



PM and VOC speciation by combustion phase

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Study Motivation

NEI 2014 reports emissions based on flaming and smoldering combustion phases of wildland fires (wild and prescribed fires).

Scant data on PM speciation by combustion phase exists and what is available in the literature had surprisingly high EC fractions.

Our objective was to validate these PM speciation profiles by combustion phase reported in the literature



Particulate and gas sampling of prescribed fires in South Georgia, USA



Sivaraman Balachandran ^{a,*}, Jorge E. Pachon ^c, Sangil Lee ^d, Michelle M. Oakes ^h, Neeraj Rastogi ^e, Wenyan Shi ^b, Efthimios Tagaris ^f, Bo Yan ^b, Aika Davis ^a, Xiaolu Zhang ^b, Rodney J. Weber ^b, James A. Mulholland ^a, Michael H. Bergin ^a, Mei Zheng ^{b,g}, Armistead G. Russell ^a

Table 3

PM_{2.5} major components (as wt.%) and metals ratios to total PM_{2.5} (mg g⁻¹ of total PM_{2.5}) in flaming and smoldering stages, averaged over two prescribed fires.

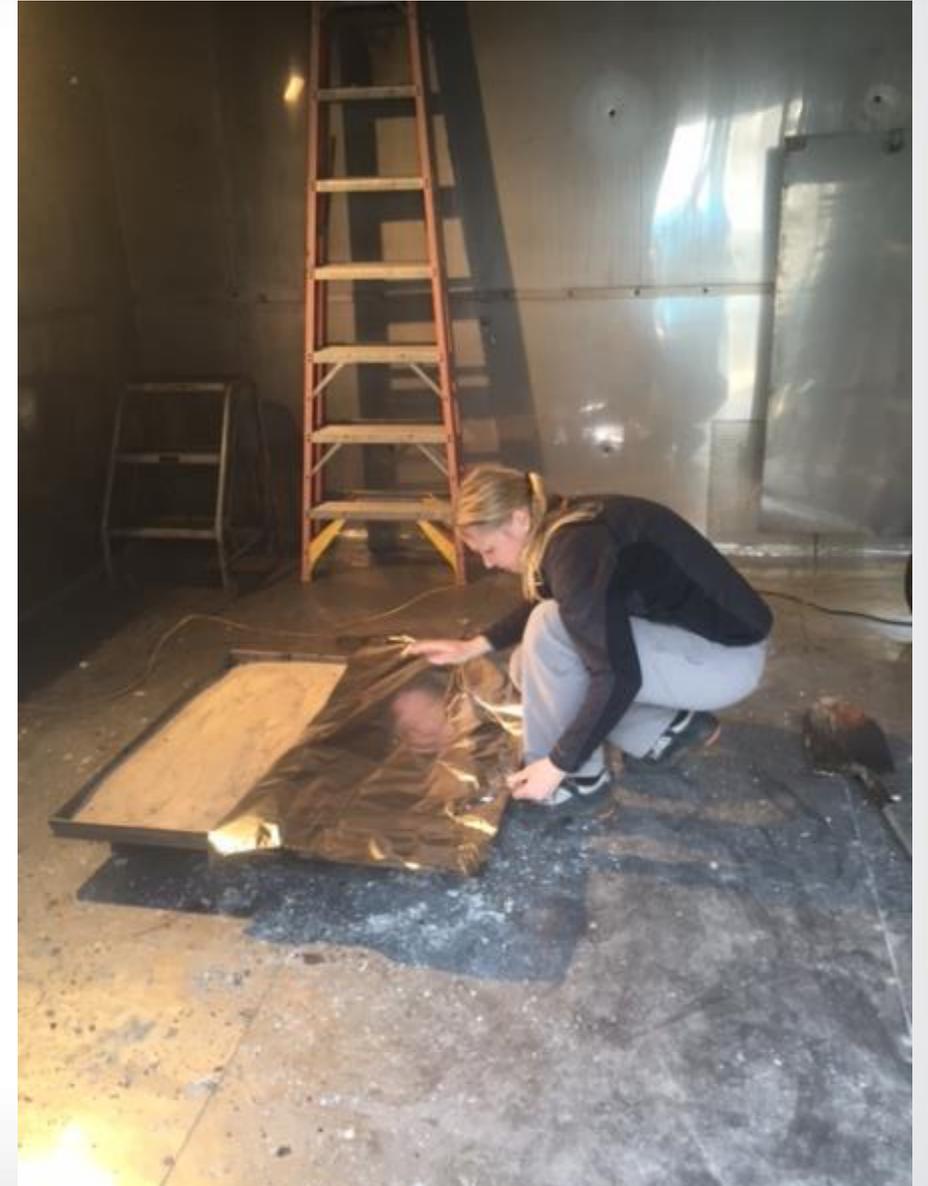
Major components units (% of total PM _{2.5})	Flaming		Smoldering	
	Avg.	St. Dev.	Avg.	St. Dev.
Other	27%	0.9%	29%	0.29%
OC	55%	1.8%	58%	0.59%
EC	11%	1.0%	10%	0.74%
Acetate	0.40%	0.16%	0.79%	0.62%
Nitrate	1.45%	0.76%	1.55%	1.36%
Sulfate	0.48%	0.08%	0.61%	0.49%
Oxalic acid	0.35%	0.34%	0.27%	0.21%
Ammonium	0.86%	0.22%	0.81%	0.07%
PM _{2.5} (μg m ⁻³)	327.15	148.32	48.52	9.45

Open Burn Test Facility

60 m³ stainless steel covered cinder block room, 1 x 1 m² burn pan

Large blower draws in ambient air to provide conditions (excess oxygen) similar to open burning conditions

Long history of open burning studies providing numerous profiles and emission factors from biomass burning and waste burning



Repeatable near separation of phases in batch burns

After ignition flaming dominates, but still mixed combustion



Toward end of burn all flames extinguish and only smoldering occurs

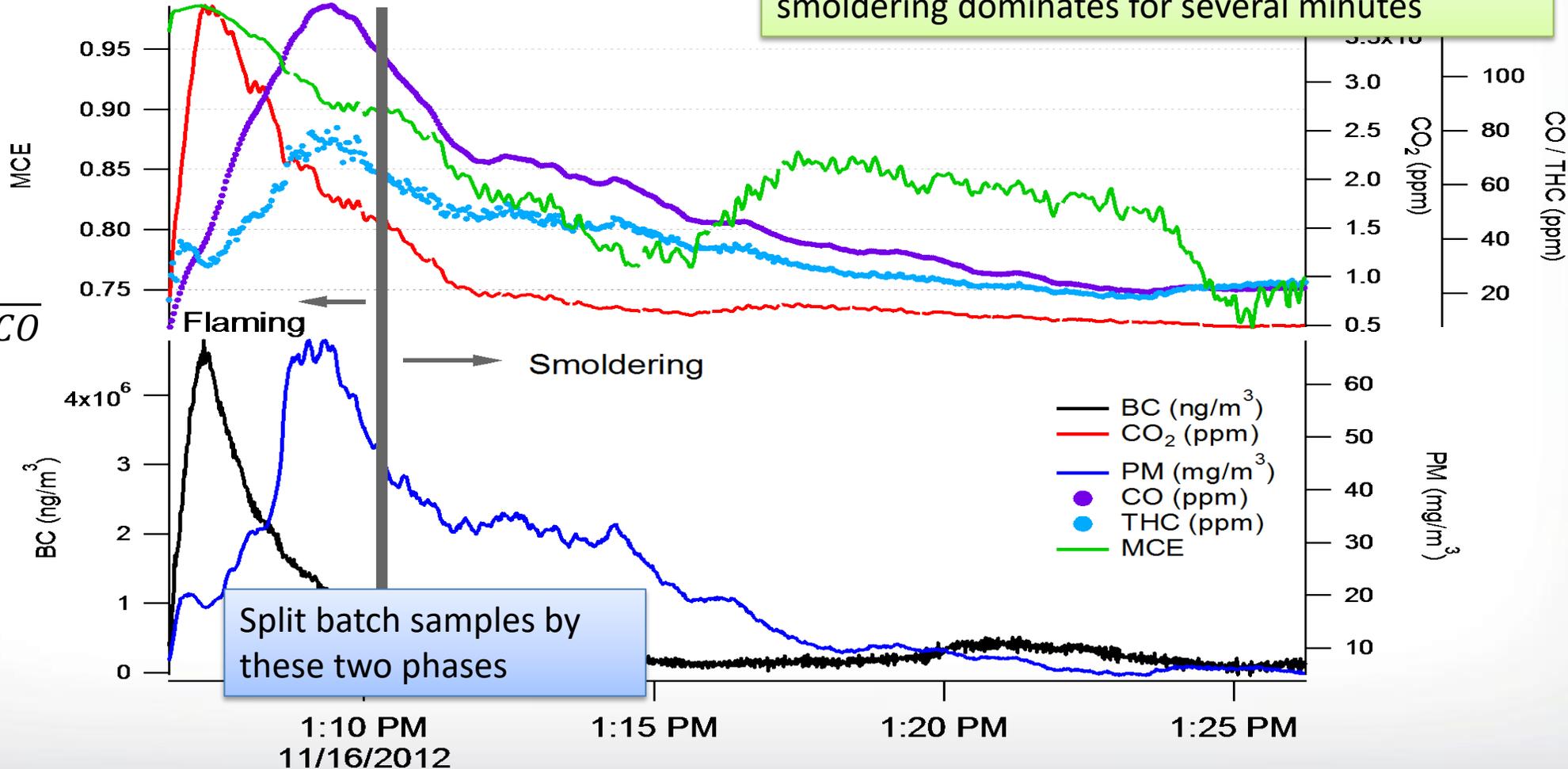


We quantify the emissions from each combustion phase by splitting the burn into two batch samples

Flaming dominated combustion occurs early and consumes most of the fuel

After all (or most) of the flames extinguish, smoldering dominates for several minutes

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



Split batch samples by these two phases

We tested this approach using fuels local to the North Carolina (mixed hardwood and pine litter)

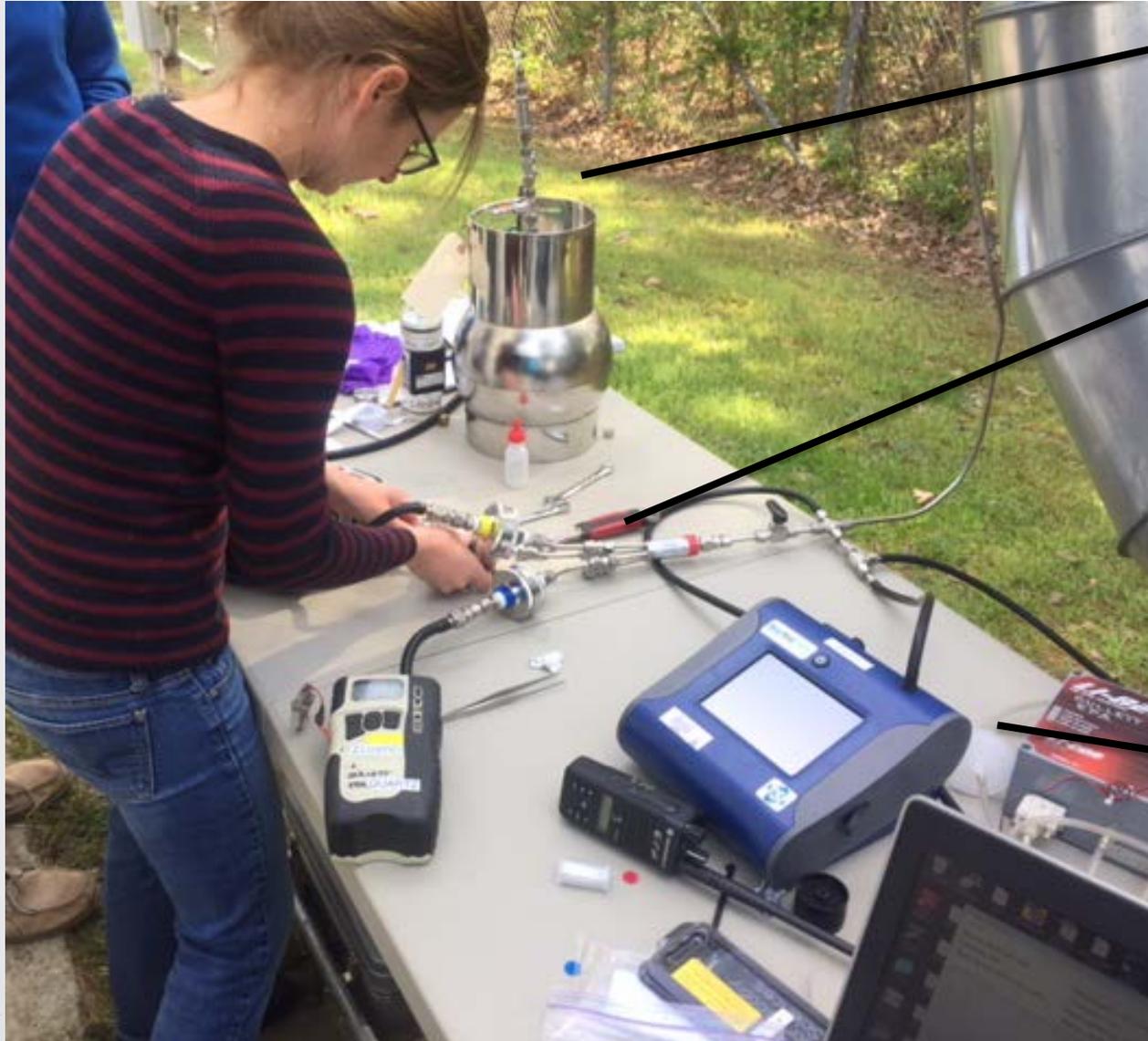


Sample emissions in the exhaust duct from the burn hut.

Switch out batch filters, canisters, and cartridges mid burn to capture flaming and smoldering phase emissions separately.

Flaming smoldering split determined visually (i.e. presence of flames) and quantified by the modified combustion efficiency

We used an assortment of methods, both continuous and batch to characterize the emissions



Summa Canister for VOCs
DNPH cartridges for aldehydes

Teflon Filters:

- ions by ion chromatography
- gravimetric mass
- trace elements by XRF
- Pb by ICP-MS

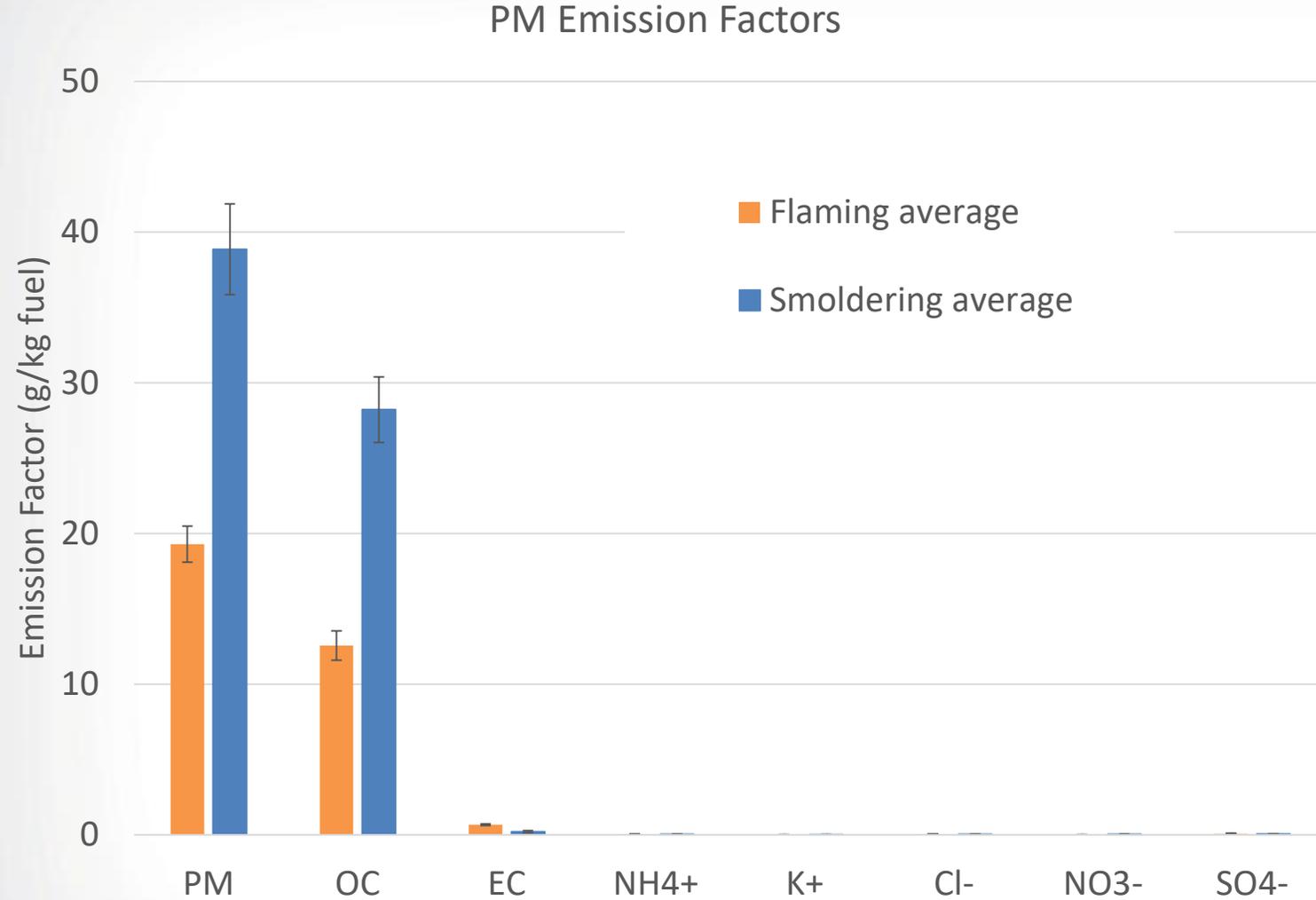
Quartz Filter:

- Organic and elemental carbon (IMPROVE TOR)

Online Measurements:

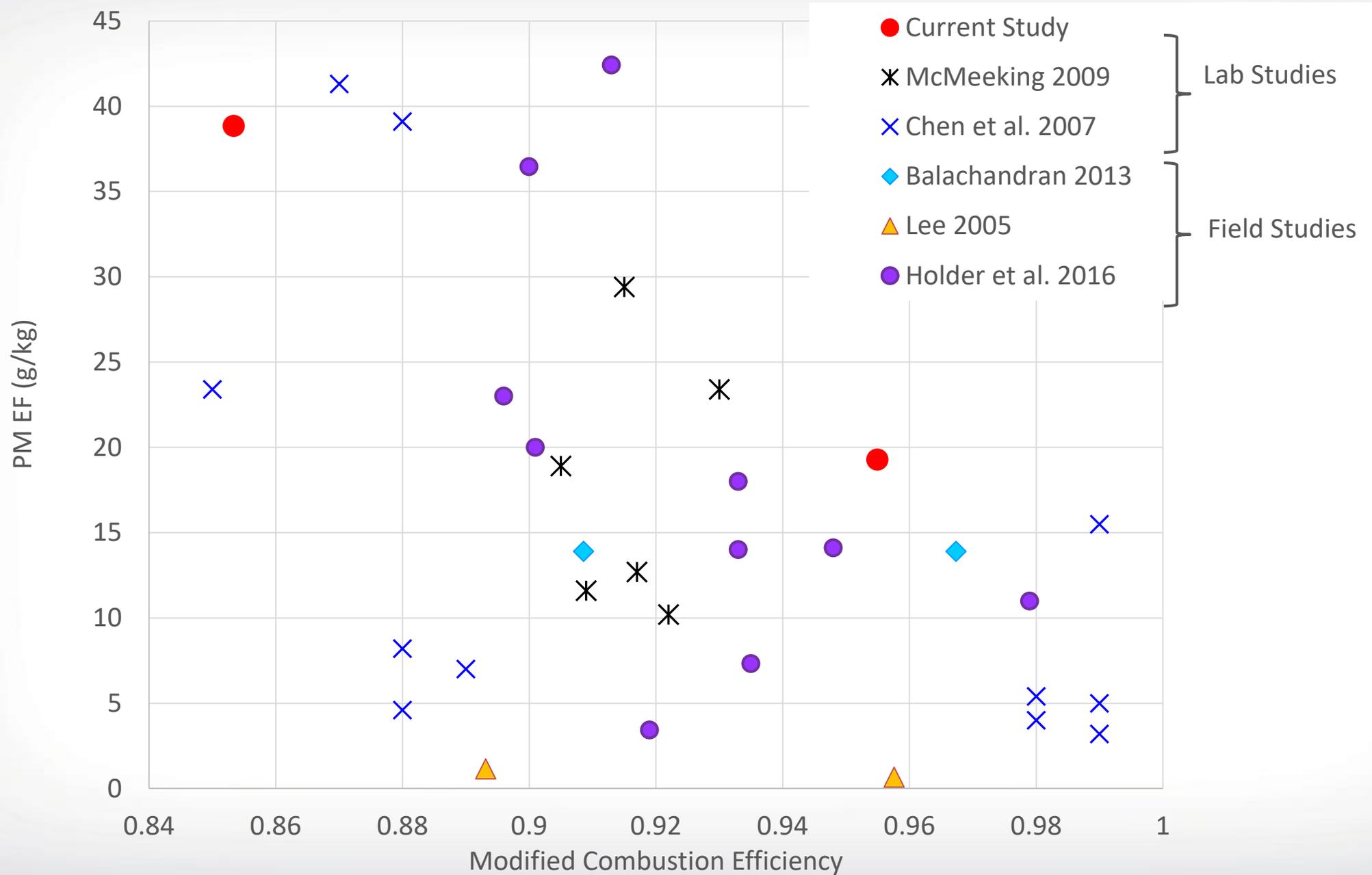
- CO₂, CO, NO, HCs by FTIR or CEMS
- Black carbon by microaethalometer
- PM mass by DustTrak

PM emission factors are strongly dependent on combustion phase

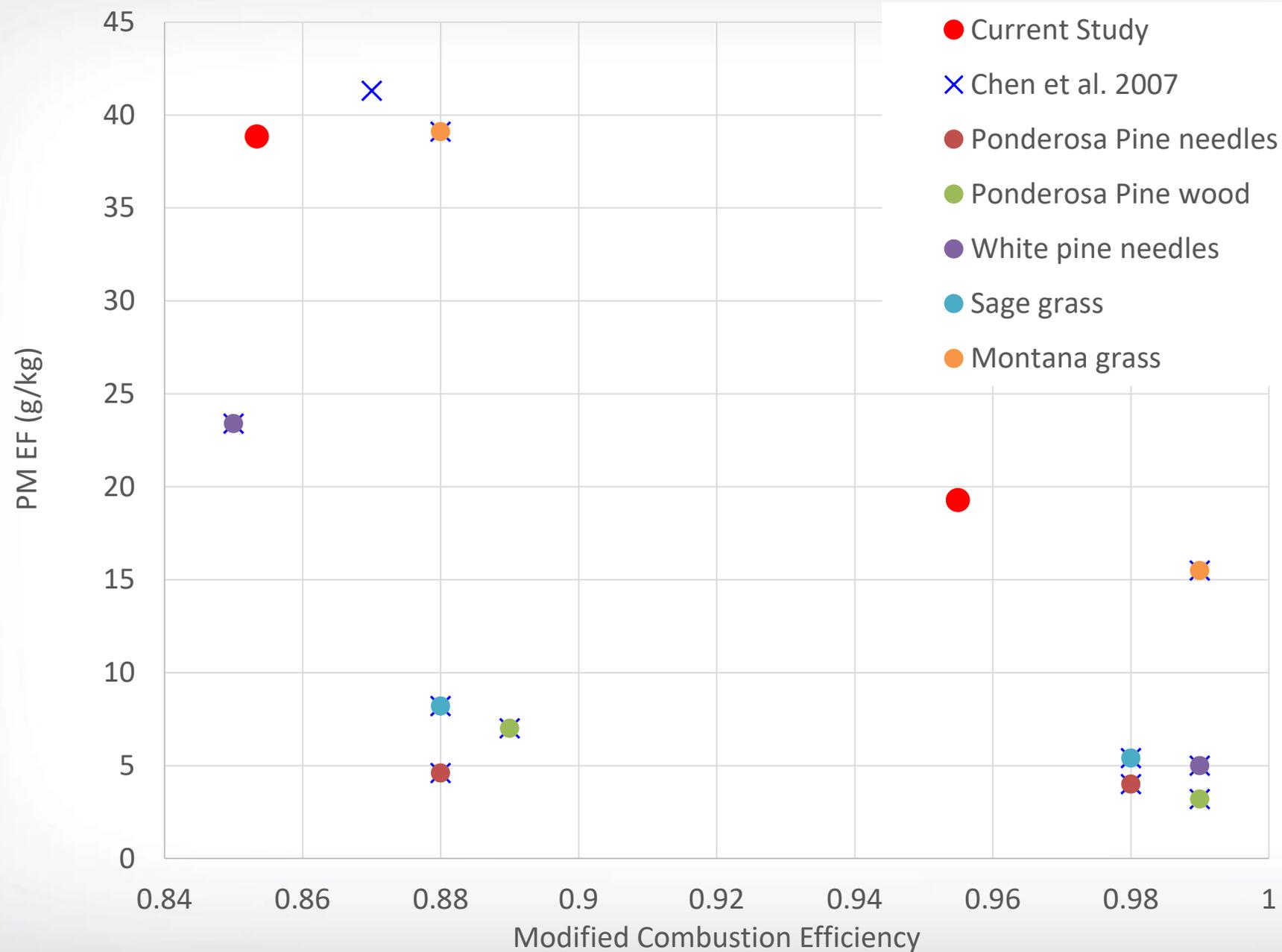


Smoldering emits almost 2x as much PM on a per fuel basis, and almost all the PM is organic carbon

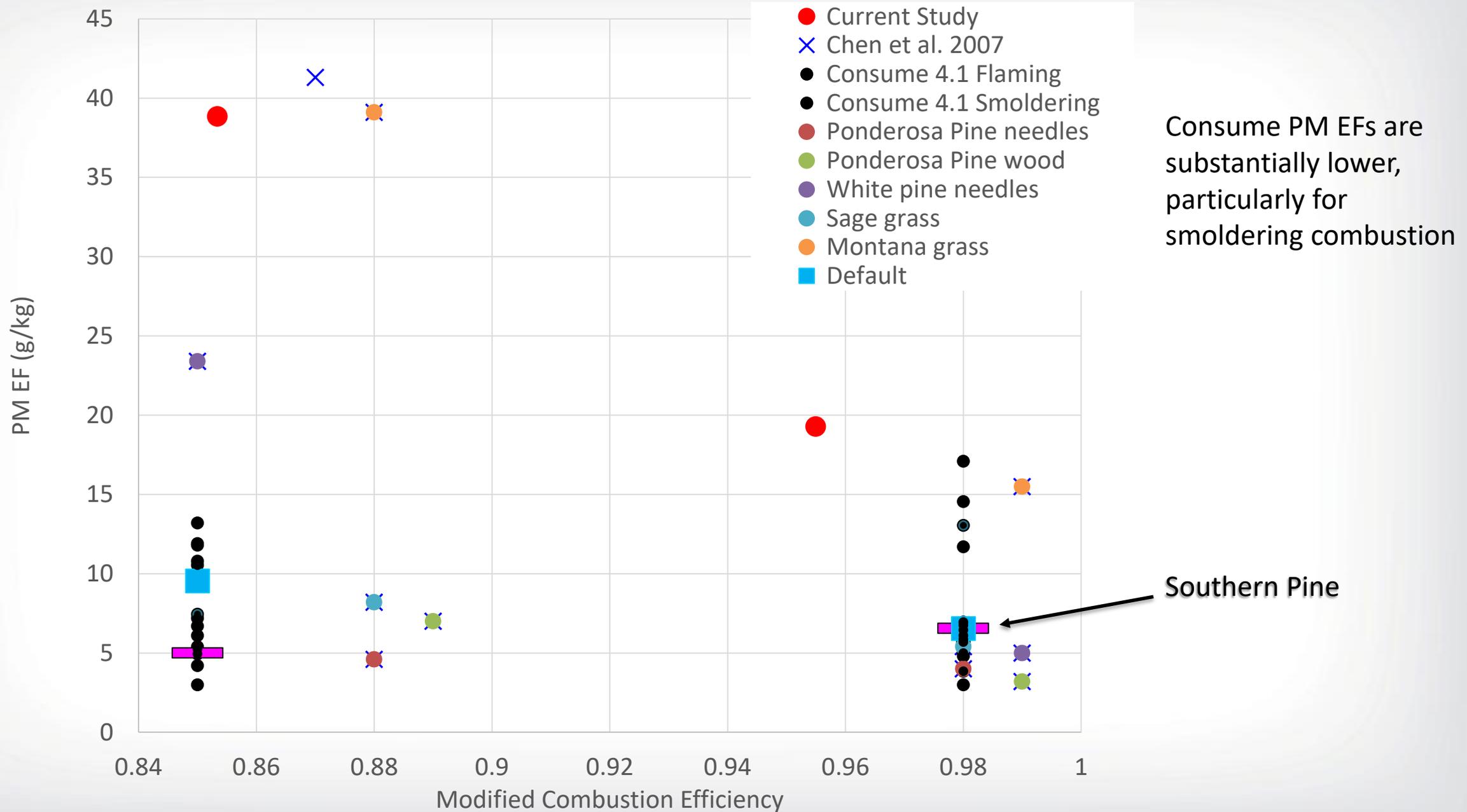
Previous PM EFs show a lot of variability



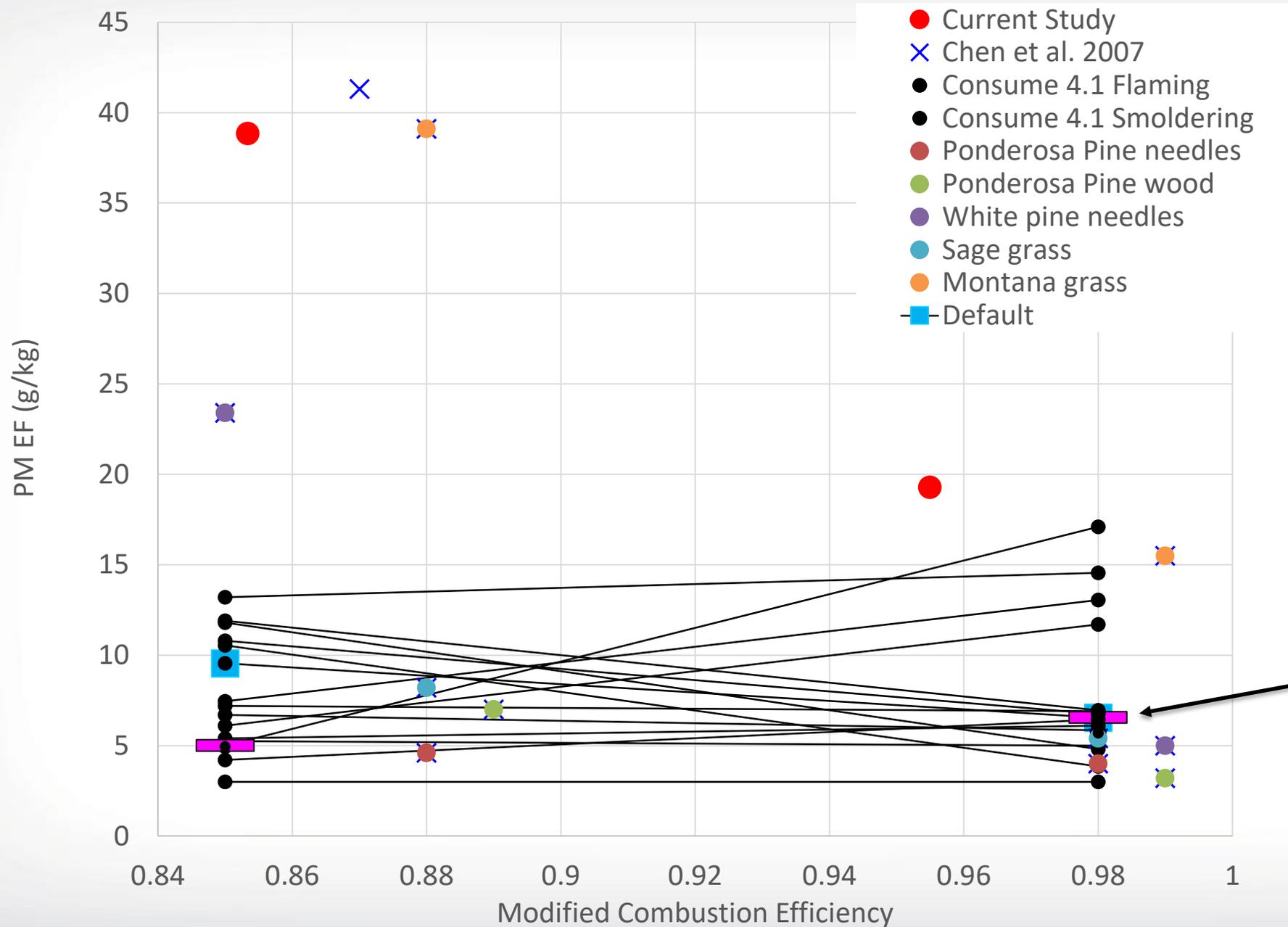
For matched smoldering and flaming PM EFs from the identical species



To compare with EFs used in the models...



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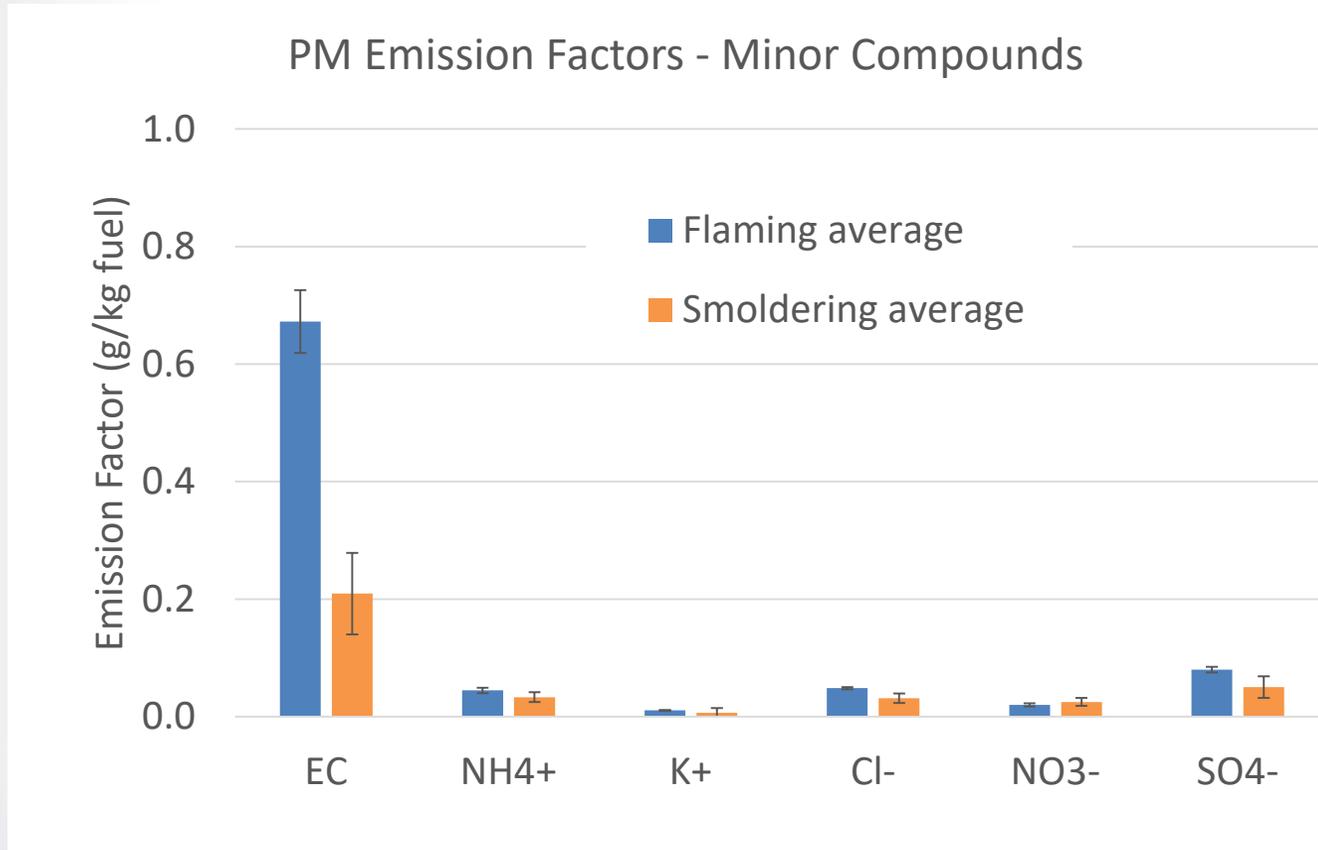


Consume PM EFs are substantially lower, particularly for smoldering combustion

Southern Pine

PM minor composition is also strongly dependent on phase

3x as much elemental carbon and 1.5x inorganic compounds are emitted during flaming.



Flaming dominated:

CO₂, NO, EC, NH₄, K, Cl, SO₄, Mg, Al, Zn, Br
...and Cd at very low concentrations

Smoldering dominated:

CO, CH₄, PM, OC, NO₃, Si, Ca, Mn, Fe
...and Pb at very low concentrations (below
method uncertainty)

Our results are quite different from the literature PM profiles

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Flaming

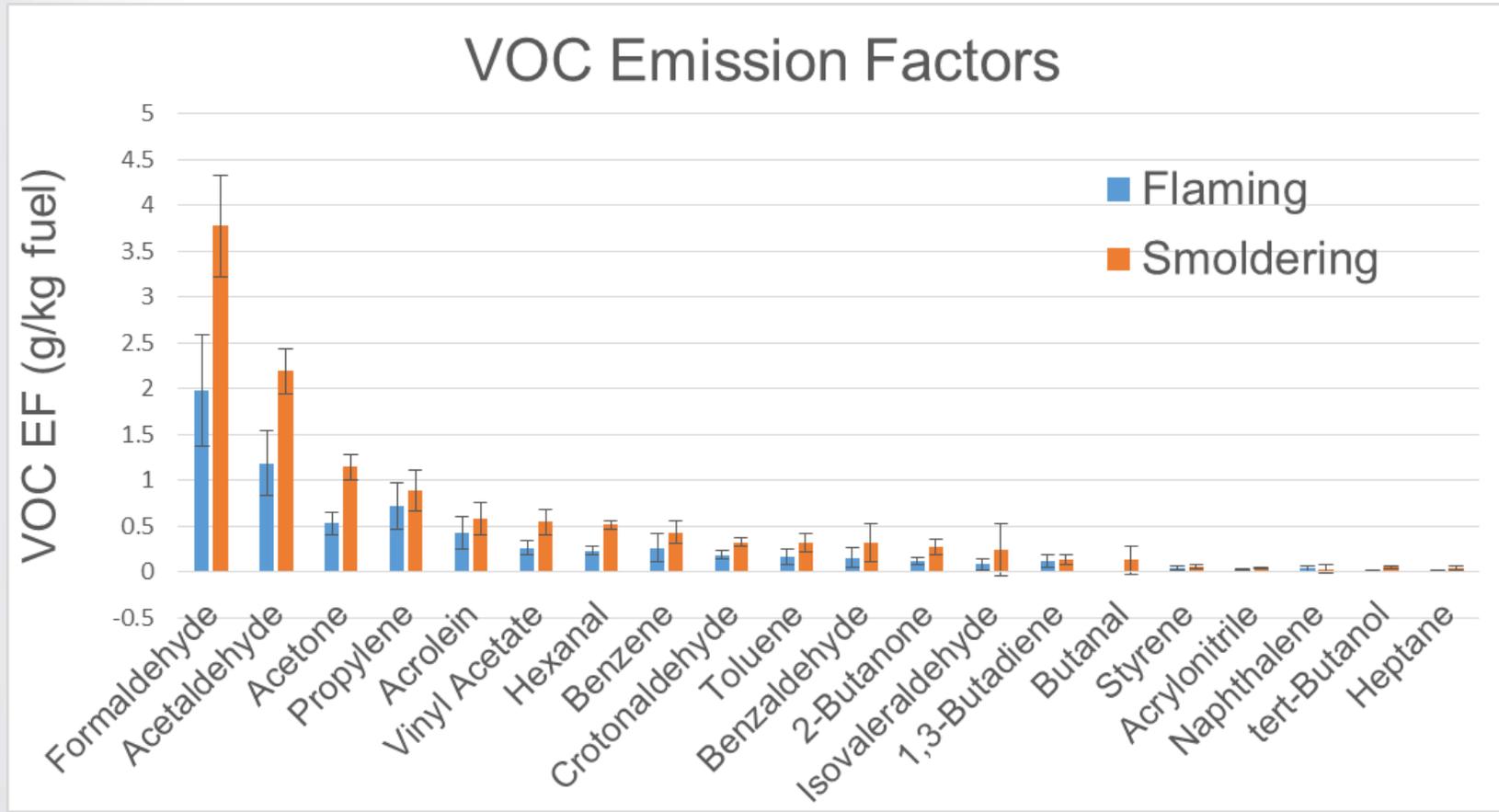
Compound	Current Study (%)	Balachandran et al. 2013 (%)
OC	56.5	≈ 55
EC	3.0	≪ 11
NO ₃	0.09	≪ 1.45
SO ₄	0.36	≈ 0.48
NH ₄ ⁺	0.20	≪ 0.86

Smoldering

Compound	Current Study (%)	Balachandran et al. 2013 (%)
OC	58.4	≈ 58
EC	0.4	≪ 10
NO ₃	0.05	≪ 1.55
SO ₄	0.10	≪ 0.61
NH ₄ ⁺	0.07	≪ 0.81

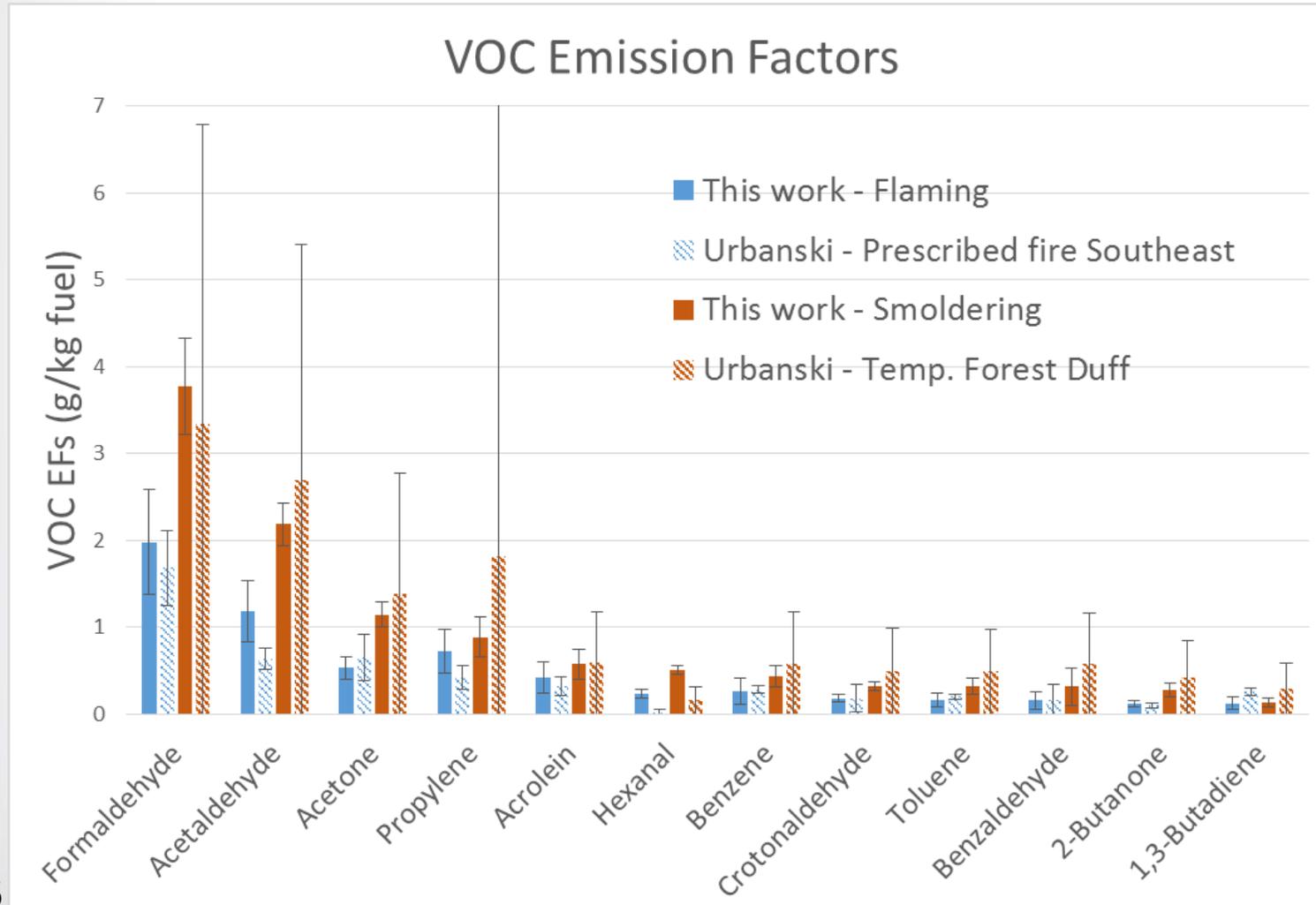
VOC Emission Factors by Phase

VOC emission factors were nearly twice as much during smoldering compared to flaming;
Urbanski 2014 Σ VOC EF vs MCE relationship predicts 7 times increase



VOC Emission Factors comparison with Urbanski 2014

Trends in VOC EF changes with phase are generally consistent with Urbanski 2014 emission profiles for flaming and smoldering fuels



Urbanski's temp. forest duff/org. soils profile has approx. 4 times greater VOC emissions compared to prescribed fire Southeast conifer forest profile (MCE = 0.752 vs 0.933)

Conclusions

- There is a large amount of variability in the PM EFs by combustion phase
- Some of this variability may be due to species differences
- Initial results indicate larger PM EFs for smoldering conditions for the same species
- Our PM speciation results are very different from the field PM speciation data and indicate 1.5– 3 x larger for the minor constituents during the flaming phase
- Trace constituents were enriched in both the flaming and smoldering emissions
- VOC EFs consistently greater from smoldering conditions, in agreement with VOC EFs split by fuels representing diverse combustion phases

Future Work

- Current efforts are to:
 - Expand the number of fuel species, including critical species: Hg, Pb, and NH_4^+
 - Explore fire intensity in the laboratory and determine how it impacts EFs and speciation
- Ultimate goal is to validate speciation observed in the lab with field measurements...if possible.