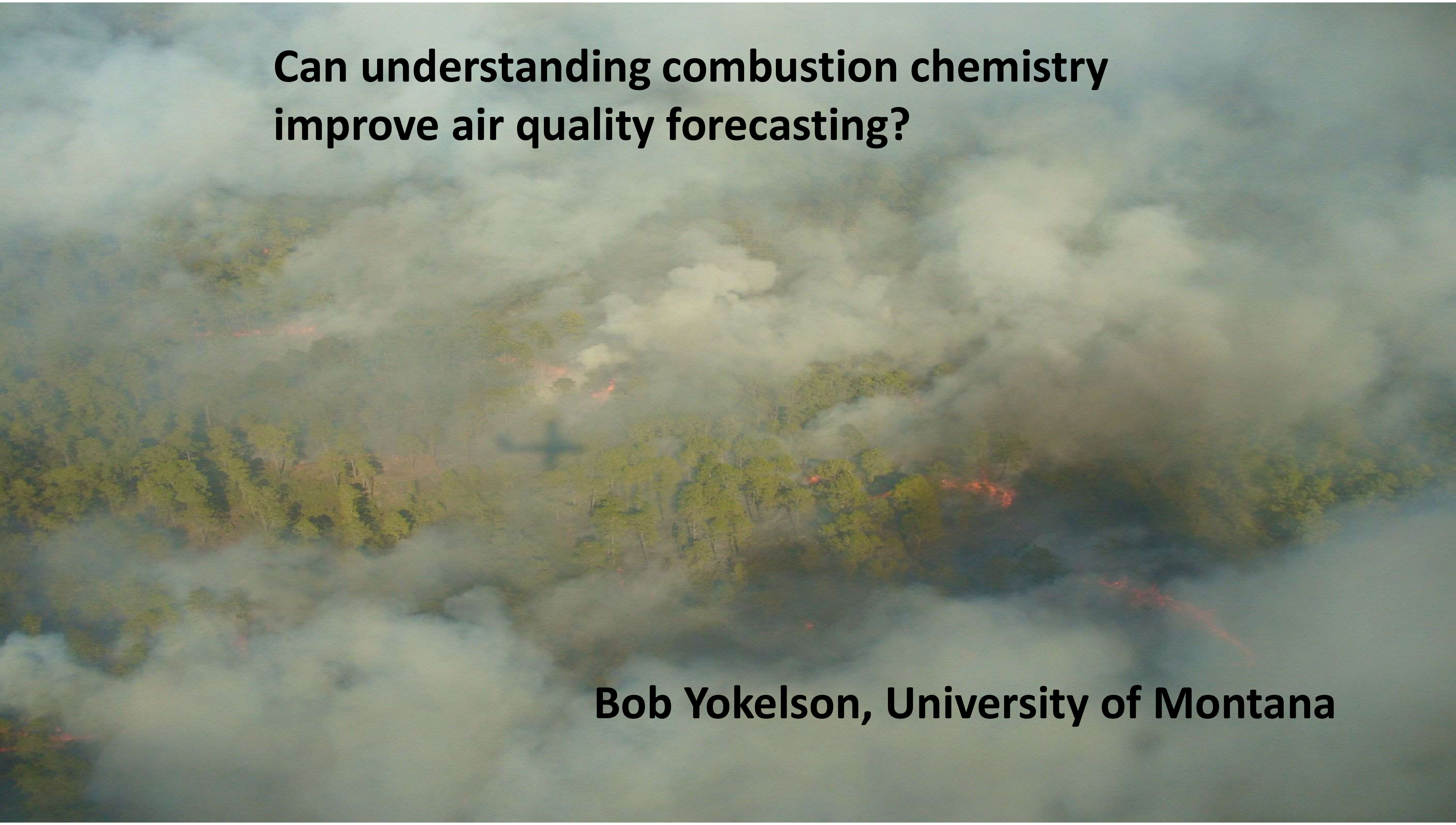


Can understanding combustion chemistry improve air quality forecasting?

Bob Yokelson, University of Montana

3 plumes from 1-day, 200 acre Williams Fire.

Overview of sampling of 257,314 acre Rim Fire.

Rim Fire Event/Study	Date (2013)	ΔCH4/ΔCO2 ppb/ppm	Main Transport
Ignition	Aug 17		
Liu et al	Aug 26	8, flaming	NE-up
Yates et al	Aug 29	6.5, flaming	NE-up
Yates et al	Sep 10	18.3, smolder	W-down
Containment	Oct 24		

List of Forecasting Issues/Difficulties and Major Uncertainties

When will it be smoky, when will it go away?

Smoke production/chemistry/exposure:

- **Missing fires** AND/OR saturated fires (clouds, cloud mask, orbital gaps, size, etc)
- **Fuel consumption**: amount, type, timing
- **Plume rise,** fall, removal, timing of variable injection distribution, complex transport
- Unknown, variable **emission factors** and emission ratios
- **Sub-grid processes**: terrain flattening, dilution, fast chemistry
- Variable/unknown **evolution** of measured and unmeasured species
- **Mis-assigned sources** (e.g. haze due to multiple sources)
- (Forecasting only) **persistence**, prescribed fires?

Smoke health effects:

skin absorption, synergistic effects, variable sensitivity, co-deployed assays, metabolomics, and smoke chemistry

Solve the problem → Smoke reduction → Prescribed fire, politics!

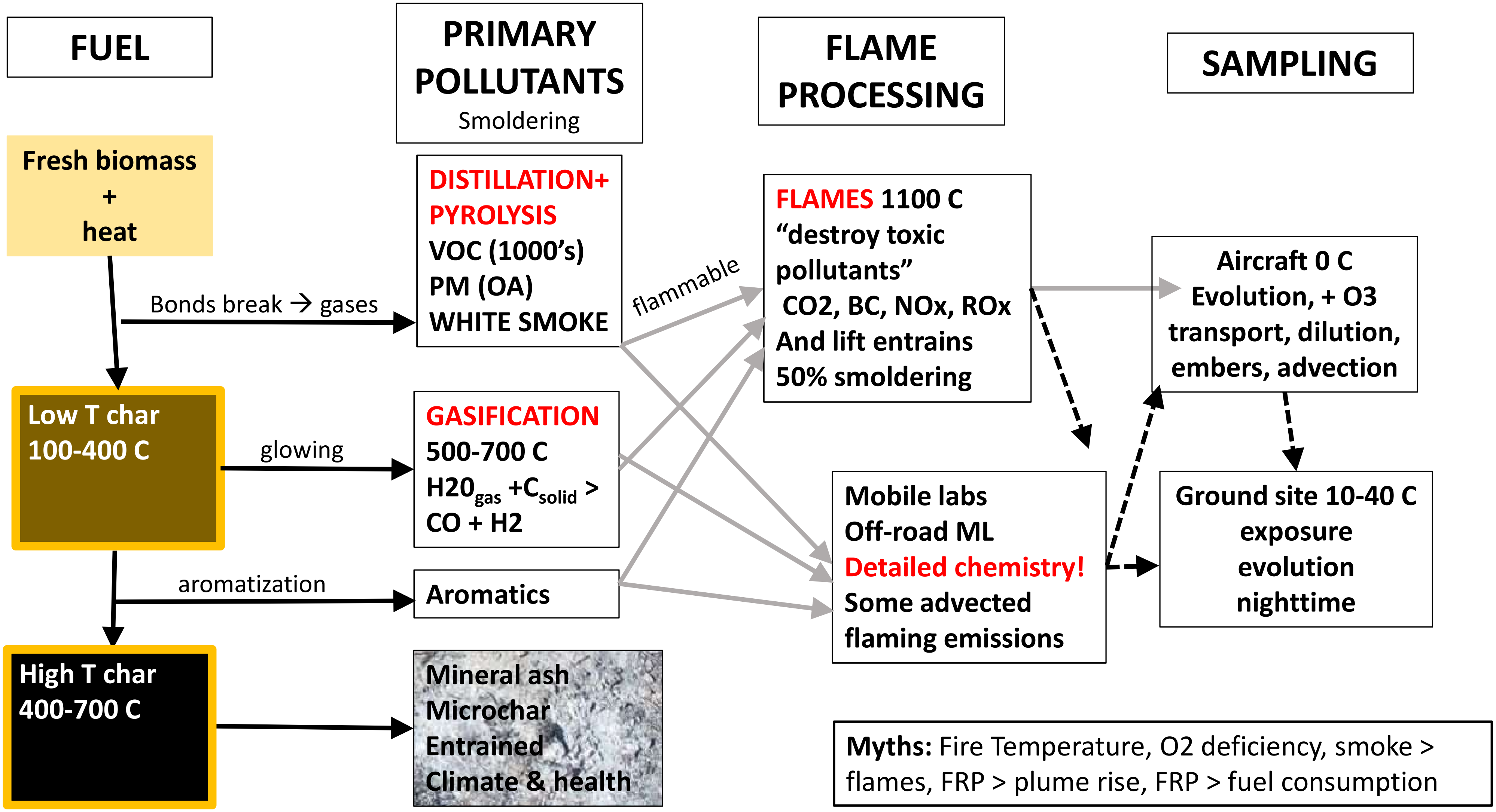
Subdominant → Dominant ↓	Fuels (EF)	Diurnal (FC, T, RH hv)	Plume rise	Dilution (“k” POA evap)	hv(λ) (OH, SOA, BrC)
Fuels (EF)	Measurement uncertainty	Fine fuel RH	heat		
Diurnal (FC, T, RH, hv)	Lower T, higher RH S/F increase FC decrease		stability		
Plume rise		Fire – generated weather		Free trop vs bdy layer	
Dilution (“k” POA evap)	Gas-particle partitioning		Entrainment and cooling		light attenuation, OH production
hv(λ) (OH, SOA, BrC)	Fuel moisture			No!	

There are many more important variables: fire heat, wind, fuel geometry, chemistry, moisture, etc,.

Biomass burning is a complex, chemical, physical system with many degrees of freedom often with non-linear interactions

So is the human body!

A simplified view of biomass combustion



FUEL

PRIMARY POLLUTANTS
Smoldering

FLAME PROCESSING

SAMPLING

Fresh biomass
+
heat

Bonds break → gases

DISTILLATION+
PYROLYSIS
VOC (1000's)
PM (OA)
WHITE SMOKE

flammable

FLAMES 1100 C
"destroy toxic pollutants"
CO2, BC, NOx, ROx
And lift entrains
50% smoldering

Aircraft 0 C
Evolution, + O3
transport, dilution,
embers, advection

Low T char
100-400 C

glowing

GASIFICATION
500-700 C
$H20_{gas}$ +C_{solid} >
CO + H2

Mobile labs
Off-road ML
Detailed chemistry!
Some advected
flaming emissions

Ground site 10-40 C
exposure
evolution
nighttime

aromatization

Aromatics

High T char
400-700 C

Mineral ash
Microchar
Entrained
Climate & health

Myths: Fire Temperature, O2 deficiency, smoke > flames, FRP > plume rise, FRP > fuel consumption


Flaming


Subsurface glowing


gasification


Mix of all three

more common in wildfires

PRIMARY POLLUTANTS
Smoldering/Flaming

a) All pollutants efficiently processed in flames > CO_2, BC, NO_x, SO_2, HCl, K^+

b) No flame processing of smoke generated by subsurface gasification > VOC, OA or OC, etc.

c) Pure gasification (glowing), CO_2, CO, H_2

d) “Normal” flaming, glowing, and pyrolysis

“Cooking” canopy and smoldering organic soils tend to make > PM/mass-fuel in wildfires!

SAMPLING

Combustion without flames:
firefighter health

FTIR, canister, (100 gases), Filters. Sampling inside burn perimeter with firefighters.

OP-FTIR “Fence-line” along fire line and airborne lab on Twin Otter (HR-AMS, SP2, PILS, WSOC, Picarro, FTIR, WAS, AIMS-20).

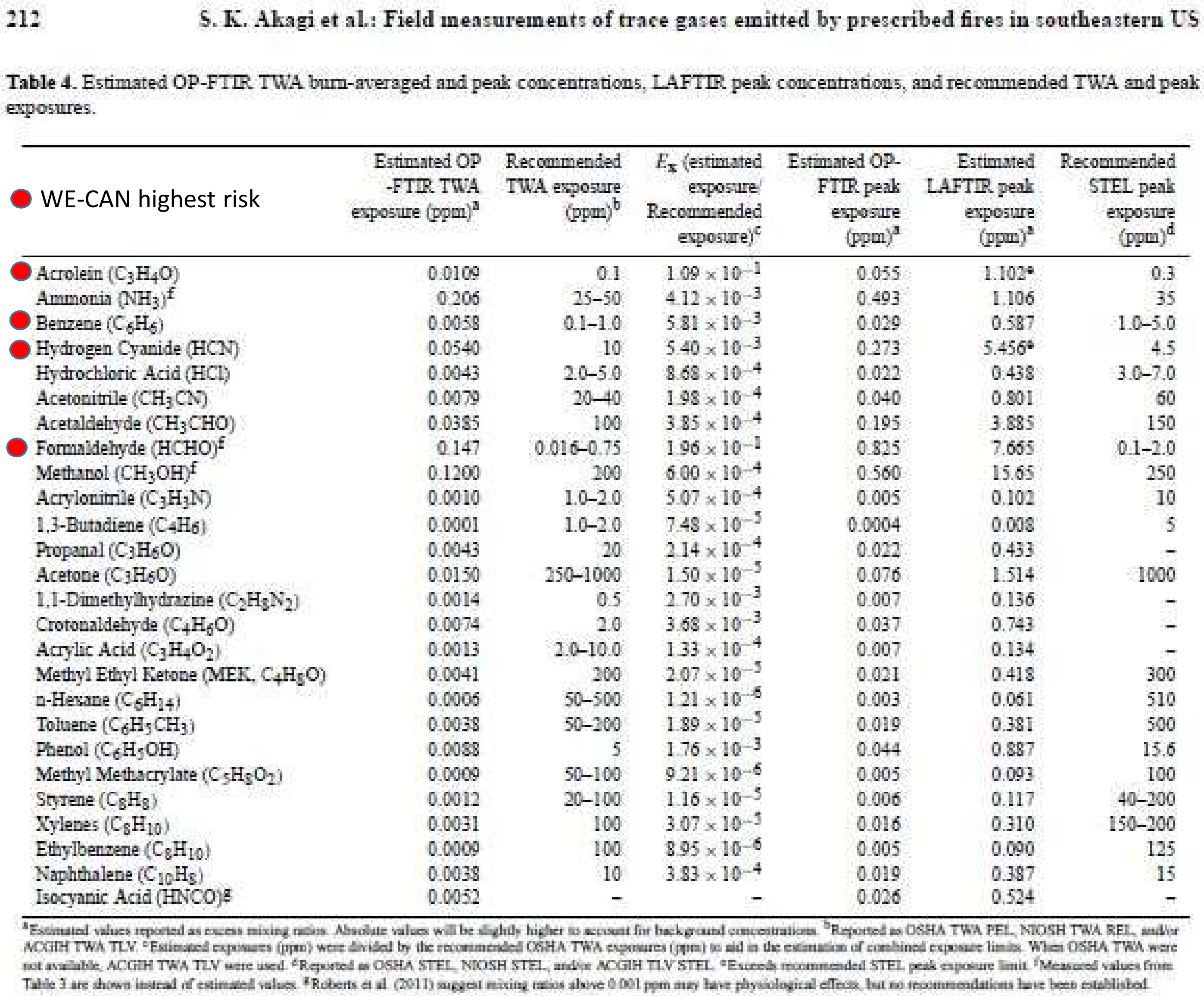
Smoke filled valleys:
mobile laboratories

Detailed Chemical Measurements:
AERODYNE MOBILE LAB: N2O, CO, H2O, C2H6, CH4, HCHO, HCOOH, HCN, C2H2, NO2, NO, Ozone, CO2, Vocus PTR-ToF-MS, HR-SP-AMS, SMPS, CPC, NOx, CO, PM, jNO2 filter radiometer, Spectral radiometer, SP2, MIPN, DEFCON, OFR, GC-EI-TOF.

Plus 4 other MLs!

NASA MACH2, PM, UNH, GT > ROS!

Firefighter Exposure to HAPs on prescribed fire



212 S. K. Akagi et al.: Field measurements of trace gases emitted by prescribed fires in southeastern US

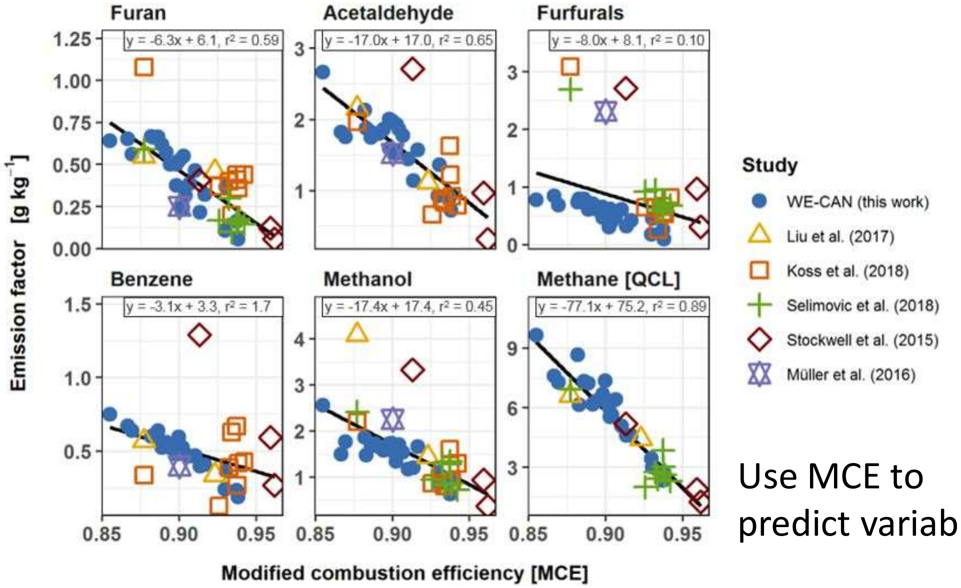
Table 4. Estimated OP-FTIR TWA burn-averaged and peak concentrations, LAFTIR peak concentrations, and recommended TWA and peak exposures.

● WE-CAN highest risk

	Estimated OP-FTIR TWA exposure (ppm)[a]	Recommended TWA exposure (ppm)[b]	E_x (estimated exposure/ Recommended exposure)[c]	Estimated OP-FTIR peak exposure (ppm)[a]	Estimated LAFTIR peak exposure (ppm)[a]	Recommended STEL peak exposure (ppm)[d]
● Acrolein (C_3H_4O)	0.0109	0.1	1.09×10^{-1}	0.055	1.102[e]	0.3
Ammonia (NH_3)[f]	0.206	25–50	4.12×10^{-3}	0.493	1.106	35
● Benzene (C_6H_6)	0.0058	0.1–1.0	5.81×10^{-3}	0.029	0.587	1.0–5.0
● Hydrogen Cyanide (HCN)	0.0540	10	5.40×10^{-3}	0.273	5.456[e]	4.5
Hydrochloric Acid (HCl)	0.0043	2.0–5.0	8.68×10^{-4}	0.022	0.438	3.0–7.0
Acetonitrile (CH_3CN)	0.0079	20–40	1.98×10^{-4}	0.040	0.801	60
Acetaldehyde (CH_3CHO)	0.0385	100	3.85×10^{-4}	0.195	3.885	150
● Formaldehyde (HCHO)[f]	0.147	0.016–0.75	1.96×10^{-1}	0.825	7.665	0.1–2.0
Methanol (CH_3OH)[f]	0.1200	200	6.00×10^{-4}	0.560	15.65	250
Acrylonitrile (C_3H_3N)	0.0010	1.0–2.0	5.07×10^{-4}	0.005	0.102	10
1,3-Butadiene (C_4H_6)	0.0001	1.0–2.0	7.48×10^{-5}	0.0004	0.008	5
Propanal (C_3H_6O)	0.0043	20	2.14×10^{-4}	0.022	0.433	–
Acetone (C_3H_6O)	0.0150	250–1000	1.50×10^{-5}	0.076	1.514	1000
1,1-Dimethylhydrazine ($C_2H_8N_2$)	0.0014	0.5	2.70×10^{-3}	0.007	0.136	–
Crotonaldehyde (C_4H_6O)	0.0074	2.0	3.68×10^{-3}	0.037	0.743	–
Acrylic Acid ($C_3H_4O_2$)	0.0013	2.0–10.0	1.33×10^{-4}	0.007	0.134	–
Methyl Ethyl Ketone (MEK, C_4H_8O)	0.0041	200	2.07×10^{-5}	0.021	0.418	300
n-Hexane (C_6H_{14})	0.0006	50–500	1.21×10^{-6}	0.003	0.061	510
Toluene ($C_6H_5CH_3$)	0.0038	50–200	1.89×10^{-5}	0.019	0.381	500
Phenol (C_6H_5OH)	0.0088	5	1.76×10^{-3}	0.044	0.887	15.6
Methyl Methacrylate ($C_5H_8O_2$)	0.0009	50–100	9.21×10^{-6}	0.005	0.093	100
Styrene (C_8H_8)	0.0012	20–100	1.16×10^{-5}	0.006	0.117	40–200
Xylenes (C_8H_{10})	0.0031	100	3.07×10^{-5}	0.016	0.310	150–200
Ethylbenzene (C_8H_{10})	0.0009	100	8.95×10^{-6}	0.005	0.090	125
Naphthalene ($C_{10}H_8$)	0.0038	10	3.83×10^{-4}	0.019	0.387	15
Isocyanic Acid (HNCO)[g]	0.0052	–	–	0.026	0.524	–

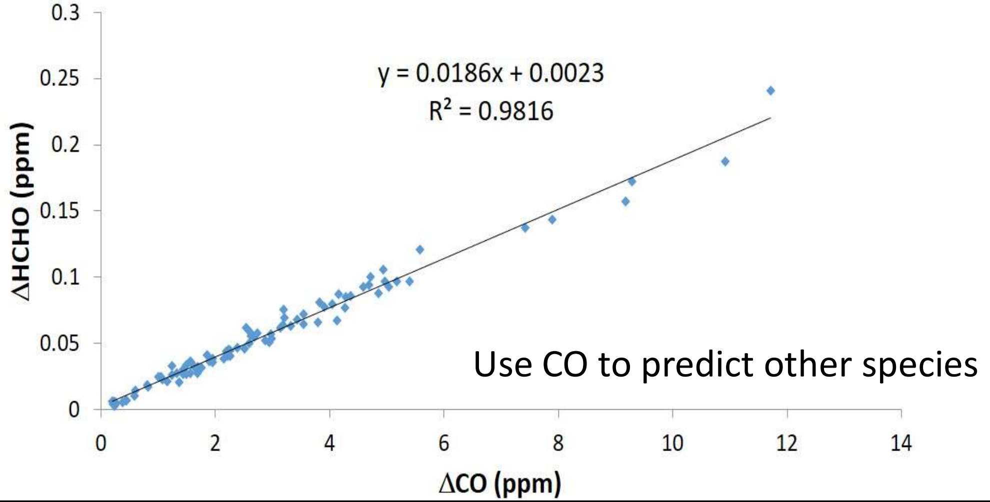
[a] Estimated values reported as excess mixing ratios. Absolute values will be slightly higher to account for background concentrations. [b] Reported as OSHA TWA PEL, NIOSH TWA REL, and/or ACGIH TWA TLV. [c] Estimated exposures (ppm) were divided by the recommended OSHA TWA exposures (ppm) to aid in the estimation of combined exposure limits. When OSHA TWA were not available, ACGIH TWA TLV were used. [d] Reported as OSHA STEL, NIOSH STEL, and/or ACGIH TLV STEL. [e] Exceeds recommended STEL peak exposure limit. [f] Measured values from Table 3 are shown instead of estimated values. [g] Roberts et al. (2011) suggest mixing ratios above 0.001 ppm may have physiological effects, but no recommendations have been established.

- No 8h exposure limits exceeded for individual compounds, but some large peaks possible, Akagi et al., 2014 (prescribed)
- Updating/improving with 2018-2019 mobile lab data! HAPS/PM, wildfires day + night
- Most complete EF of VOCs Hatch et al. 2015, 2017
- Most complete PM chemistry, Jen et al. 2019
- Missing: Exposure, sensitivity, synergistic effects? Metabolomics

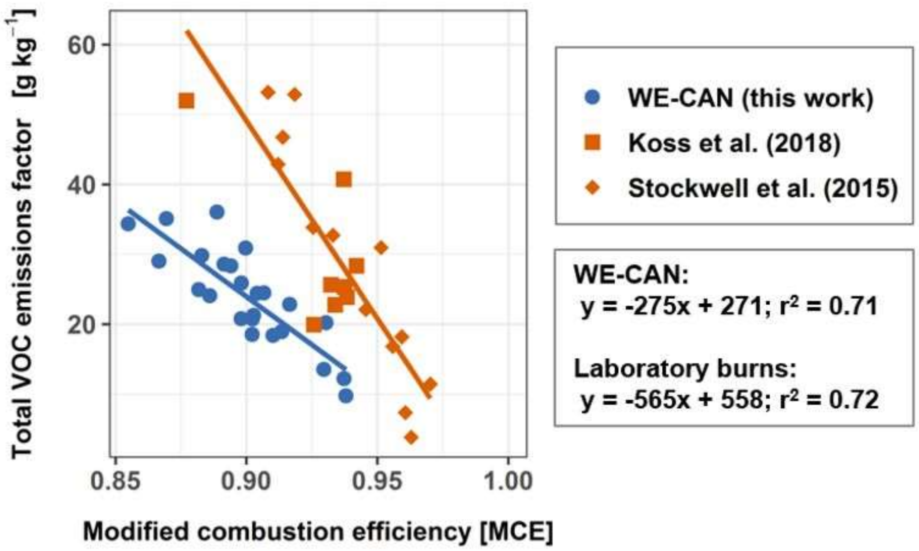


Use MCE to predict variability

UMT airborne FTIR: HCHO vs CO for a NC prescribed fire: example ER



Use CO to predict other species

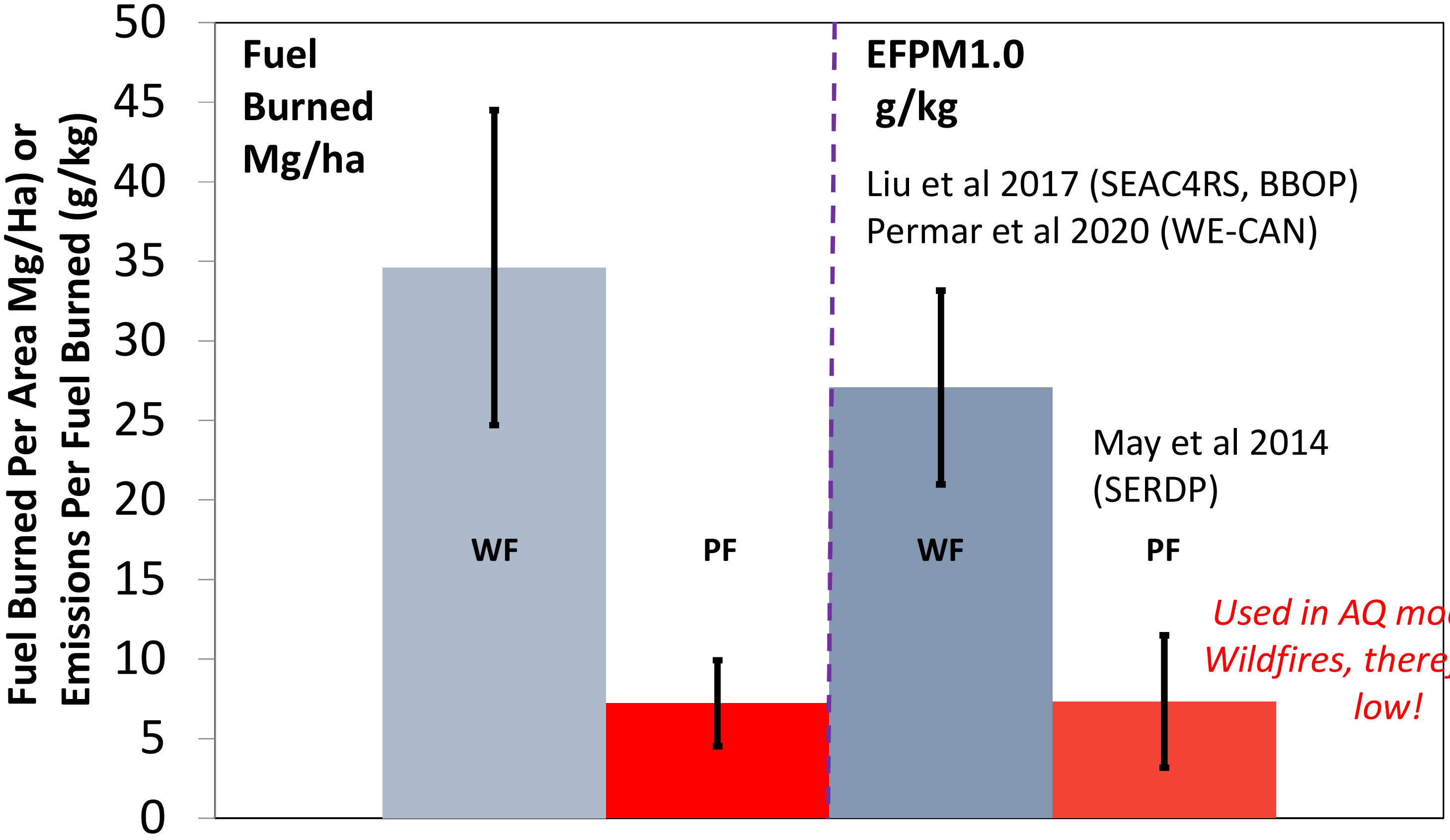


- **Combustion chemistry-based relationships like ERs and EFs vs MCE have been exploited for decades!**
- **WE-CAN EFHAPs, PM & EFVOC(tot) vs MCE for 161 VOCs from 24 wildfires! Permar et al 2020**
- MCE from space by TROPOMI?
- van der Velde et al.: **Biomass burning combustion efficiency observed from space using measurements of CO and NO_2 by TROPOMI**, Atmos. Chem. Phys. Discuss.

Towards solving the problem with smoke reductions with spring/fall prescribed fires

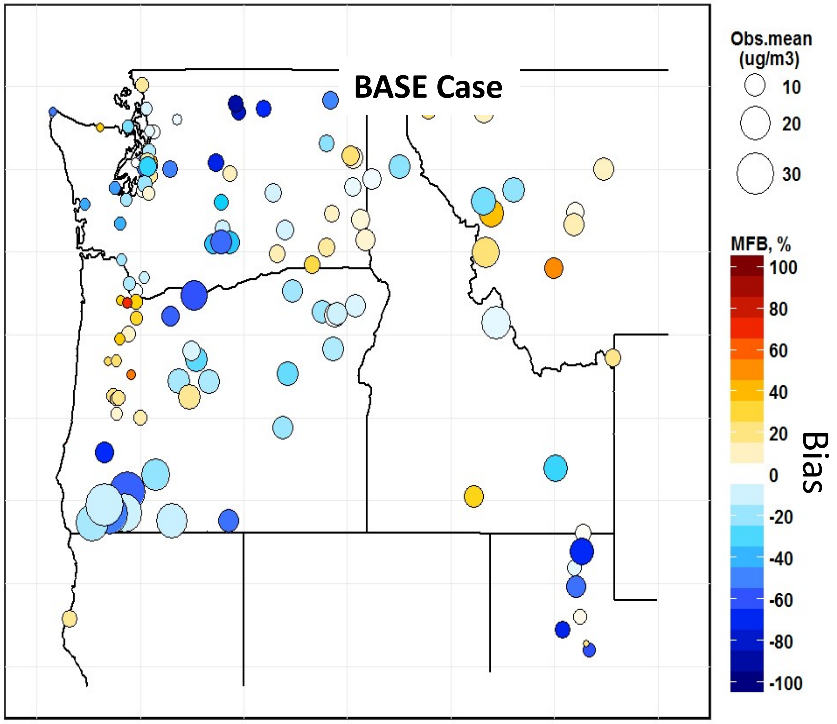
1) ~18X < PM pollution per area burned than wildfires
2) can be burned when smoke impacts and structure risks are minimized
3) reducing hazardous fuels
4) easier to forecast

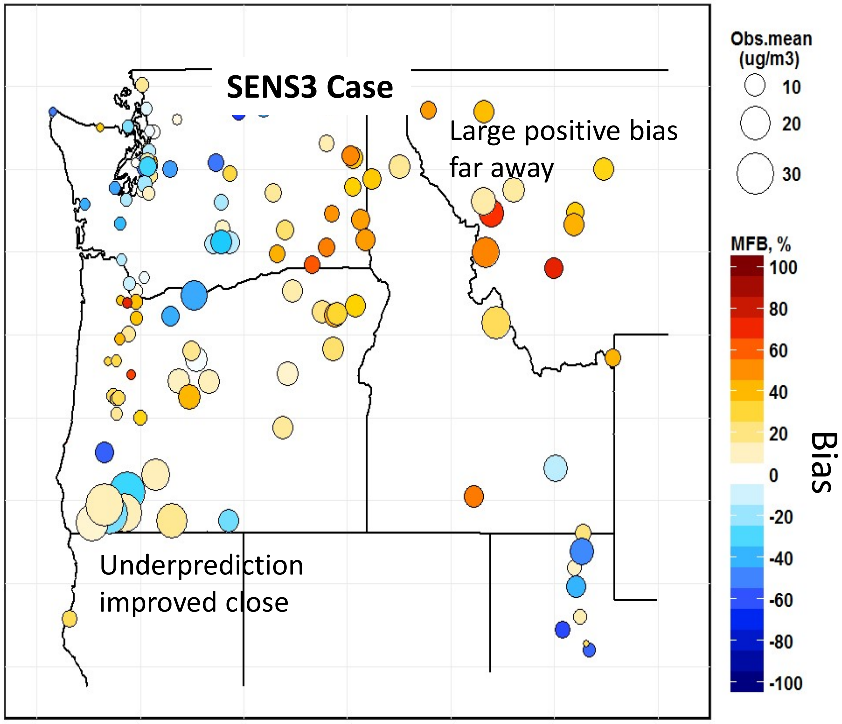
For coniferous ecosystems



Used in AQ models for Wildfires, therefore too low!

Will larger WF EFPM improve surface PM forecast? Test month Aug 2013


BASE Case

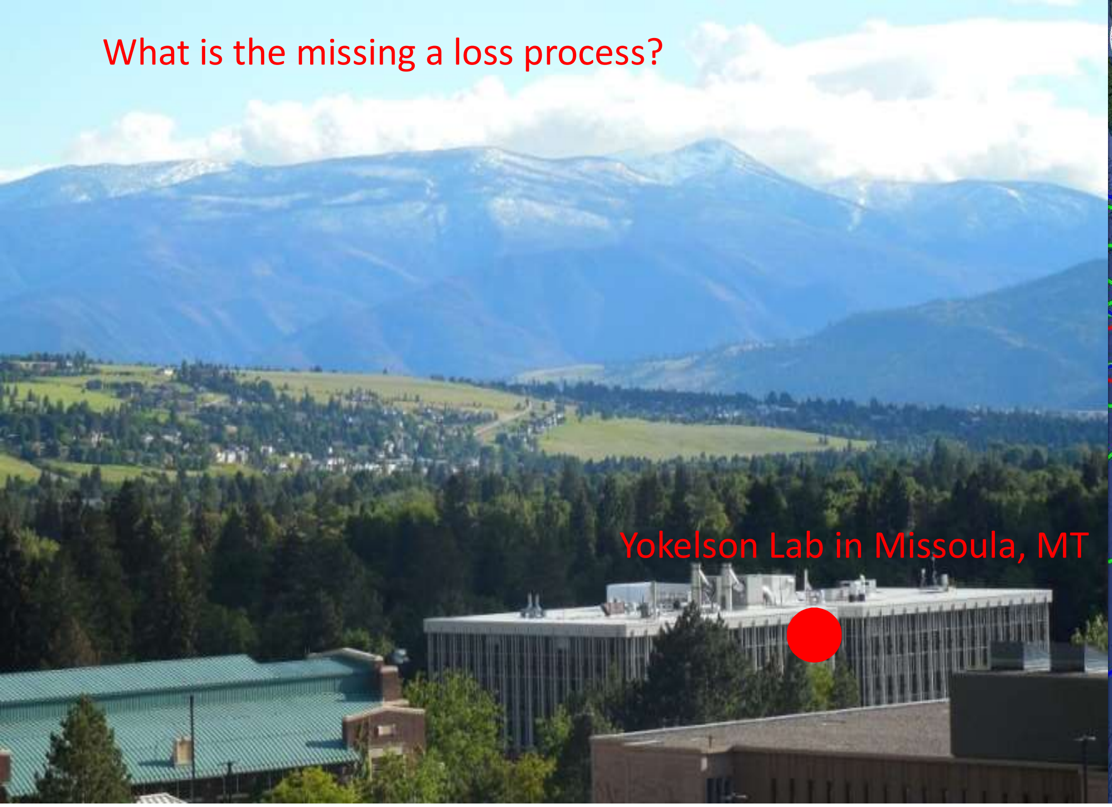

SENS3 Case

Large positive bias far away

Underprediction improved close

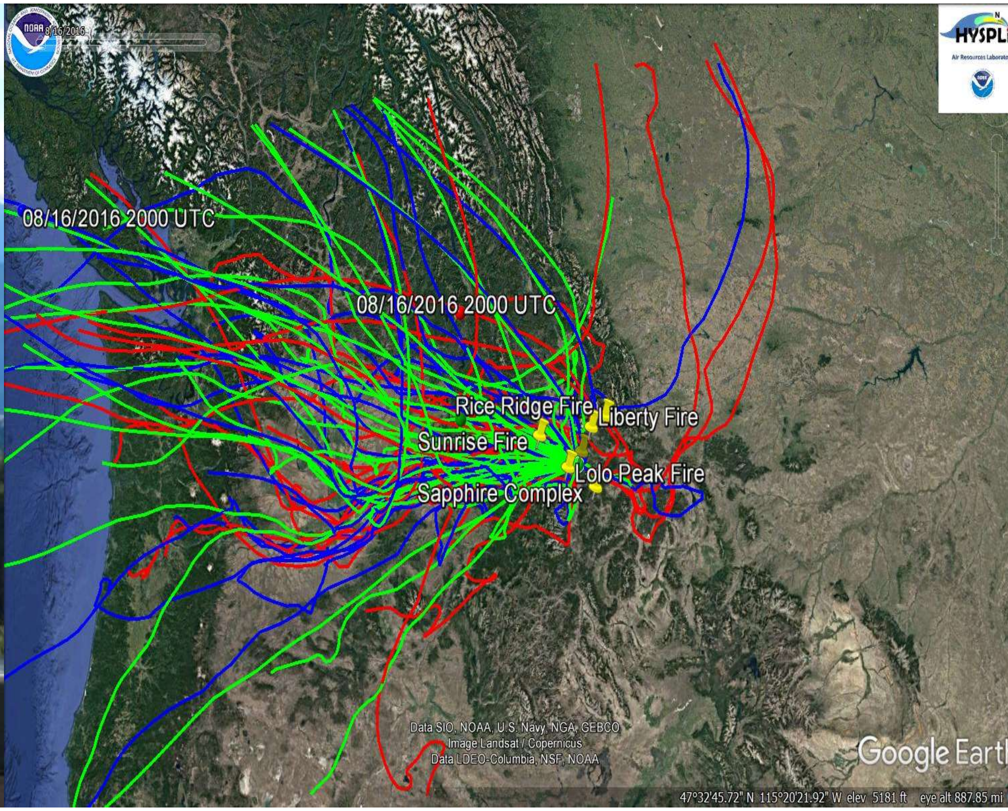
Kelley Barsanti, Tsengel Nergui , Yunha Lee, Brian Lamb, etc., Washington State University, AIRPACT
http://www.lar.wsu.edu/airpact/:

Step 1: Change emissions, needs broad-scale evaluation (any single case study misleading)
Step 2: missing a loss process, PM conserved in most aircraft studies, need data.



What is the missing a loss process?

Yokelson Lab in Missoula, MT

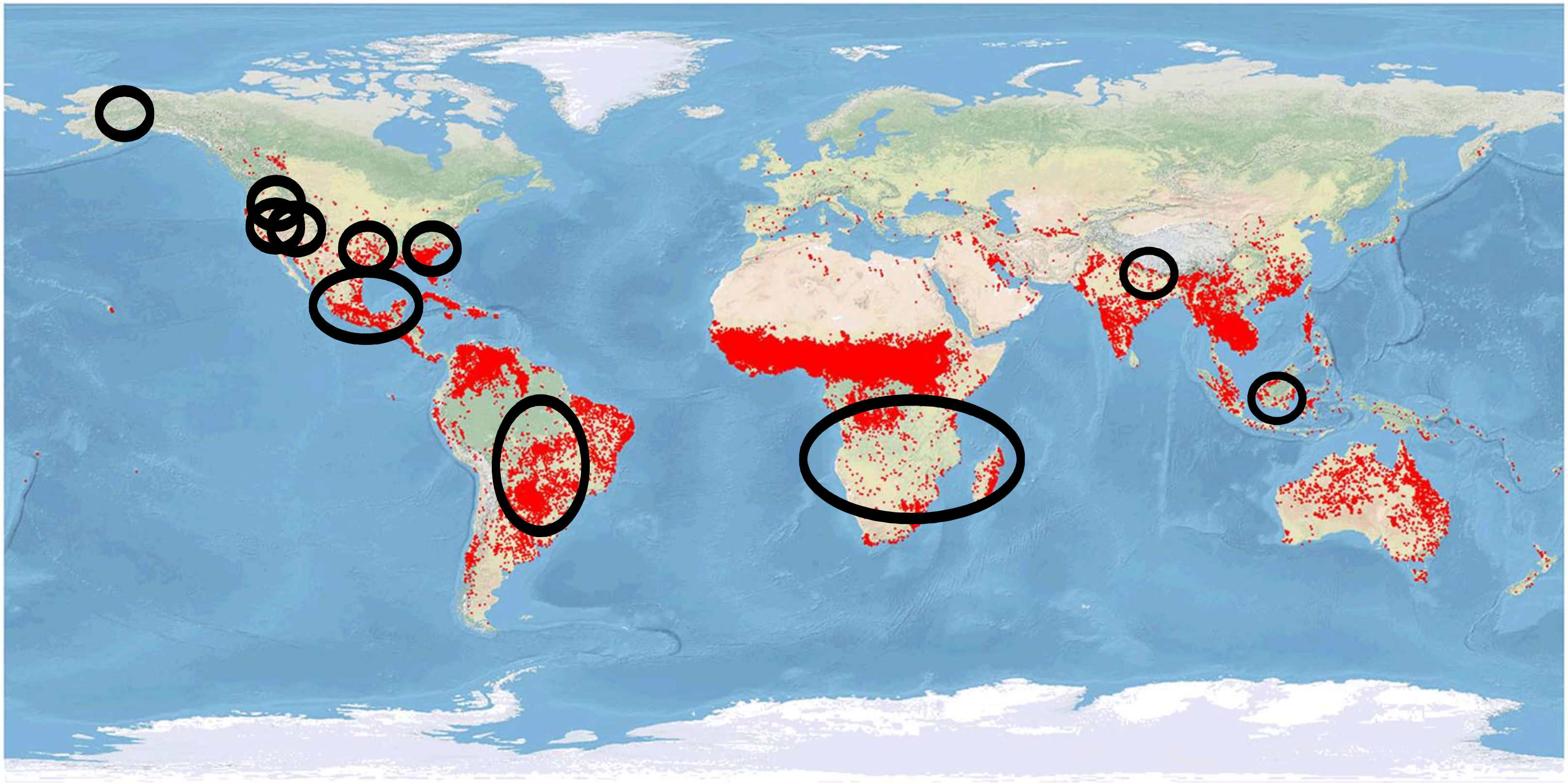


Missoula 2017-2020 > 1200 hours of “regionally representative surface smoke”: **Selimovic et al., (2020)**

1) PM/CO in Missoula is about half of aircraft measurements (age-independent): 40^{0}C Temp difference
2) Thermally driven OA evaporation at surface for SOA 1-2 days old
3) O3 enhanced in dilute smoke, suppressed in thick smoke → chemical mechanisms
4) inert tracers time series.

2013 MODIS Active Fire Detections from the Aqua and Terra satellites

CPU time devoted to what task?



January February March April May June July August September October November December

Active fires, shown in red, are detected using MODIS data from the Aqua and Terra satellites.
Source: NASA Fire Information for Resource Management System (FIRMS) https://earthdata.nasa.gov/firms

Take home points:

- Lot’s of challenges, where to focus most? Timing of impacts #1?
- PM evaporation is more dominant at the surface, this also impacts VOC, nitrogen
- Chemistry differs air/ground, day/night, rural/urban
- More ground-based, downwind data needed for model evaluation
- Smoke chemistry co-deployed with metabolomics, assays, long-term follow-up needed to better understand health risks
- Wildfires emit more PM than spring/fall prescribed fires
- Prescribed fires could help reduce smoke!

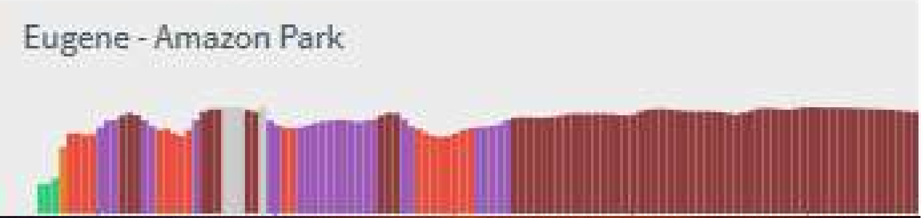
Questions? **bob.yokelson@umontana.edu**

Thank you to: NSF, NASA, NOAA, JFSP, SERDP, DOE, DOD, USFS, CSU

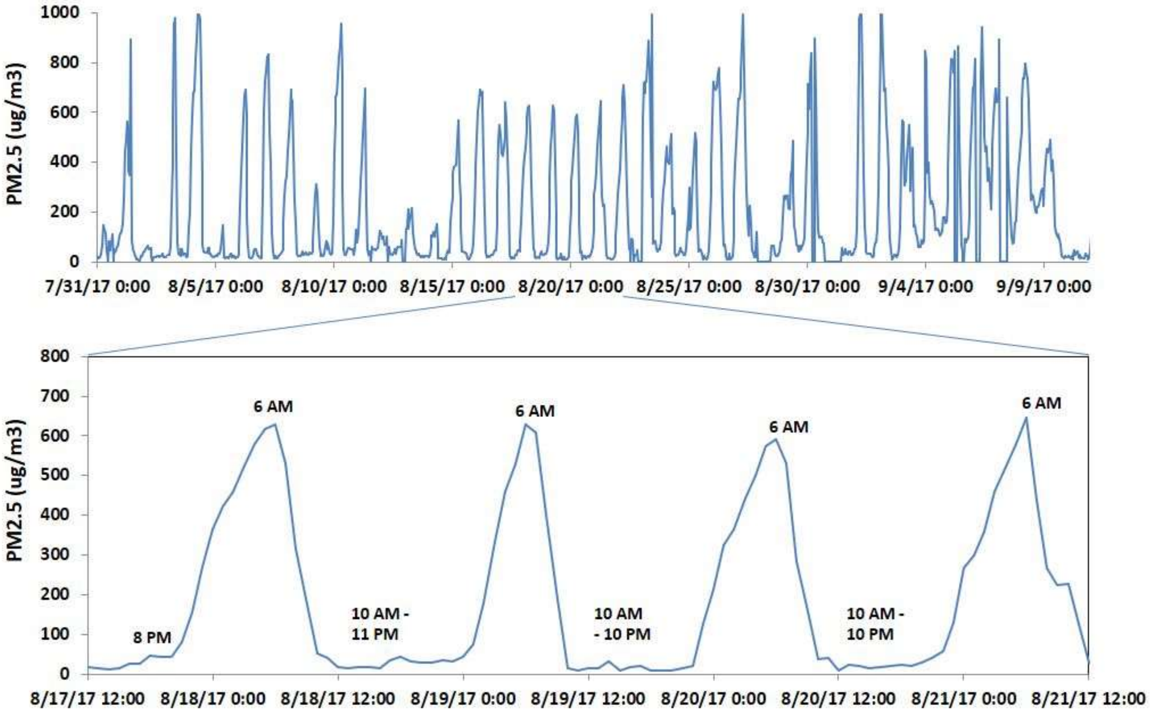
References: Akagi 2014 doi:10.5194/acp-14-199-2014, Hatch 2015 doi:10.5194/acp-15-1865-2015, Hatch 2017 doi:10.5194/acp-17-1471-2017, Jen 2019 doi.org/10.5194/acp-19-1013-2019, Liu 2017 doi:10.1002/2016JD026315, May 2014 doi:10.1002/2014JD021848, Nergui 2017 Integrating measurement based new knowledge on wildland fire emissions and chemistry into the AIRPACT air quality forecasting for the Pacific Northwest. New Orleans, LA: American Geophysical Union Fall Meeting. Abstract# A41L-06, Permar 2020 http://hs.umt.edu/luhu/documents/permar_submit.docx, Selimovic 2020 https://agupubs.onlinelibrary.wiley.com/doi/full/10.1029/2020JD032791, Yates 2016 doi.org/10.1016/j.atmosenv.2015.12.038, Yokelson 1996 J. Geophys. Res., 101, 21067-21080

Back up slides

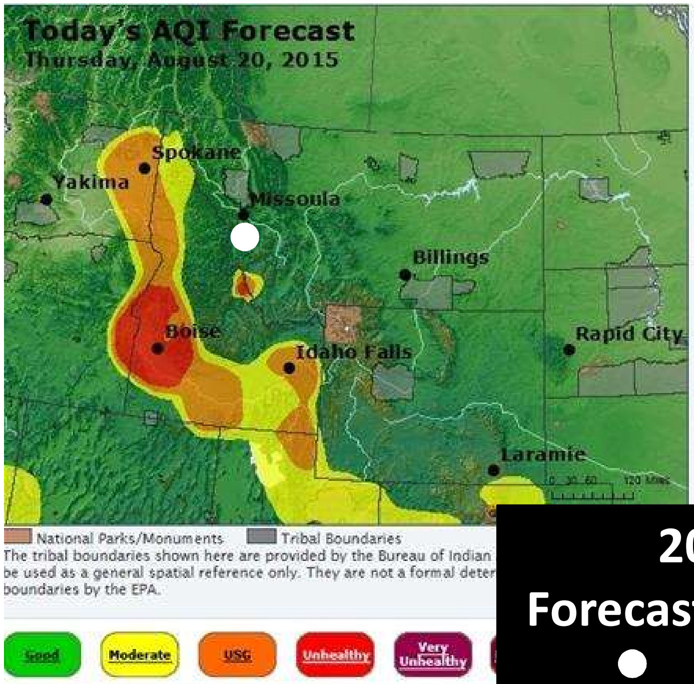
Orofino-45423 US-12



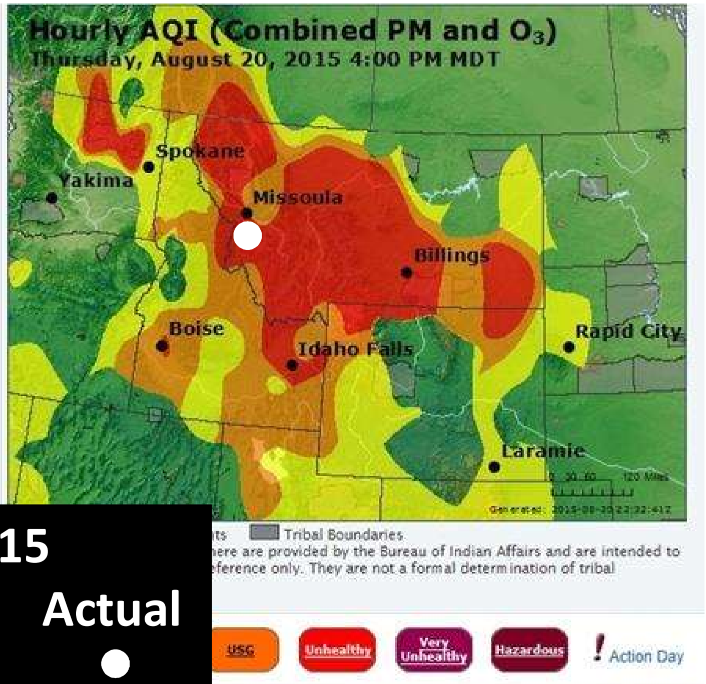
Eugene - Amazon Park



Ground-based impact types: downslope flow (above), elevated layers mixing down (~inverse of above), boundary layer plume strike, “synoptic scale smoke fronts” (Eugene).



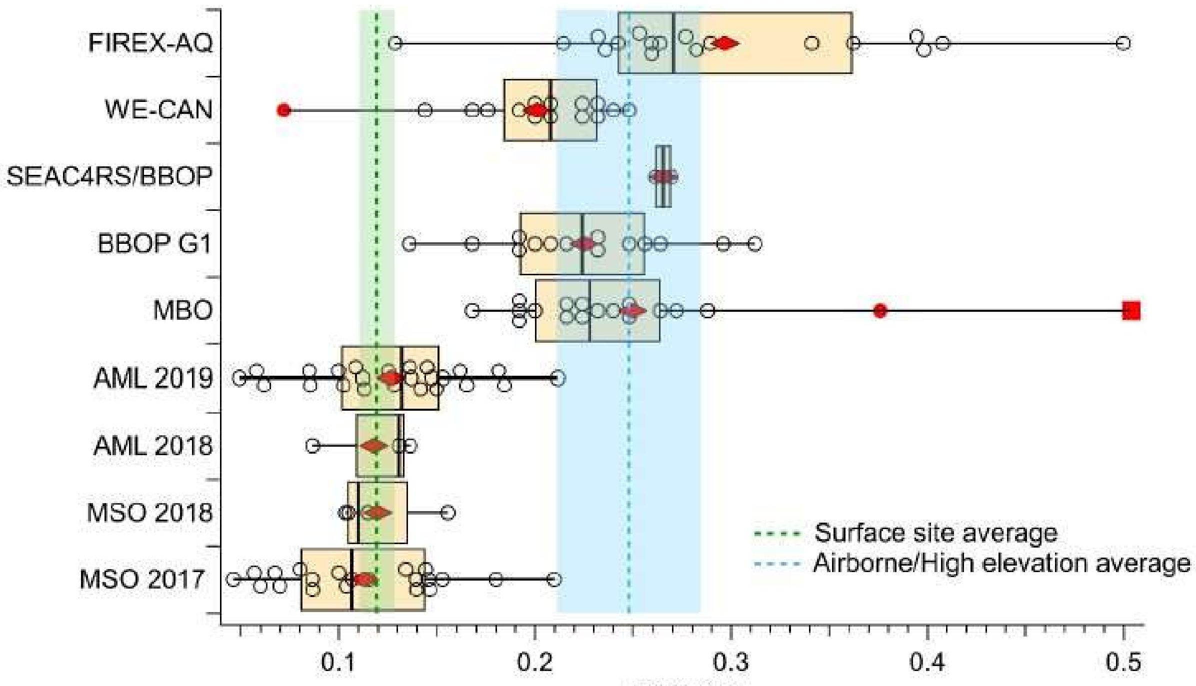
The tribal boundaries shown here are provided by the Bureau of Indian
be used as a general spatial reference only. They are not a formal deter
boundaries by the EPA.

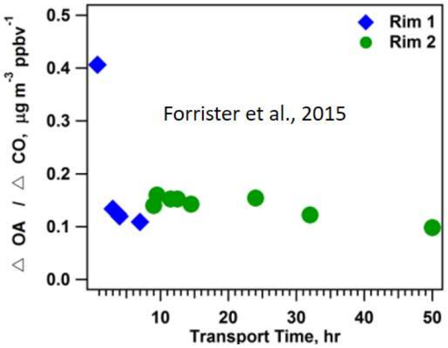


ere are provided by the Bureau of Indian Affairs and are intended to
eference only. They are not a formal determination of tribal

2015

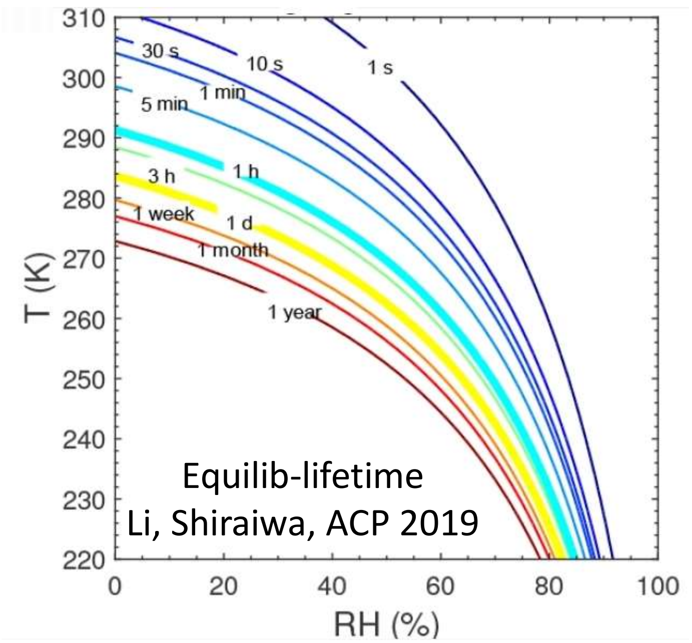
Forecast ● **Actual** ●





Forrister et al., 2015

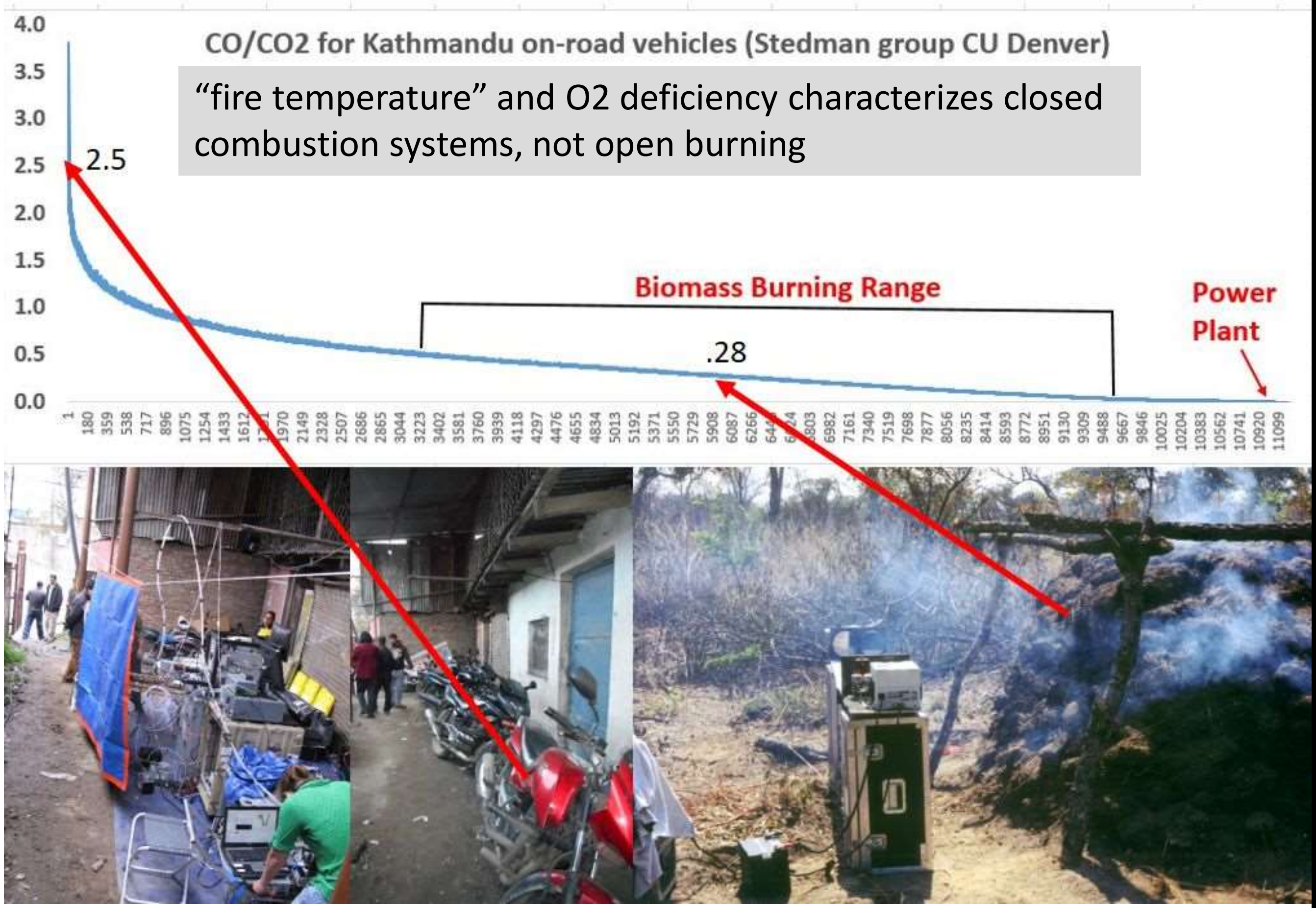
2006-2017 Boise WF PM/CO 0.12(.01)
McCLure and Jaffe (2018)



Equilib-lifetime
Li, Shiraiwa, ACP 2019

T-glass BBOA between 0C and surface T, Schum et al., 2018; DeRieux et al., 2018; Schmedding et al., 2020

BB efficiency compared to idling motorcycles (2015), on road fleet (1993)



“fire temperature” and O2 deficiency characterizes closed combustion systems, not open burning

Learn from the study of people who build open fires in their house!