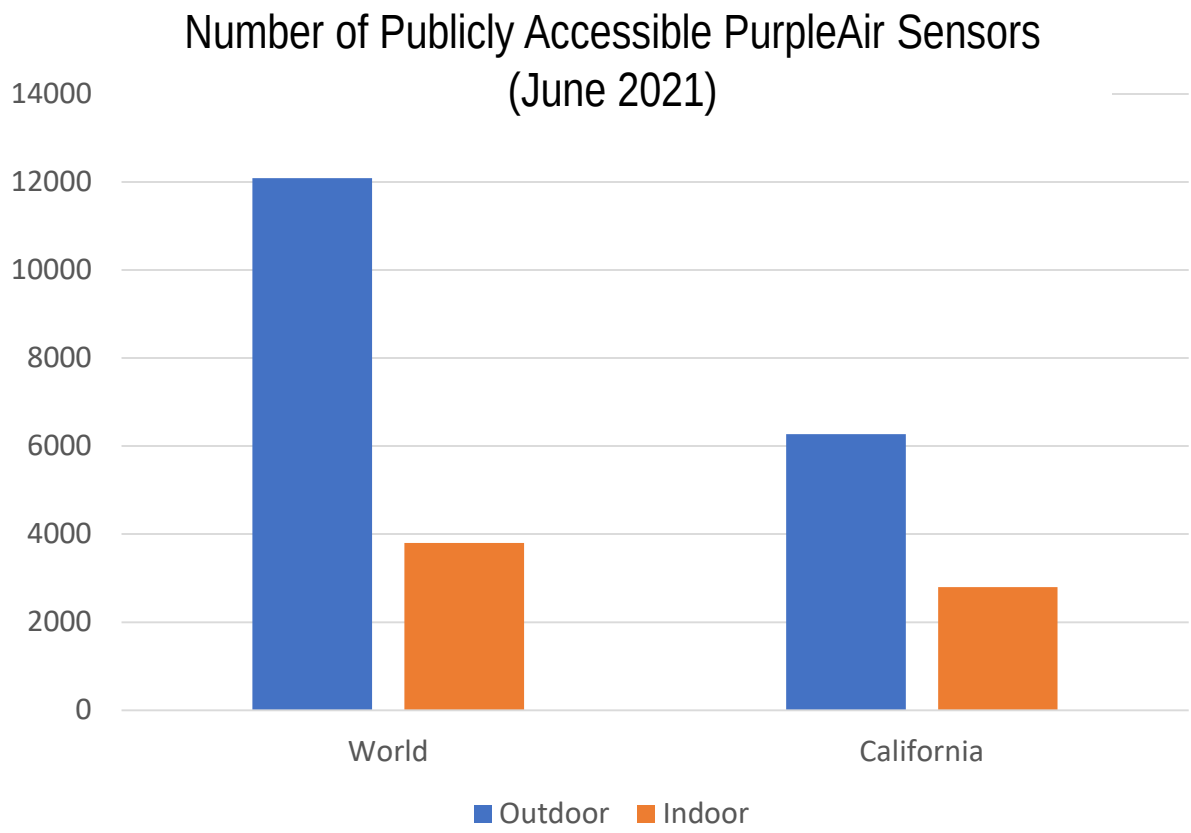


- PA network is extensive, especially in California (CA)
- Measures PM in real-time
- We used data from >1400 indoor sensors in CA during 2018 & 2020 to assess PM infiltration
- Covers the six largest fires in the recorded history of CA

www.bloomberg.com/news/articles/2020-09-14/mapping-the-wildfire-smoke-choking-the-western-u-s

Number of indoor PA sensors grew rapidly in direct response to wildfire events

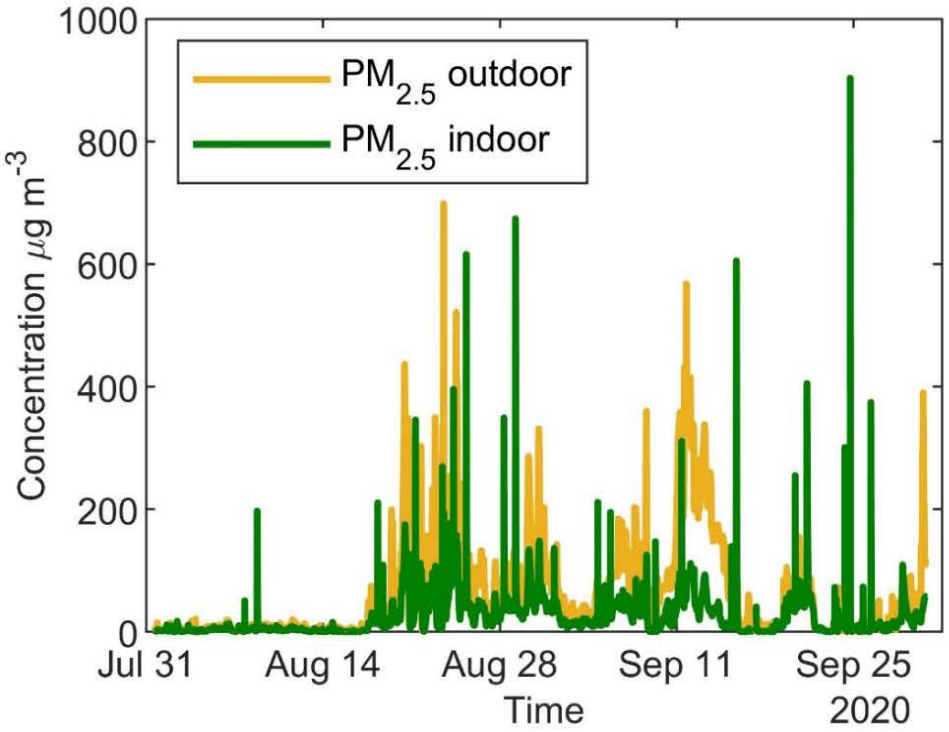




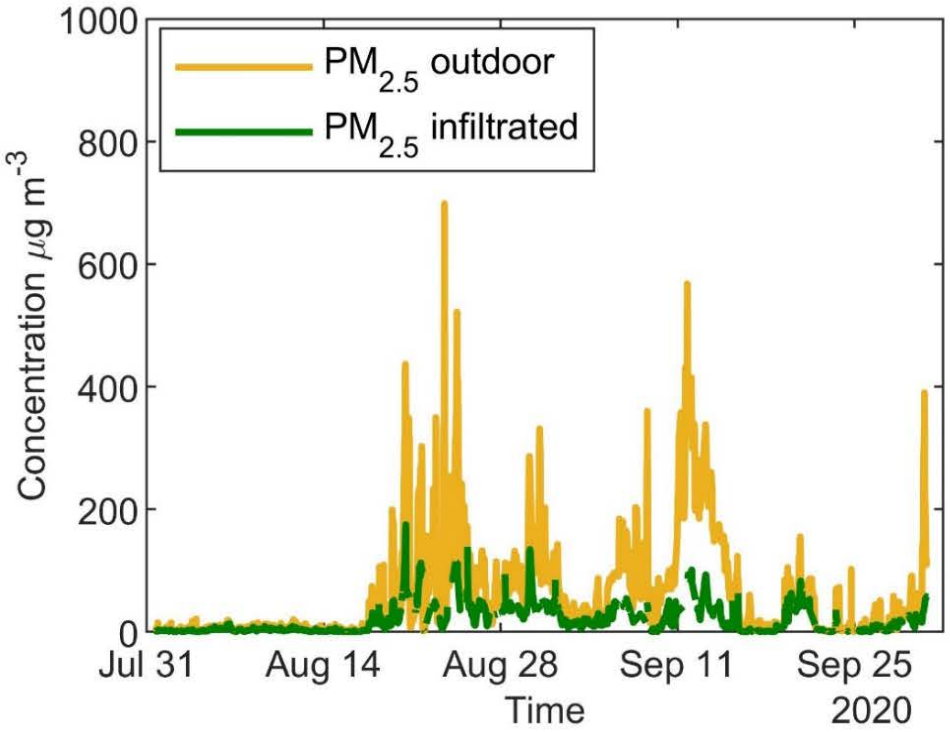
Liang et al. in review, Data sources: $PM_{2.5}$ EPA, # sensors PurpleAir, wildfires CalFire

Indoor/outdoor $PM_{2.5}$ relationship of an example residence (measured using PA sensors)

All Data



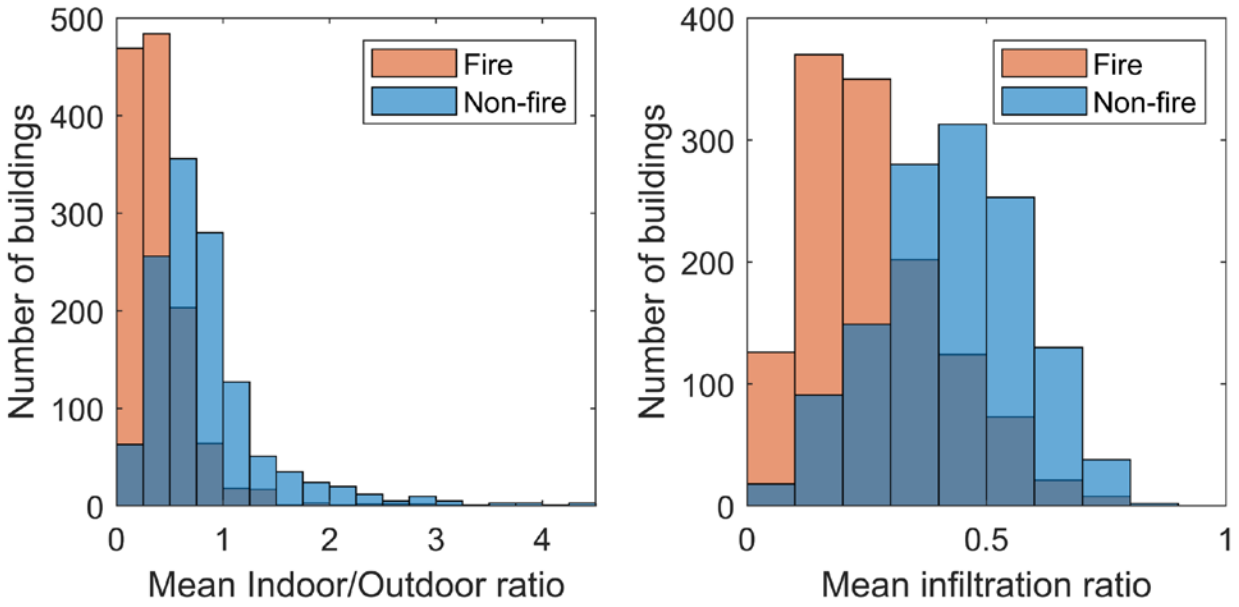
Indoor Emission Events Removed



Liang et al. in review

Indoor air quality was affected by wildfire smoke
Buildings were protective (less infiltration on fire days)

	Mean outdoor conc µg m^{-3}	Mean indoor conc µg m^{-3}
	Mean ± s.d.	Mean ± s.d.
Non-fire days	16 ± 7	7 ± 5
Fire days	85 ± 32	21 ± 16
Unhealthy days	115 ± 39	25 ± 20



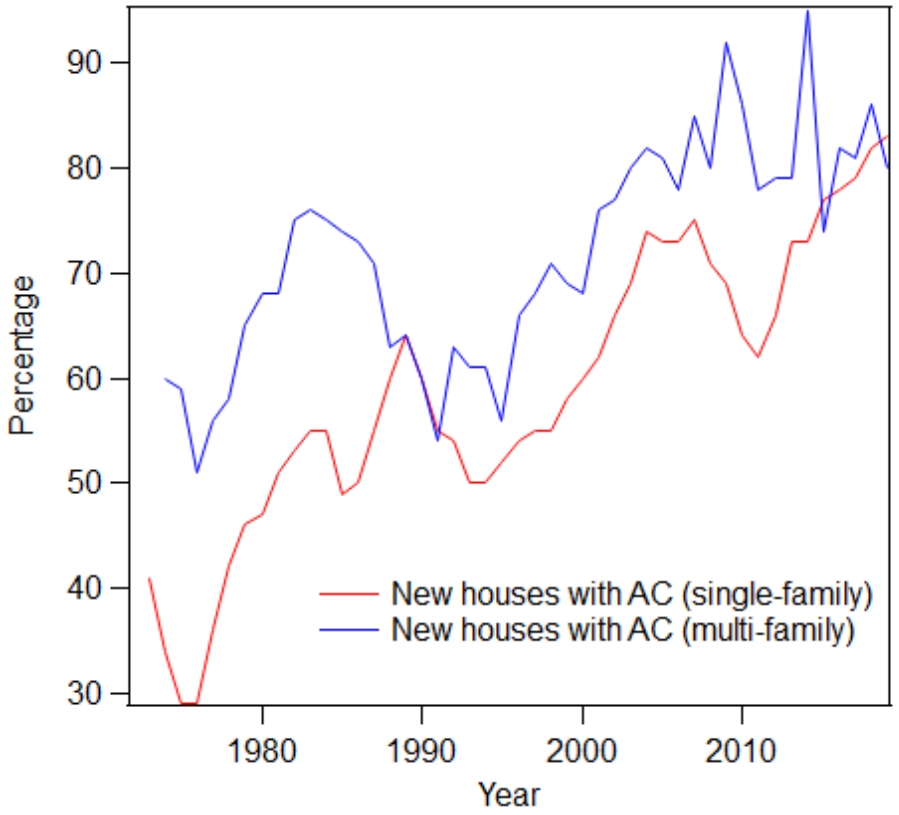
Infiltration ratio: (indoor $PM_{2.5}$ of outdoor origin/outdoor $PM_{2.5}$)

Data from 1274 indoor PA sensors, San Francisco Bay Area, Aug → Sept 2020

Liang et al. in review

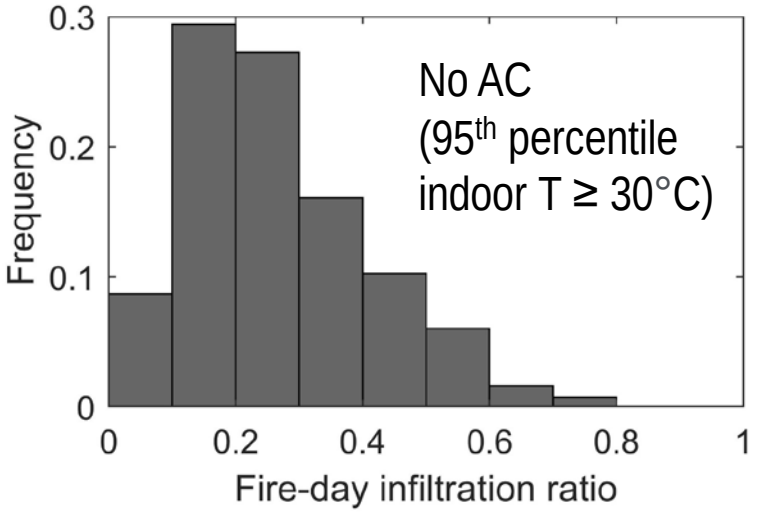
Air-conditioned buildings have lower PM infiltration ratios

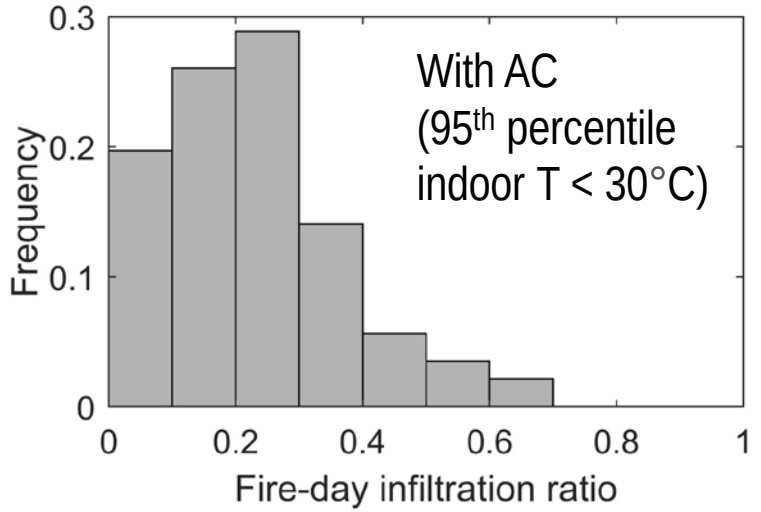
New western US houses more likely to have AC
(US Census data)



Air conditioning (AC)

- Shutting windows and doors
- Likely indoor filtration devices





Liang et al. in review

Conclusions

- Despite burning at WUI, no evidence of “non-biomass fuels” in Berkeley 2017 wildfire smoke
- Substantial changes in chemical composition of wildfire smoke occur during transport
- No change in PM OC mass during transport (evaporation ≈ secondary production)
- Infiltration ratios reduced by ~50% (0.4 --> 0.2) during wildfire days, while $PM_{2.5}$ ~tripled
- Widely available real-time PM data have potential for educating people and altering behavior

Some Key Knowledge Gaps

- Chemical emission profiles from WUI wildfires are relatively unknown
- Thousands of chemicals are observed in smoke, but health effects of most remain largely uncertain
- Secondary organics are important components of aged smoke, yet remain poorly characterized
- Indoor penetration & persistence of organic chemicals from smoke is poorly understood
- PurpleAir data is widely accessed during wildfire events, but available data is skewed by income