O_3 formation in urban areas from fire emissions

Dan Jaffe, University of Washington (djaffe@uw.edu)

Seattle, Aug. 21, 2018. $PM_{2.5}$ = 110 ug/m^3

Seattle, Sept. 14, 2020, $PM_{2.5}$ = 264 µg/m^3

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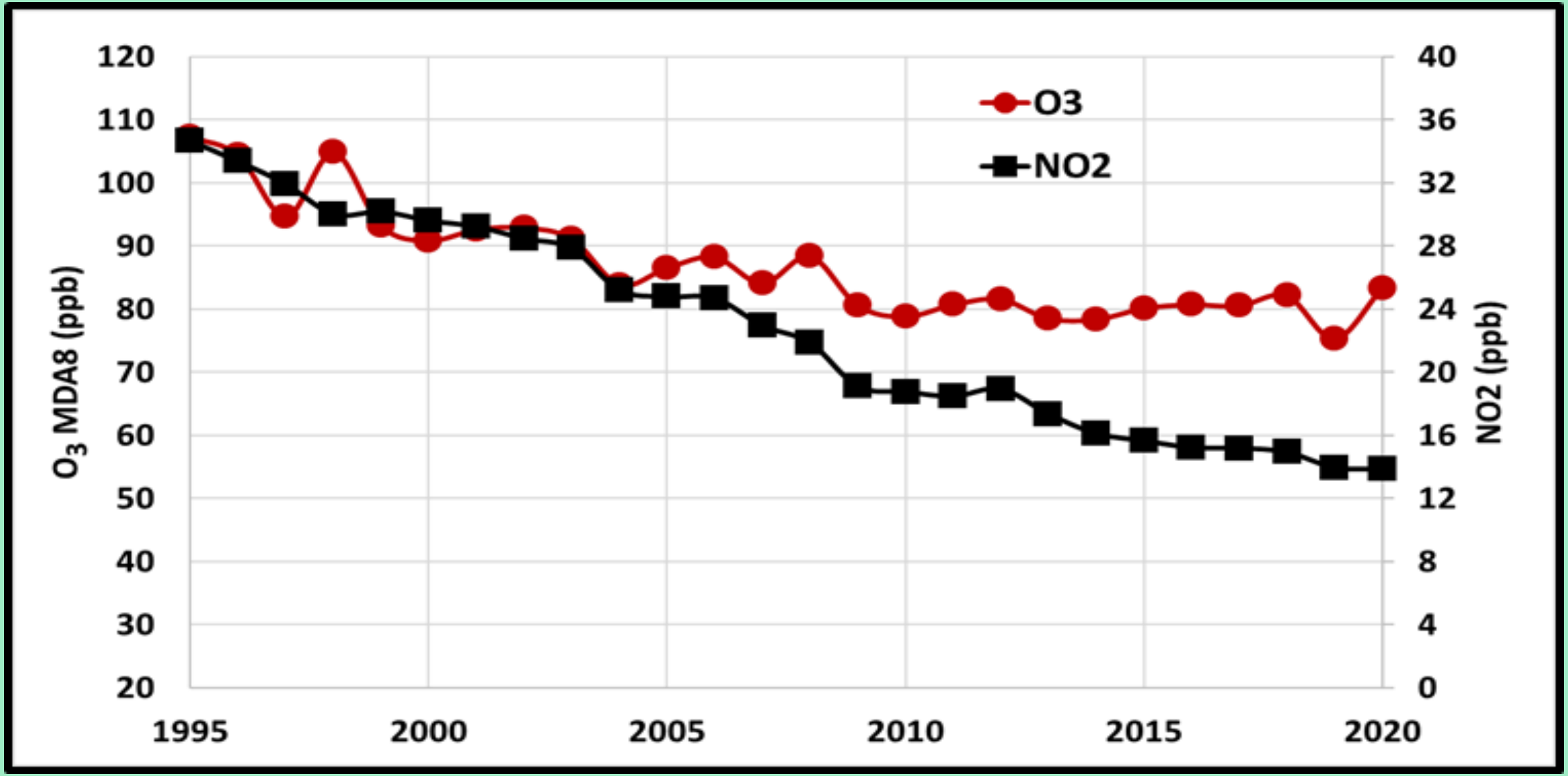
Long-term record of fourth highest MDA8 O_3 and NO_2 in 20 western NAAs



O_3: Fourth highest MDA8 in highest monitor in each metro region.
NO_2: May-Sept average of daily 1-hour maximums.

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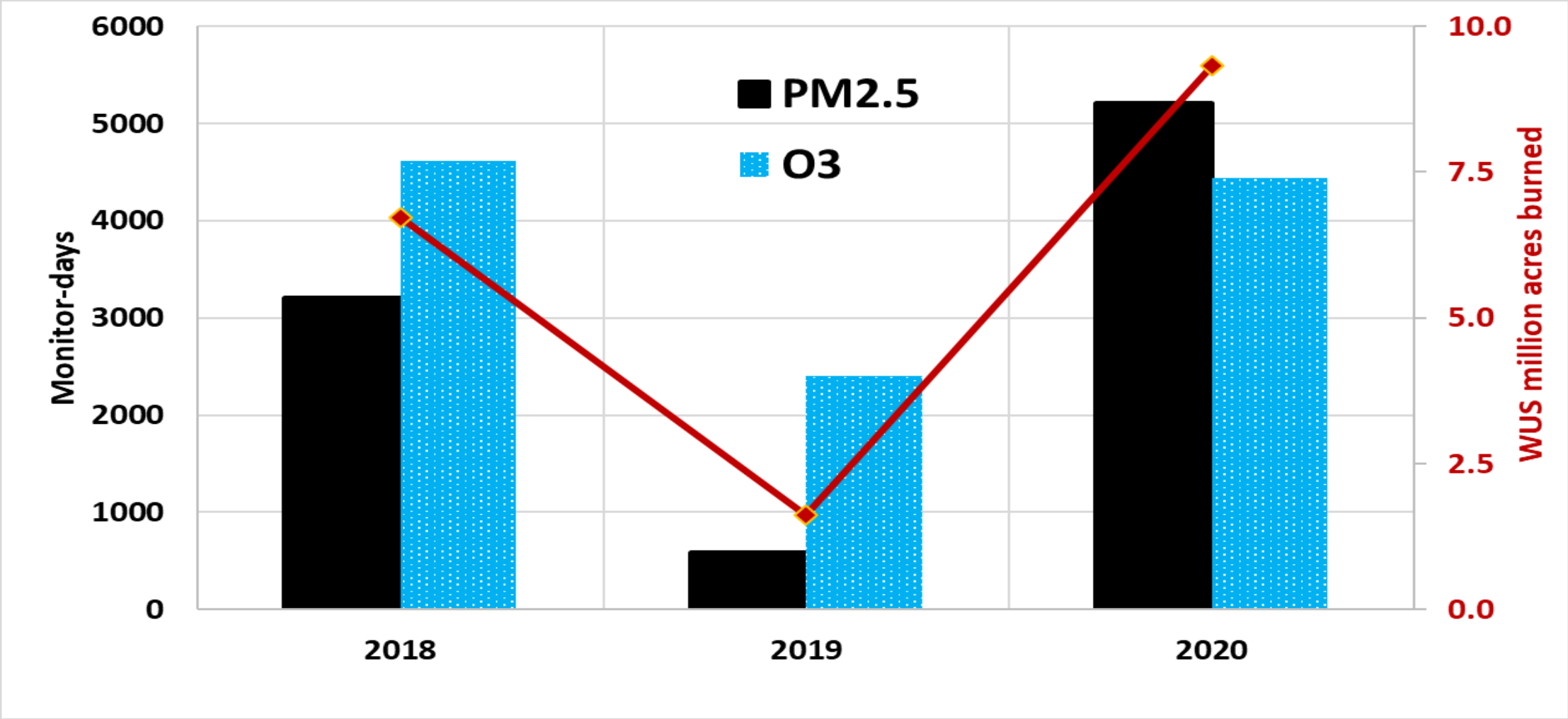
Western U.S. $PM_{2.5}$ and O_3 exceedance days and area burned

(All reg monitors, MDA8 O_3 > 70 ppb; $PM_{2.5}$ >35 ug/m3)



- For $PM_{2.5}$, 10x the number of days in 2020 compared to 2019.
- For O_3, 2x the numbers days in 2020, compared to 2019).
- For 2020, approximately ¾ of these are in Cal.

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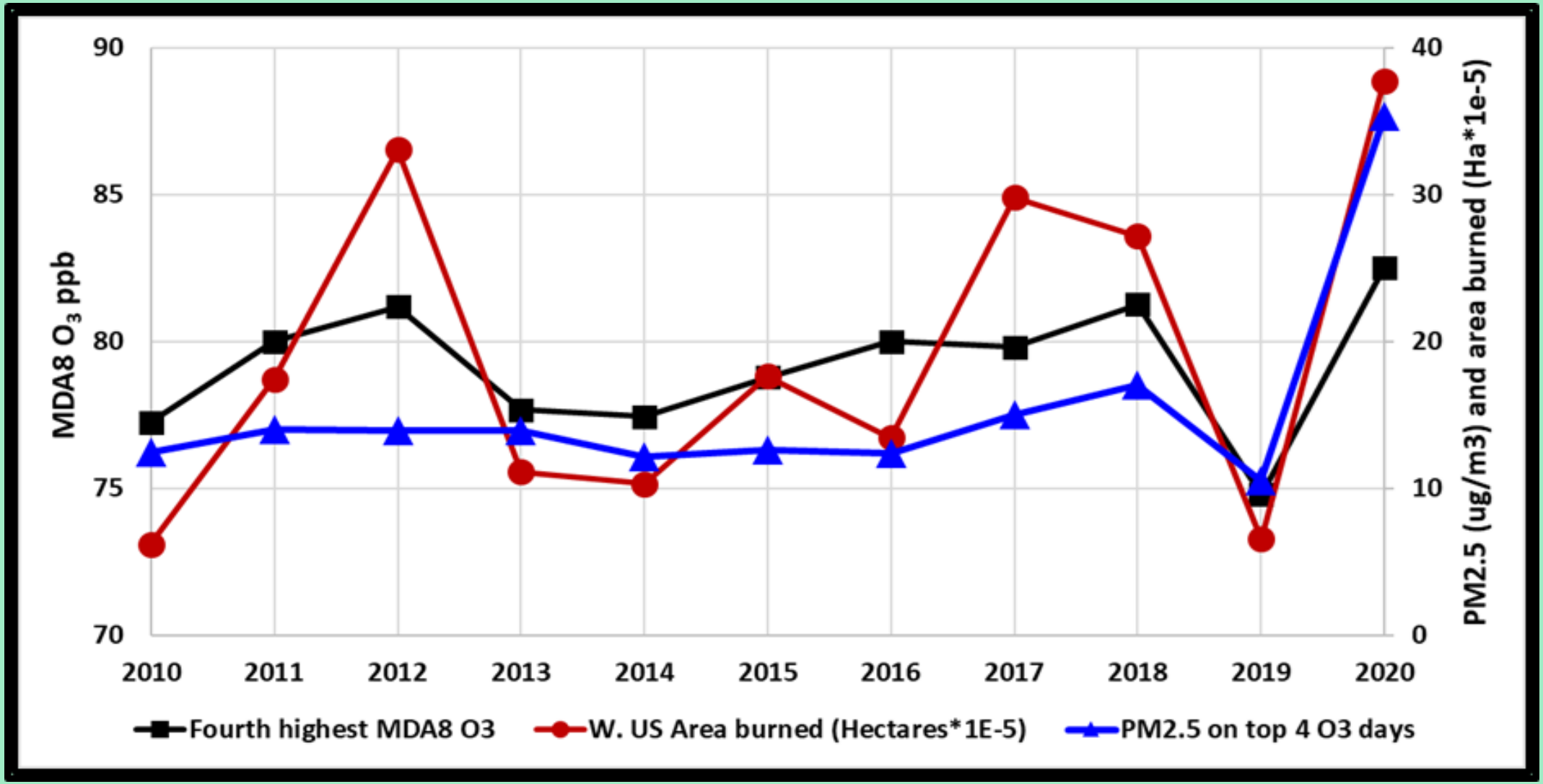
O_3, $PM_{2.5}$ and fires on top four days for 20 western NAAs



Jaffe et al 2021, in-prep.

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O_3 vs $PM_{2.5}$ exceedances by monitor

PM2.5 in West	2018	2019	2020
Number of PM2.5 monitors	308	301	300
Avg 98th percentile, all monitors	33.1	18.4	43.2
Number w/98th perc >35 ug/m3	85	11	131
Fraction exceeding 35 ug/m3	0.28	0.04	0.44
Avg of those over 35 ug/m3	62.3	40.6	69.5

Ozone in west	2018	2019	2020
Number of O3 monitors	440	413	411
Avg fourth highest, all monitors	69.8	65.6	70.0
Number with fourth highest >70 ppb	209	105	174
Fraction exceeding 70 ppb	0.48	0.25	0.42
Avg of those over 70 ppb	79.4	78.8	82.0

O_3 exceedances are much more subtle!

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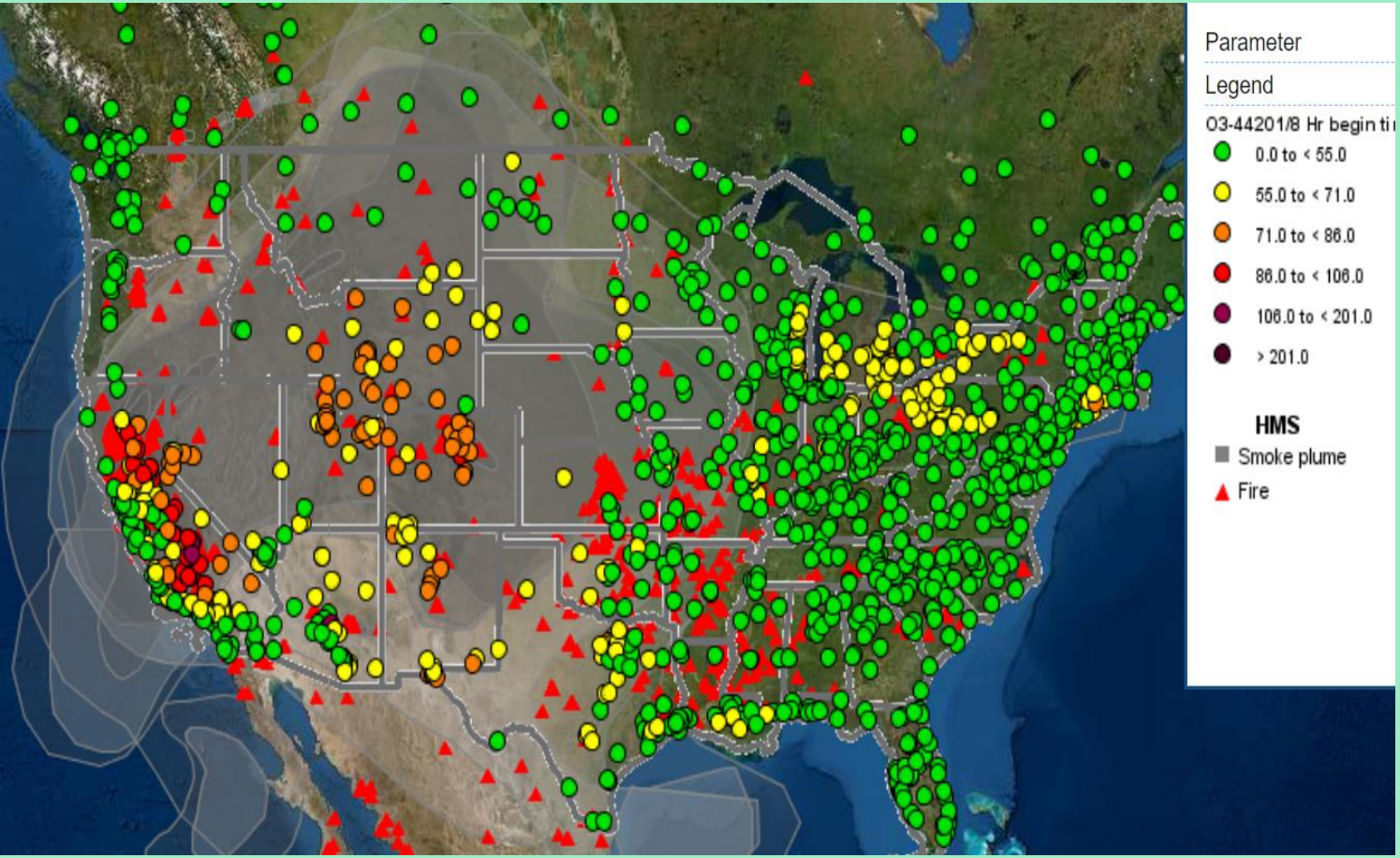
Photochemistry, O_3 and smoke



MDA8 O_3 values for Aug 22, 2020

- We know that that smoke contributes to O_3 exceedances in urban areas, but processes poorly understood. (Jaffe et al 2004, 2008; 2018; 2020; Buysse et al 2019).
- Large amount of variability due to: emissions; photolysis, local VOC/NOx ratio, transport pathway, meteorology, etc.

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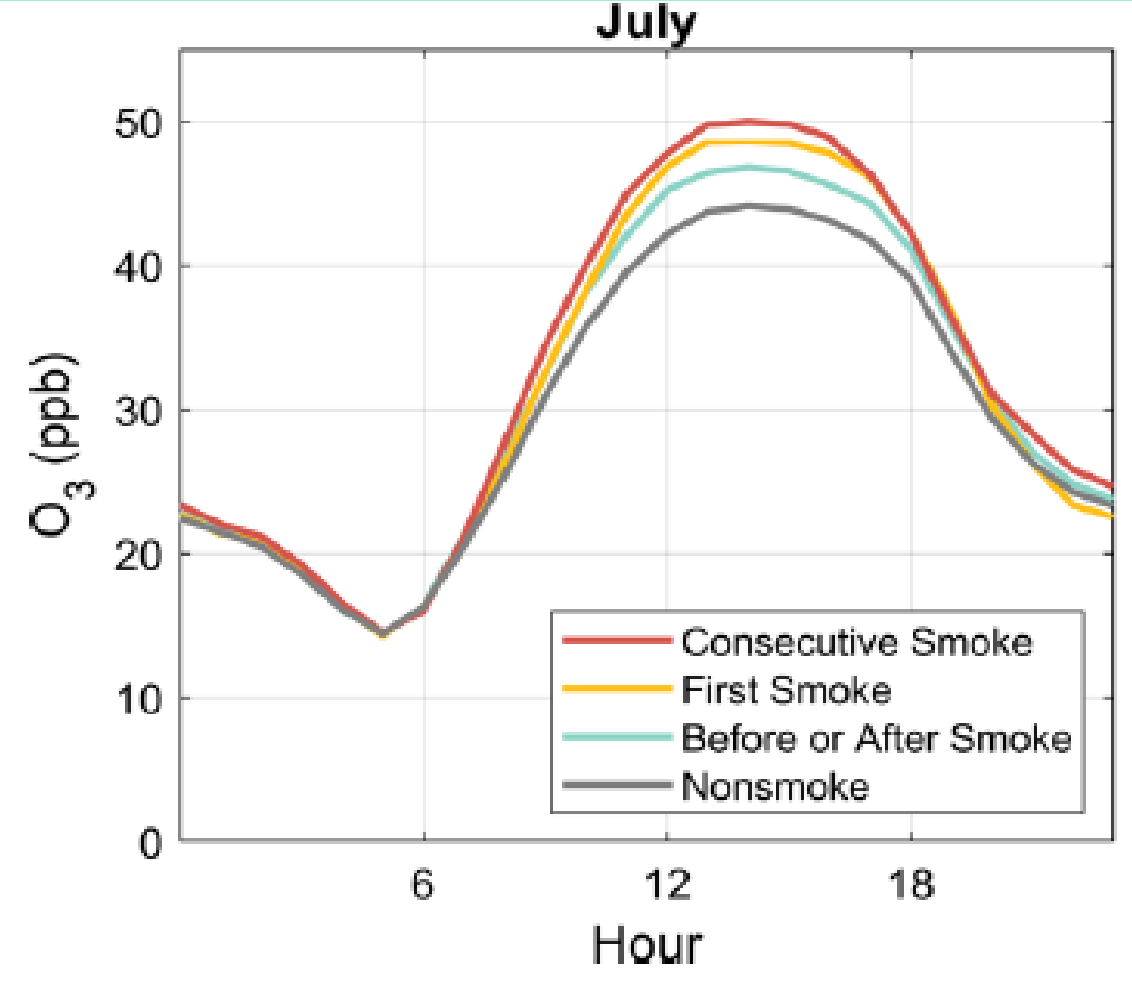
Outline for rest of this talk

- What do the observations show?
- What can we learn from machine learning/statistical modeling?
- What can we learn from photochemical modeling?
- Evidence for/against instrumental bias.
- How to identify smoke in urban areas?

What do observations show about smoke and O_3?

- O_3 is enhanced during smoke by photochemistry and is not correlated with $PM_{2.5}$ (Buysse et al 2019).
- Very high $PM_{2.5}$ (>100 ug/m3) *usually*, not associated with high O_3 (Buysee et al 2019);
- Smoke in urban areas leads to significant increase in VOCs (Ninneman and Jaffe 2021)
- Smoke in urban area usually lead to small or insignificant enhancements in NOx (Buysee et al 2019; McClure and Jaffe 2018; Laing et al 2017).
- Smoke days and high smoke seasons can be warmer, but this appears to be a small factor in explaining enhanced O_3 (Jaffe 2020; Jaffe et al 2021).



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How to quantify the O_3 in an urban area due to smoke? Use machine learning to predict MDA8 O_3 w/wo smoke.

- **Generalized Additive Modeling (GAM), is a type of machine learning that uses a training dataset to identify patterns and relationships. This approach can incorporate linear, non-linear and categorical relationships.**

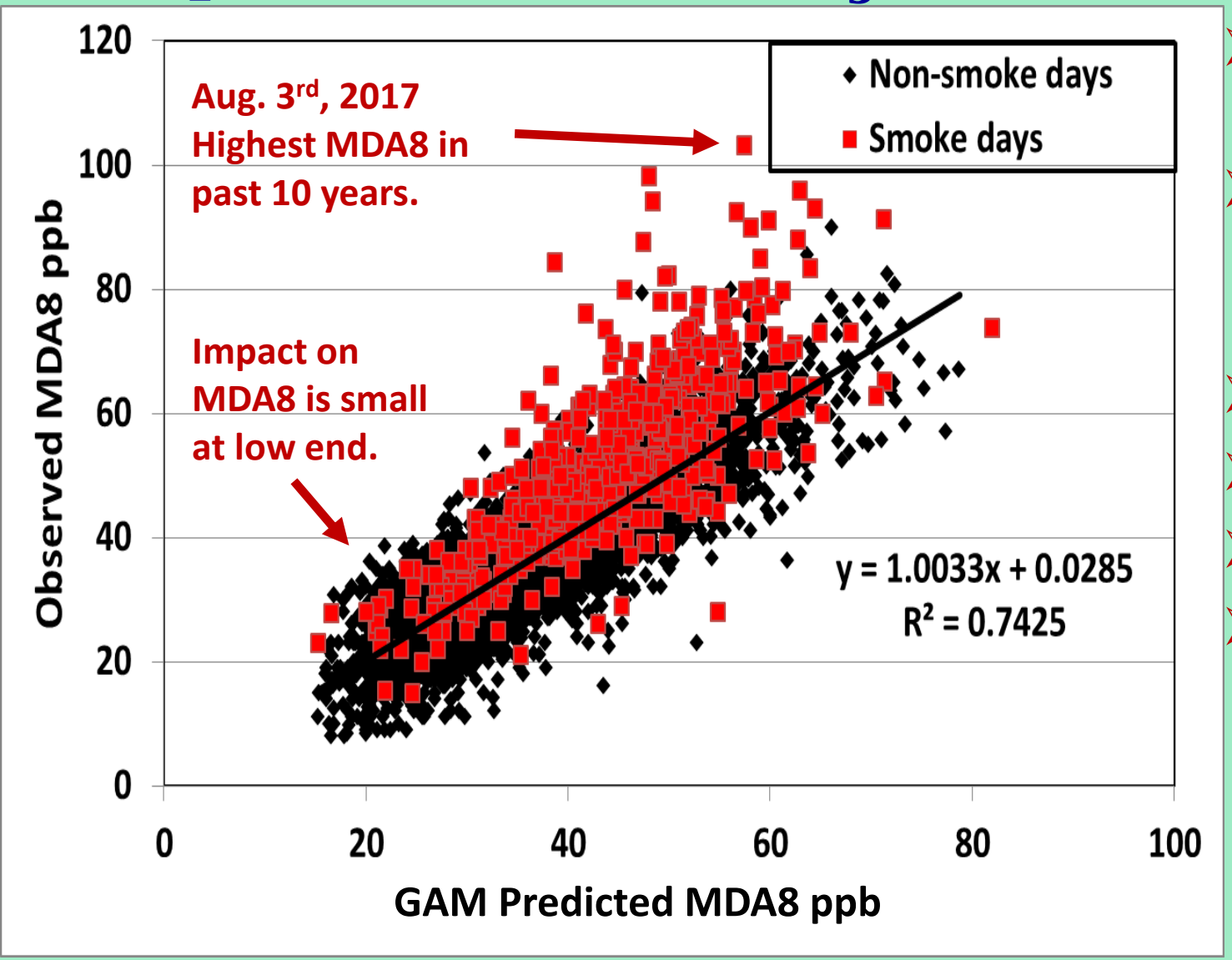
$$g(O_{3i}) = f_1(temp_i) + f_2(WS_i) + f_3(WD_i) + \ldots + residual_i$$

Where f_1, f_2, etc from spline fits to the obs. "*i*" refers to daily obs.

- **Typical predictors are daily max temp, ws, wd, trajectory distance, RH, geopotential height, etc.**
- **Various steps for model QC, including cross-validation with data that was not part of training dataset.**
- **<u>Smoke is not include in the model, so we attribute difference between modeled and predicted to smoke influence.</u>**

Camalier et al 2007; CARB 2011; Sun et al 2015; Gong et al 2017; 2018; McClure and Jaffe 2018; Jaffe et al 2018; 2021.

Impact of smoke on O_3 for 5 sites in PNW: 2007-2017 data



- Smoke only adds O_3 on warm, photochemically active days.
- This suggest that enhanced O_3 is largely driven by enhanced in-situ photochem, not O_3 transported in.
- Residual = Observed – GAM predicted
- Mean residual (non-smoke) = 0 ± 4.8
- Mean residual (smoke days) = 7.5 ± 2.9
- Results on individual days can support EE documentation.

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Selected applications of GAM by our group

City	Results
Houston, TX	Mean O_3 res. 3-5 ppb for smoke days
Enumclaw, WA	Mean O_3 res. 7.1 ppb for smoke days
Denver, CO	Mean O_3 res. 4.3 ppb for smoke days
Portland, OR	Mean O_3 res. 6.6 ppb for smoke days
El Paso, TX	Supported EE demonstration, approved by EPA.
Baton Rouge, TX	Supported EE demonstration, approved by EPA.
Beijing and 11 other cities in China	Used GAM to show impact of short term emission reductions

Gong et al 2017; 2018 McClure et al 2018; Jaffe et al 2018; Gao et al 2019.

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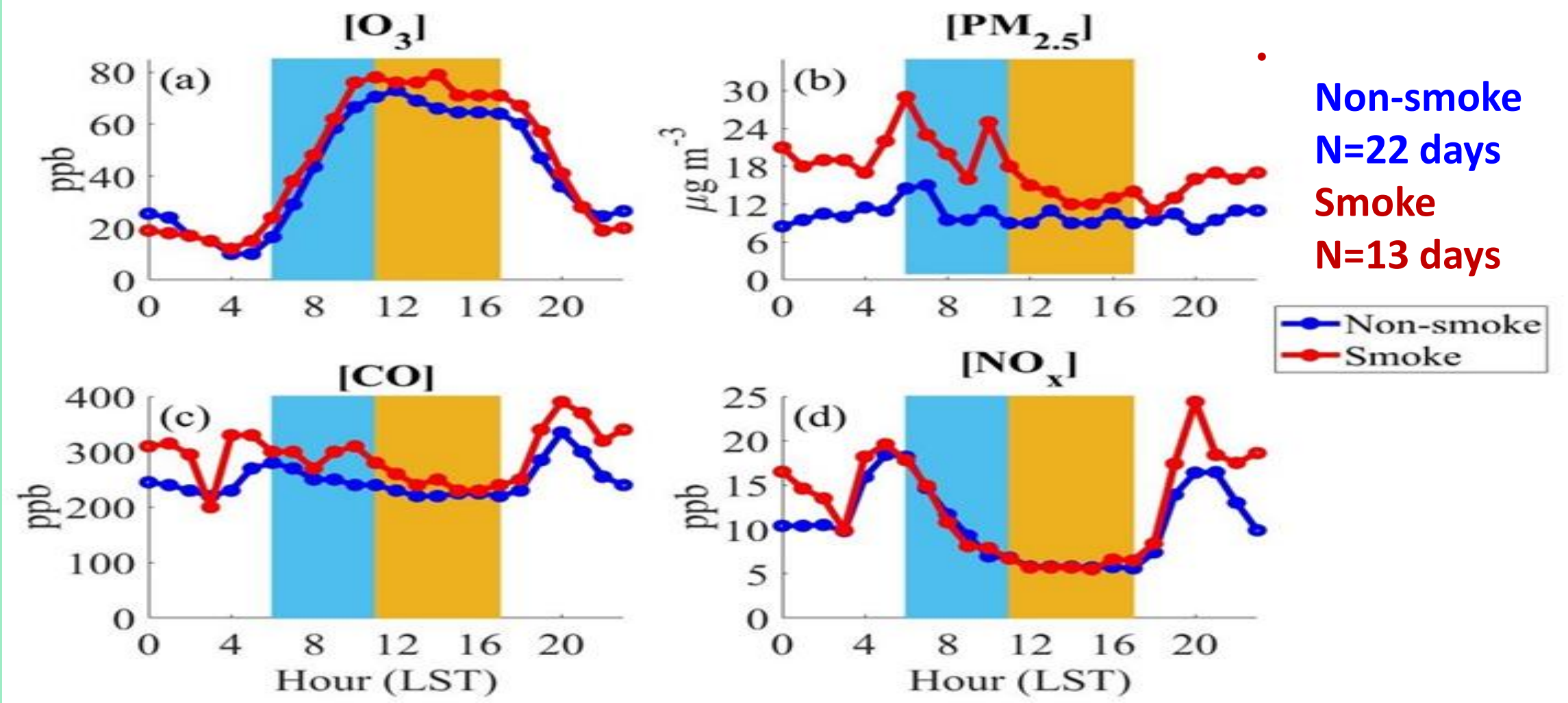
Photochemical models and smoke

- Because of complexities in emissions and chemistry, it is very difficult to model O_3 formation with typical gridded models. Keep in mind that smoke contains over 500 VOCs and this is likely key to driving photochemistry.
- We have been reasonably successful using the FOAM box model for Bakersfield, CA where urban concentrations were constrained by observations, including obs of ~40 individual VOCs.

Observed concentrations smoke vs non-smoke, Bakersfield CA



Non-smoke
N=22 days
Smoke
N=13 days

Ninneman and Jaffe, Atmos. Envir, In-review

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Obs Bakersfield CA (July + Aug 2018)

Type of day	N_{days}	Median $[O_3]$ (ppb)	Median $[PM_{2.5}]$ ($\mu g\ m^{-3}$)	Median $[NO_x]$ (ppb)	Median [CO] (ppb)	Median ∑VOCs (ppb)
Smoke	13	69.0	17.5	6.7	280.0	29.4
Non-smoke	20	61.0	10.0	6.3	240.0	19.2

- Given insignificant enhancements in NOx, we hypothesize that the additional O_3 production is driven by VOCs in smoke.
- Model was constrained by observed concs of 40 individual VOC species.

Ninneman and Jaffe, Atmos. Envir, In-review

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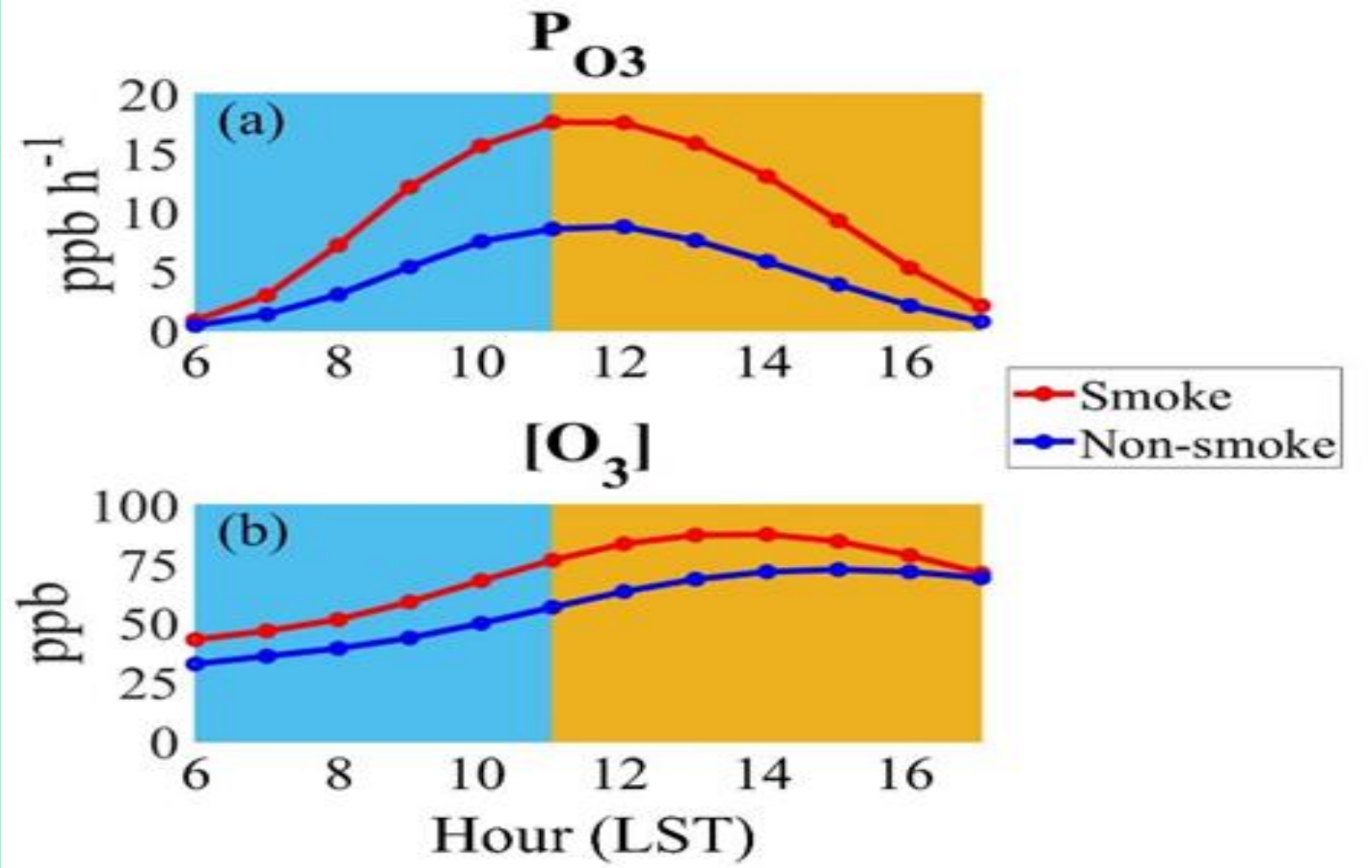
Ozone production in smoke and non-smoke



- **Based on this work, it appears that the additional VOCs in smoke drive the enhanced O_3 production.**

Ninneman and Jaffe, Atmos. Envir, In-review

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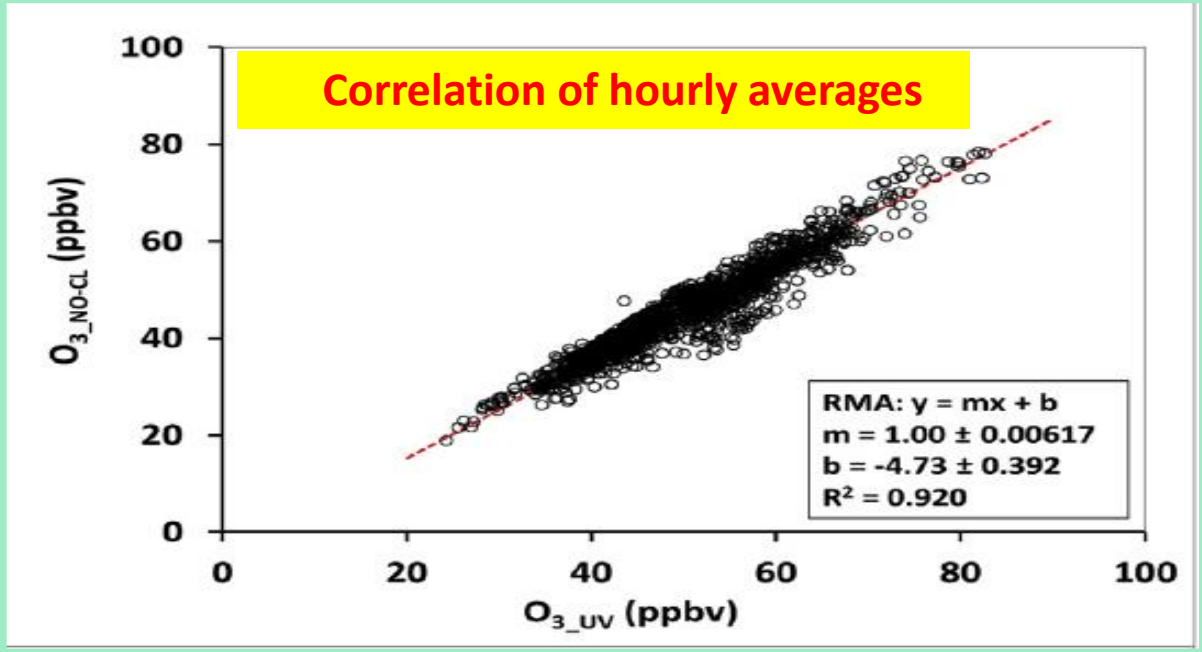
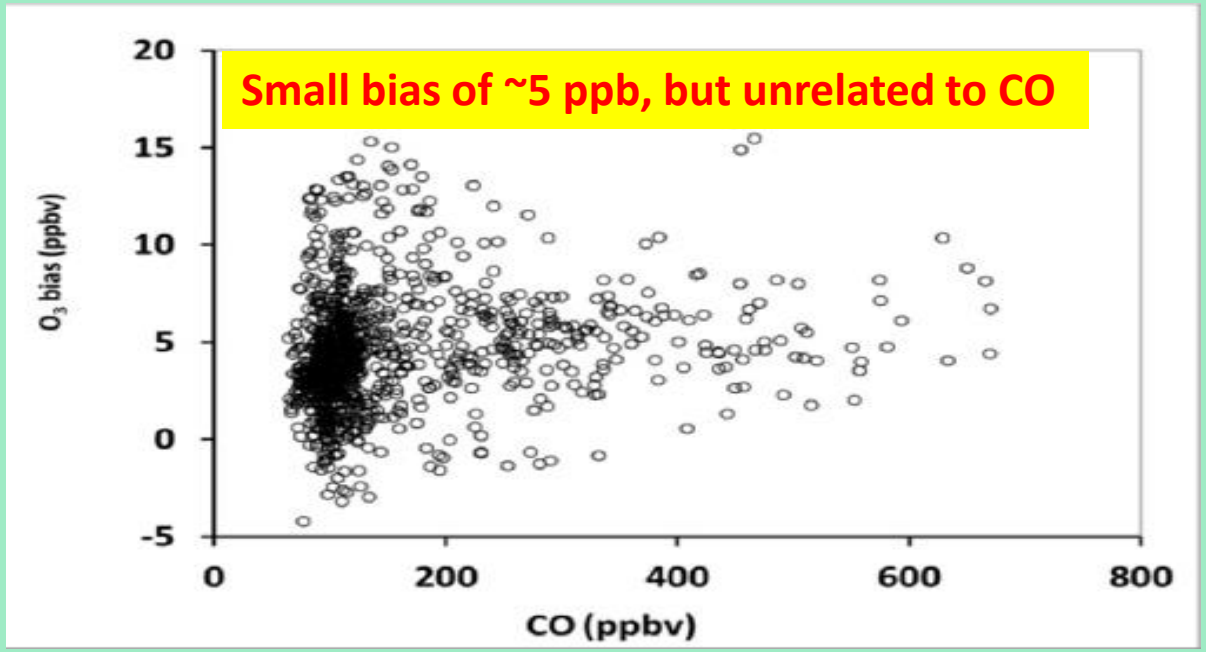
Evidence for bias in UV observations?





- Some studies have showed bias in lab fresh and/or heavy smoke plumes (e.g. Long et al 2021).
- We compared UV and chemil O_3 instruments at Mt. Bachelor in aged smoke plumes and found no evidence for bias between measurements in smoke up to 800 ppb of CO and 100 ppb of O_3 (Gao and Jaffe 2017- Atmos. Envir)
- This could be explained by different composition and concentration between aged and fresh plumes.
- The fact that O_3 peaks in midday and is uncorrelated with CO or PM in urban areas argues against a significant bias in smoke plumes.

Gao H. and Jaffe D.A., Comparison of ultraviolet absorbance and NO-chemiluminescence for ozone measurement in wildfire plumes at the Mount Bachelor Observatory. Atmospheric Environment 166, 224–233, doi: 10.1016/j.atmosenv.2017.07.007, 2017.

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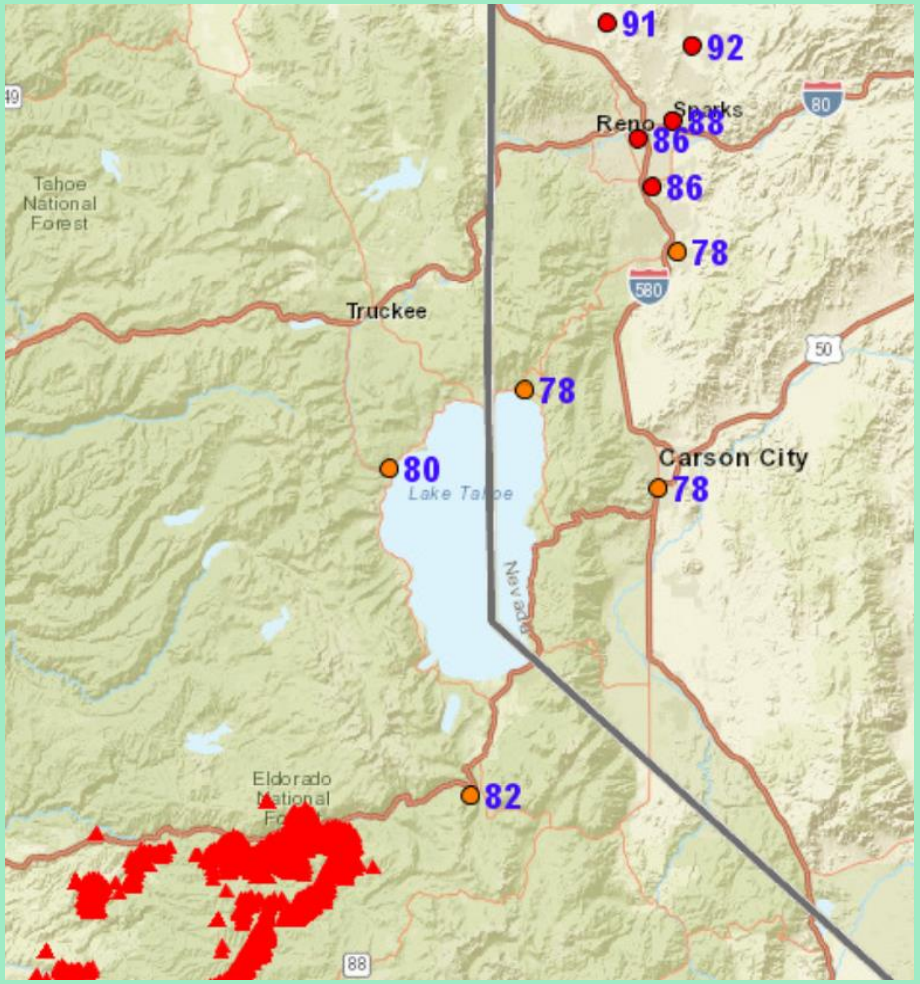
How to identify smoke in urban area?

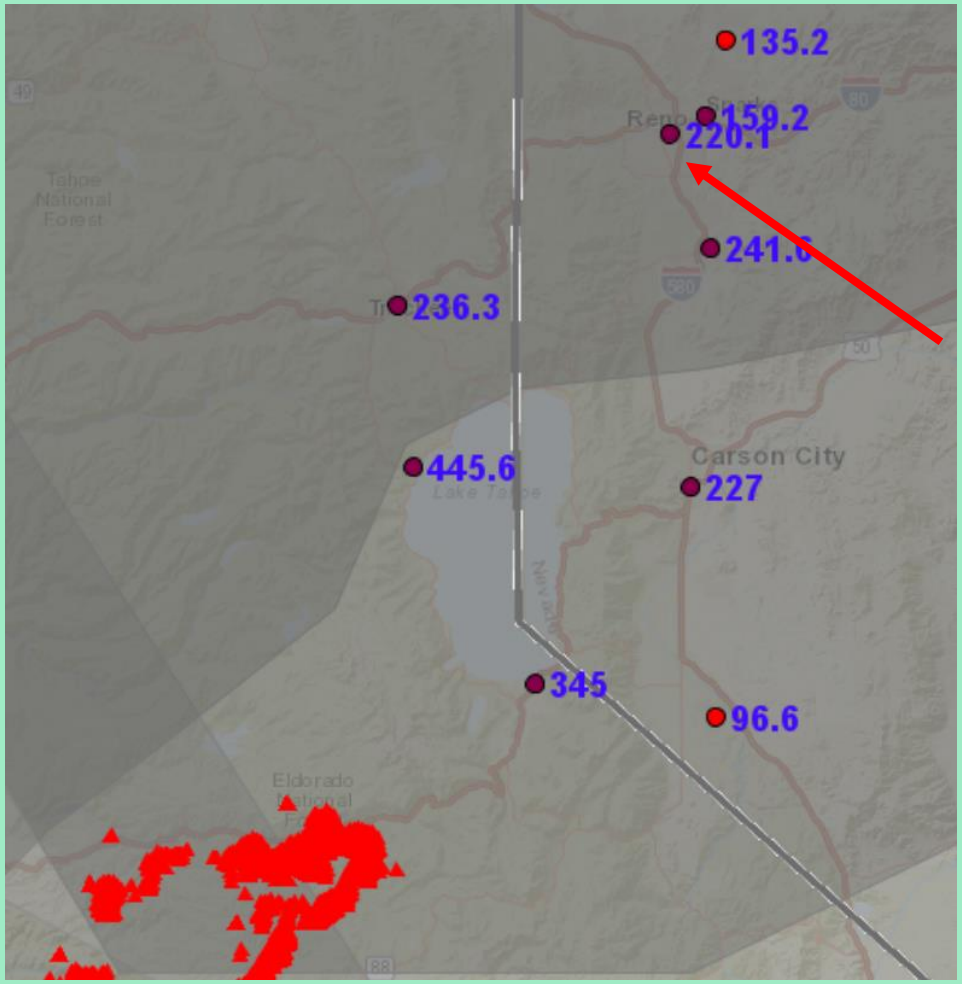
- Observations suggest we are trying to identify "smoke" in urban areas when $PM_{2.5}$ is between 10-100 ug/m^3. Hardest at low concentrations of $PM_{2.5}$.
- Best case scenario: Observations of specific smoke tracers (e.g. acetonitrile, acetone, levoglucosan, organic C, Oxygenated VOCs).
- Some ratios can be good indicator of smoke:
  - **$OC/PM_{2.5}$ should be a good indicator due to high OC fraction in smoke.**
  - **$\Delta PM_{2.5}/\Delta CO$ ratio can also indicate smoke. Laing et al 2017 reports a ratio of 0.128 ± .06 (ug/m3 per ppb) for smoke events, compared to 0.037 ± .014 for non-smoke urban data.**
- Satellite data can indicate transport and source region, but do not indicate surface impacts.

Laing J.R., Jaffe D.A., Slavens A.P., Li W., and Wang W. Can ΔPM2.5/ΔCO and ΔNOy/ΔCO Enhancement Ratios Be Used to Characterize the Influence of Wildfire Smoke in Urban Areas? Aerosol and Air Quality Research, Vol 16, 3075-3087, doi:10.4209/aaqr.2017.02.0069, 2017.

Reno O_3 and the Caldor fire, 8/23/2021



MDA8 O3, ppb



Reno4

PM2.5, ug/m3 (daily)

For reference, max temp in Reno on 8/23/2021 was 30° C.

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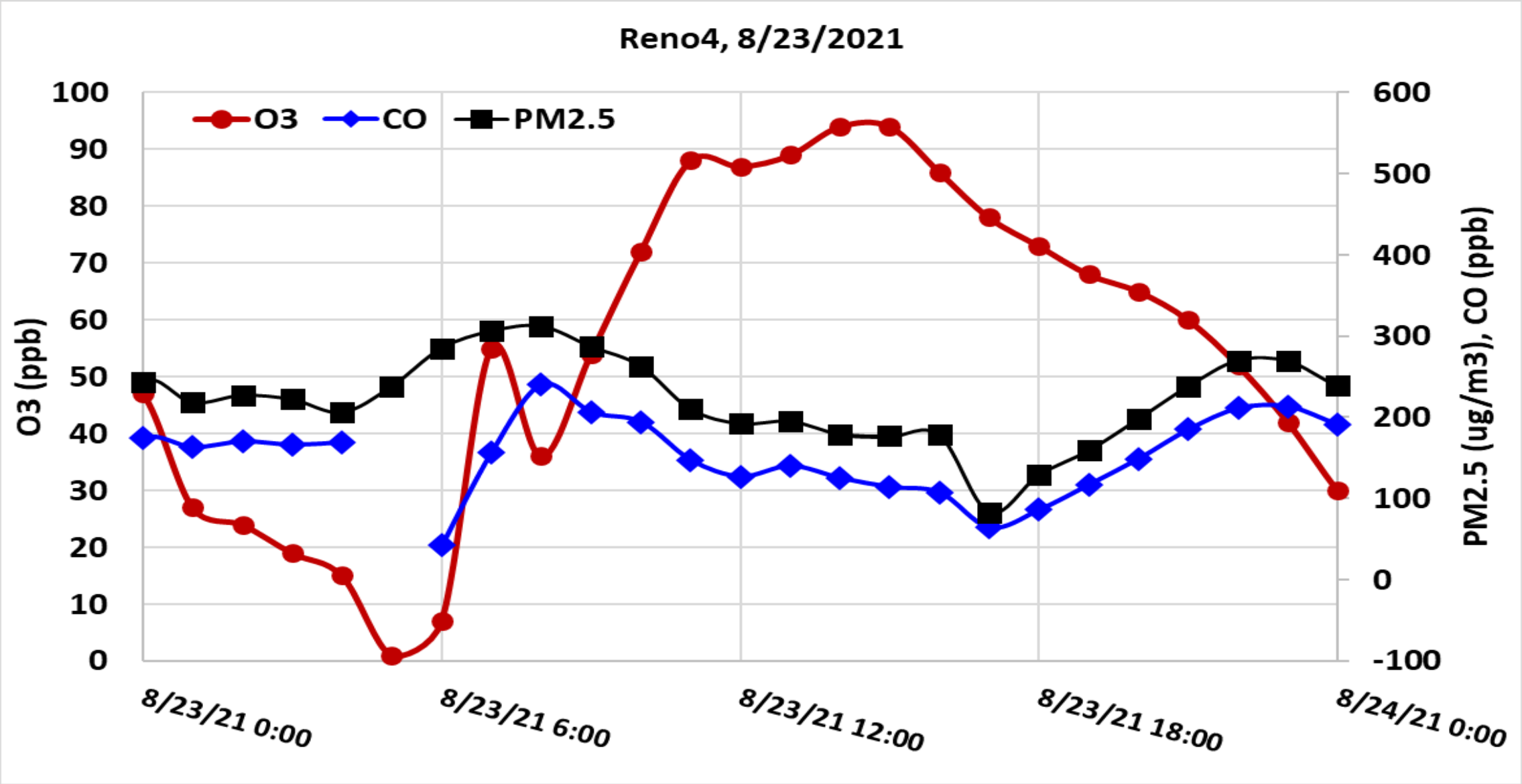

MDA8 = 86 ppb

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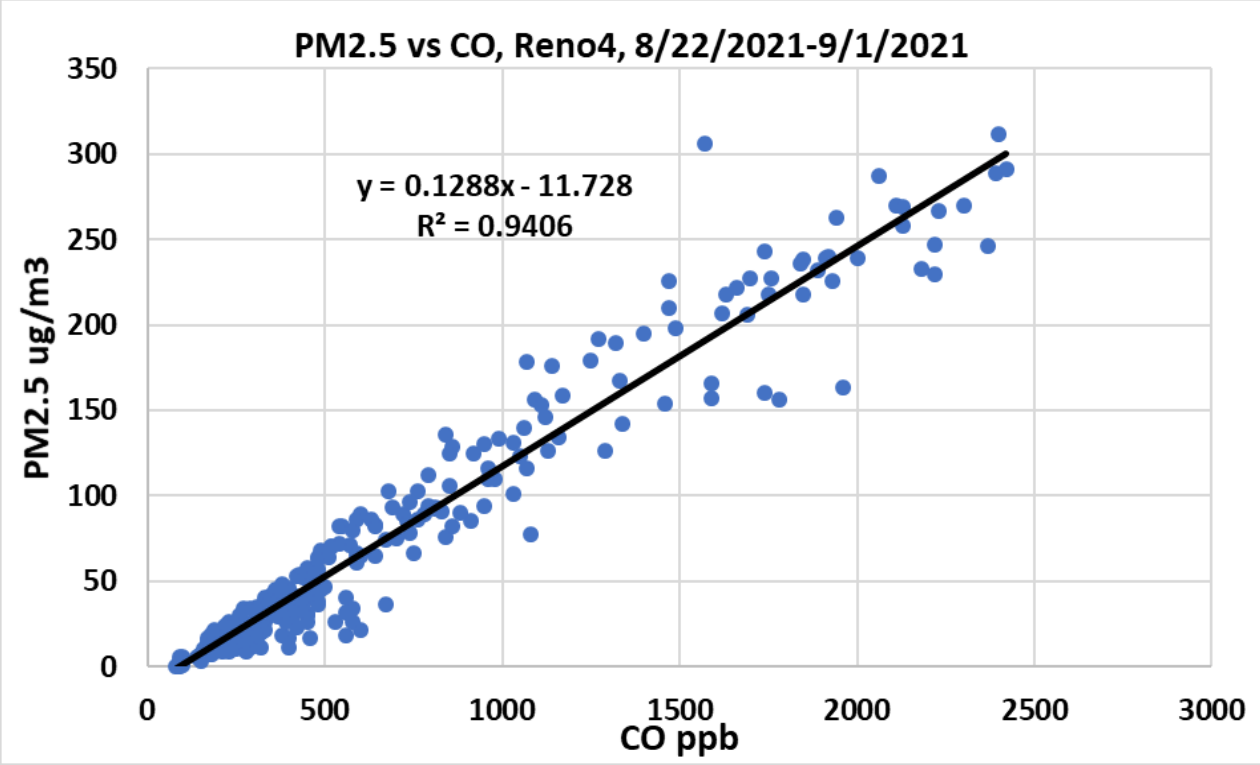
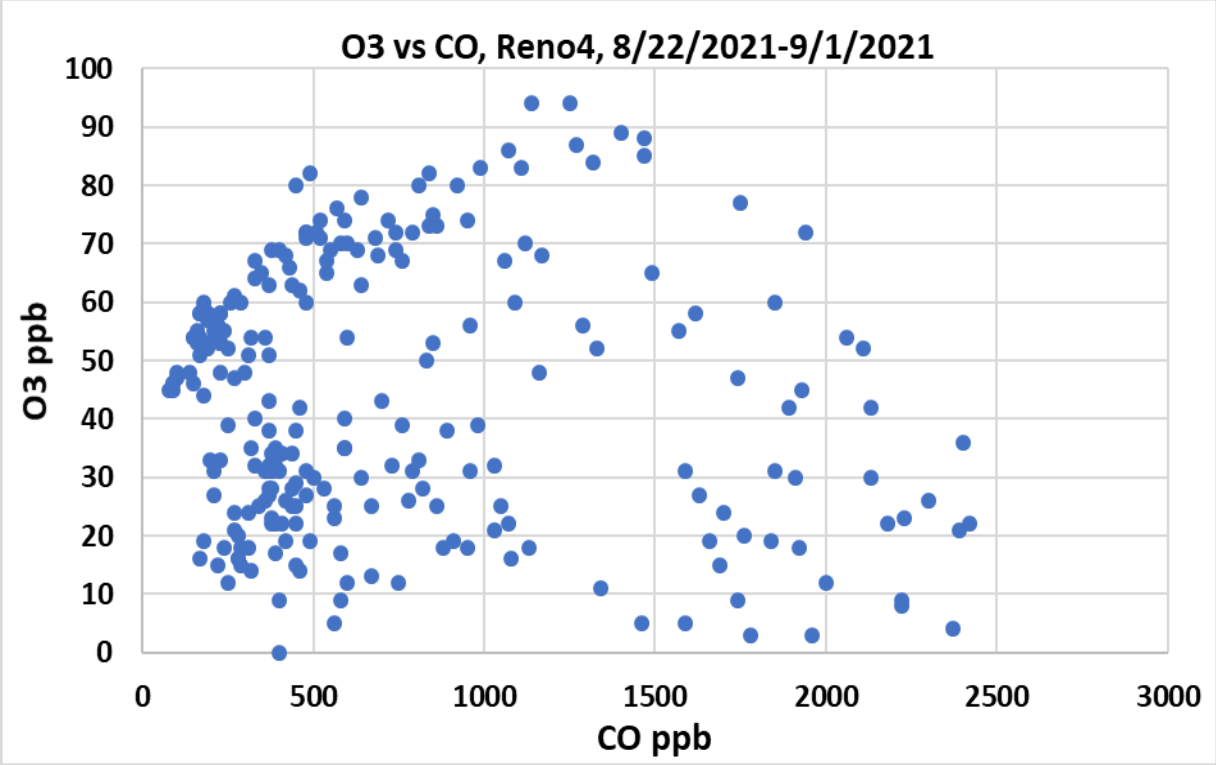
Reno4, hourly data, 8/22/2021-9/1/2021





- **Laing et al 2017 reports a ratio of 0.128 ± .06 ug/m3 per ppb for 25 smoke events, compared to 0.037 ± .014 for non-smoke urban data.**

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Summary: Implications of smoke on O_3 in urban areas

- Smoke intrusion in urban areas adds 0-30 ppb to the MDA8, with a large degree of variability.
- During smoke events, O_3 diurnal cycle is same as usual (peak in afternoon), but with faster production during daytime. Additional O_3 appears to be mostly driven by higher VOCs and photochemistry.
- For many sites, smoke days have slightly higher temps than non-smoke days. I calculate that ~25% of the extra O_3 is due to higher temps and ~75% due to enhanced photochemistry (based on the O_3–temp relationship).
- Possible bias in UV instruments in fresh or heavy smoke (Long et al 2021).
- No evidence for UV instrumental bias in aged smoke compared to chemiluminescent method (up to ~800 ppb CO). This is supported by both direct comparisons (Gao and Jaffe 2017) and non-existent relationship between O_3 and $PM_{2.5}$ in ambient data during smoke events.
- Statistical modeling and photochemical box models can help support exceptional event documentation by quantifying the O_3 that would be expected in the absence of smoke.
- Given the large number of EE cases that are likely in 2020 and 2021, how can EE documentation be simplified and/or workload shared by multiple agencies?

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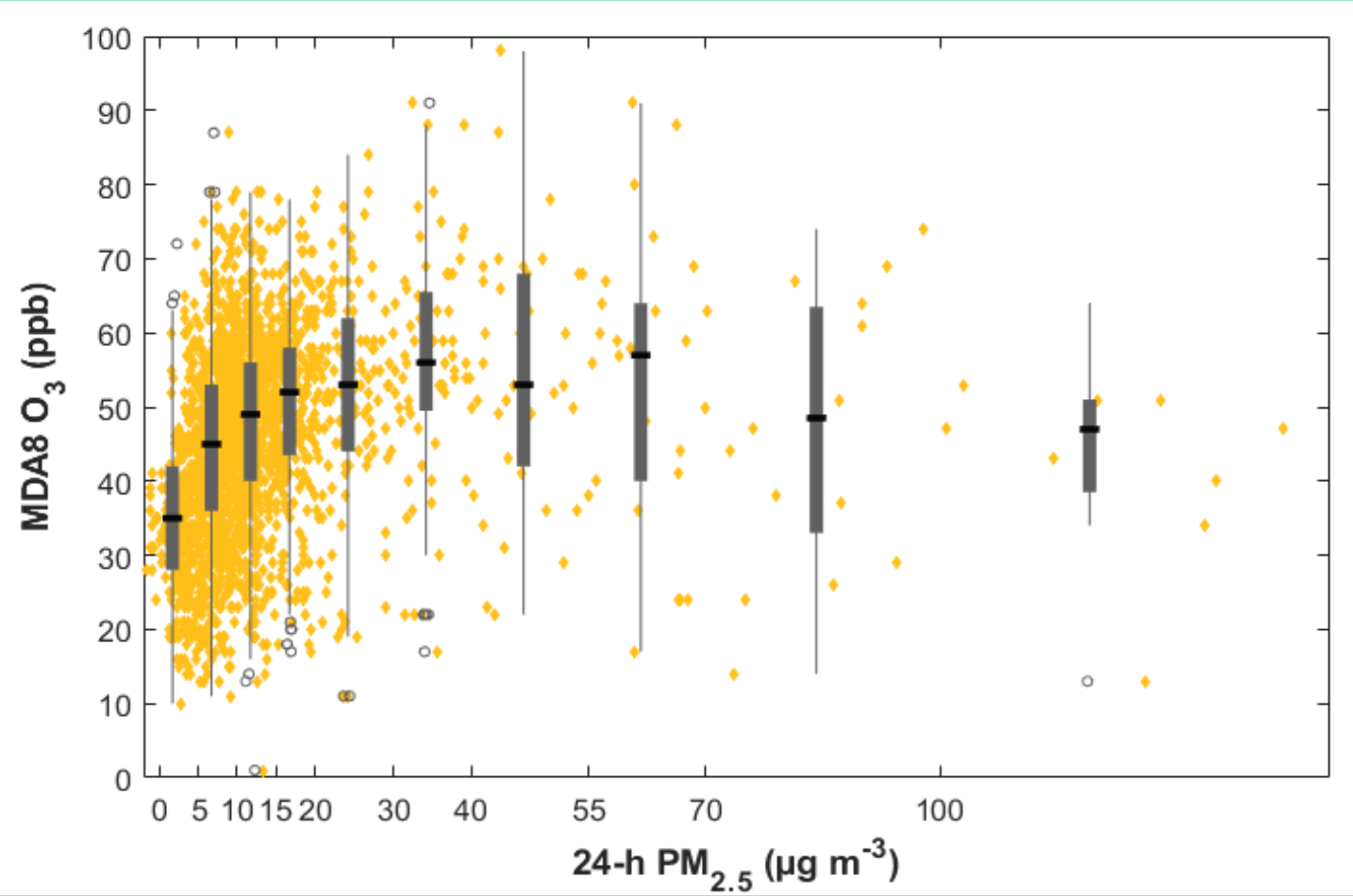
Spares

Very high $PM_{2.5}$ does not lead to high O_3 in smoke



Buysse et al 2019.

- Role of transport time and PM levels (McClure et al 2018; Buysse et al 2019); Role of UV Photolysis (Baylon et al 2018; Alvarado et al 2015).
- Role of Temperature (Gao et al 2020).
- Use of machine learning to predict O_3 MDA8 in smoke (Gong et al 2017; Gao et al 2020)

- Why not high O_3 at high $PM_{2.5}$?

Heterogenous chemistry?

Reduction in photolysis?

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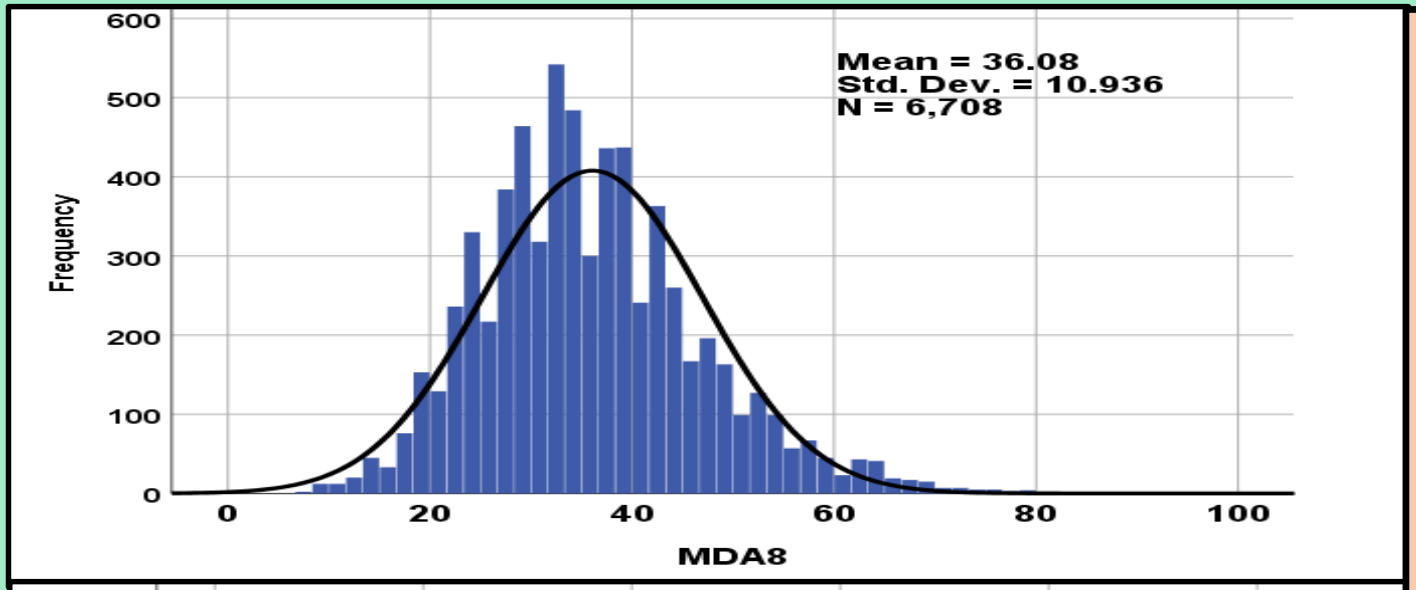
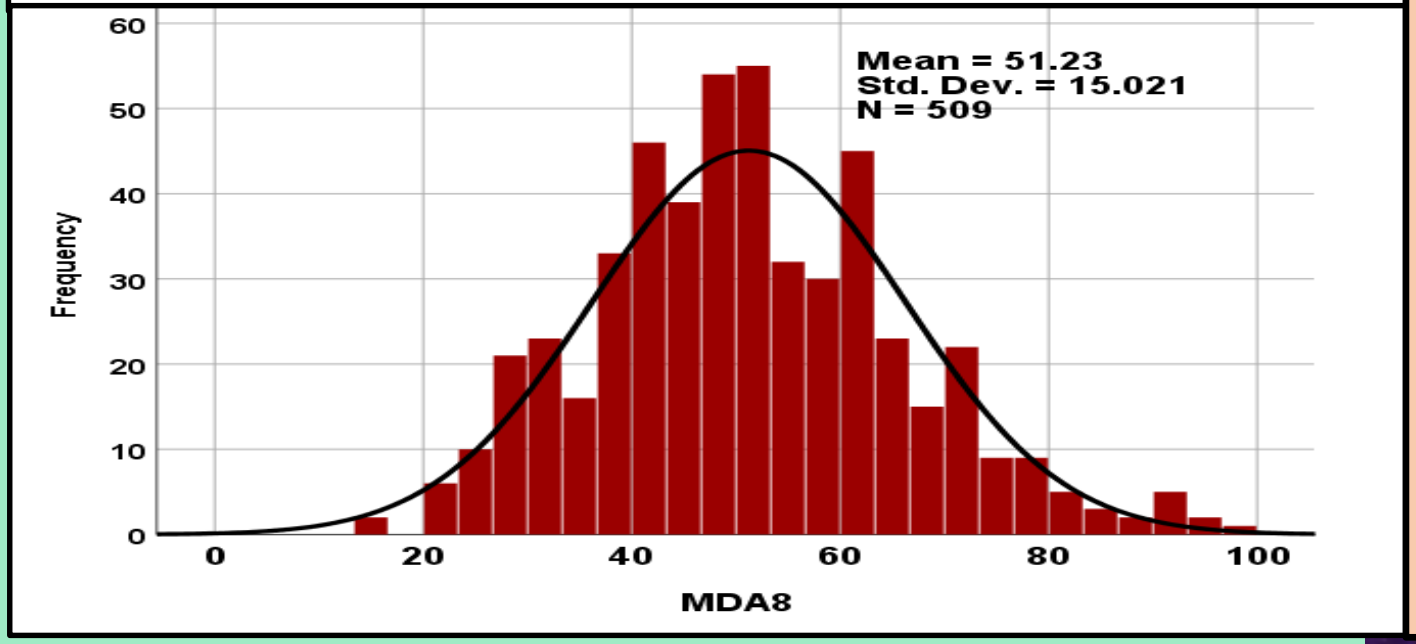
Max daily 8-hour O_3 in and out of smoke for 5 cities in the PNW: May-Sept. 2007-2017.





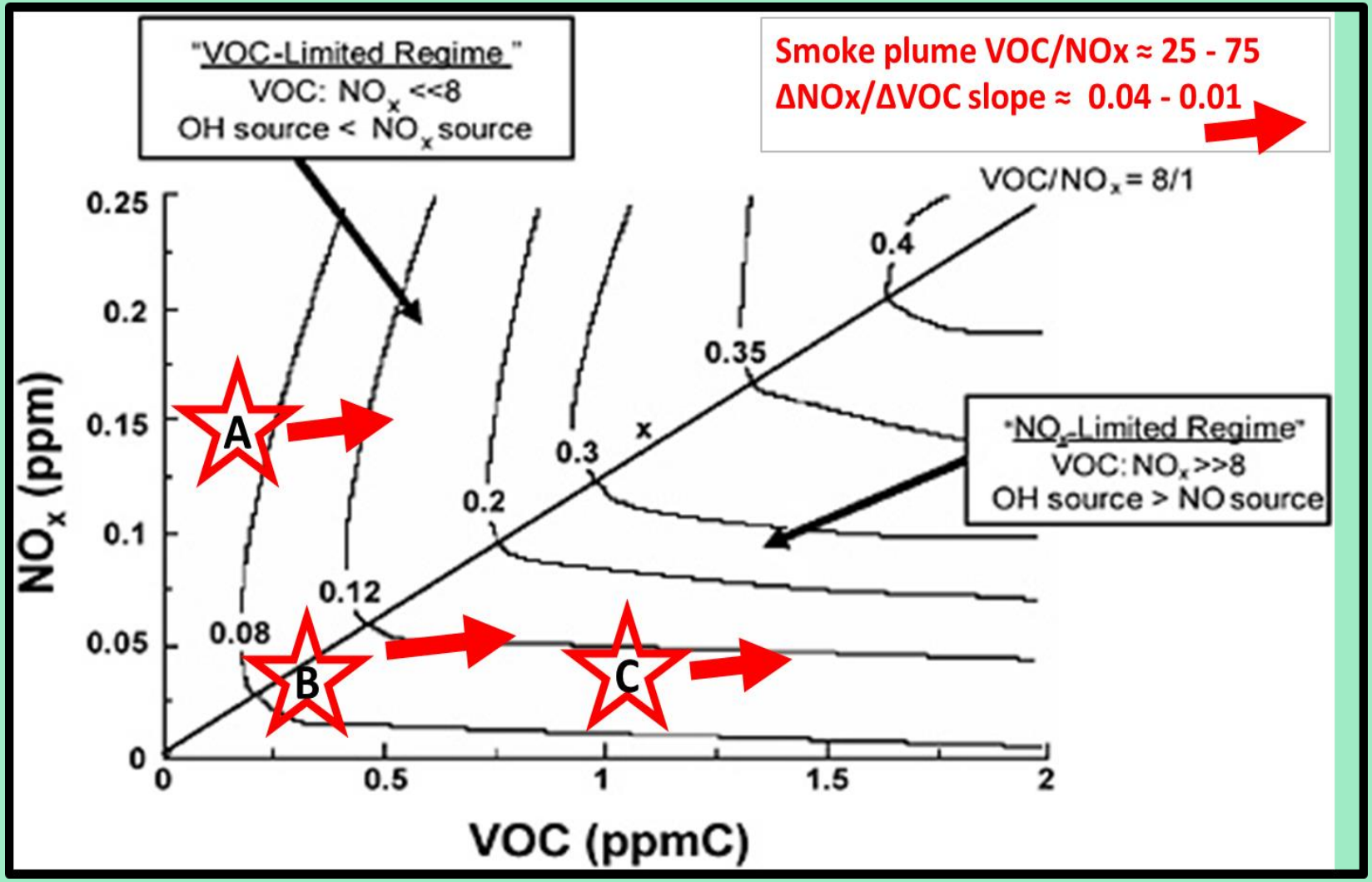
No smoke days:

- Average MDA8 = 36 ppb
- Fraction of days that have MDA8 g.t. 70 ppb = 0.4%

Smoke days:

- Average MDA8 = 51 ppb.
- Fraction of days that have MDA8 g.t. 70 ppb = 10.1%.
- Smoke days are 40% of all days with MDA8>70
- Using a machine learning algorithm, we find that smoke contributes about 8 ppb, on average, to the MDA8, but with lots of variability (Jaffe et al 2021).

Smoke can impact differently in different regions due to local VOCs and NOx regime



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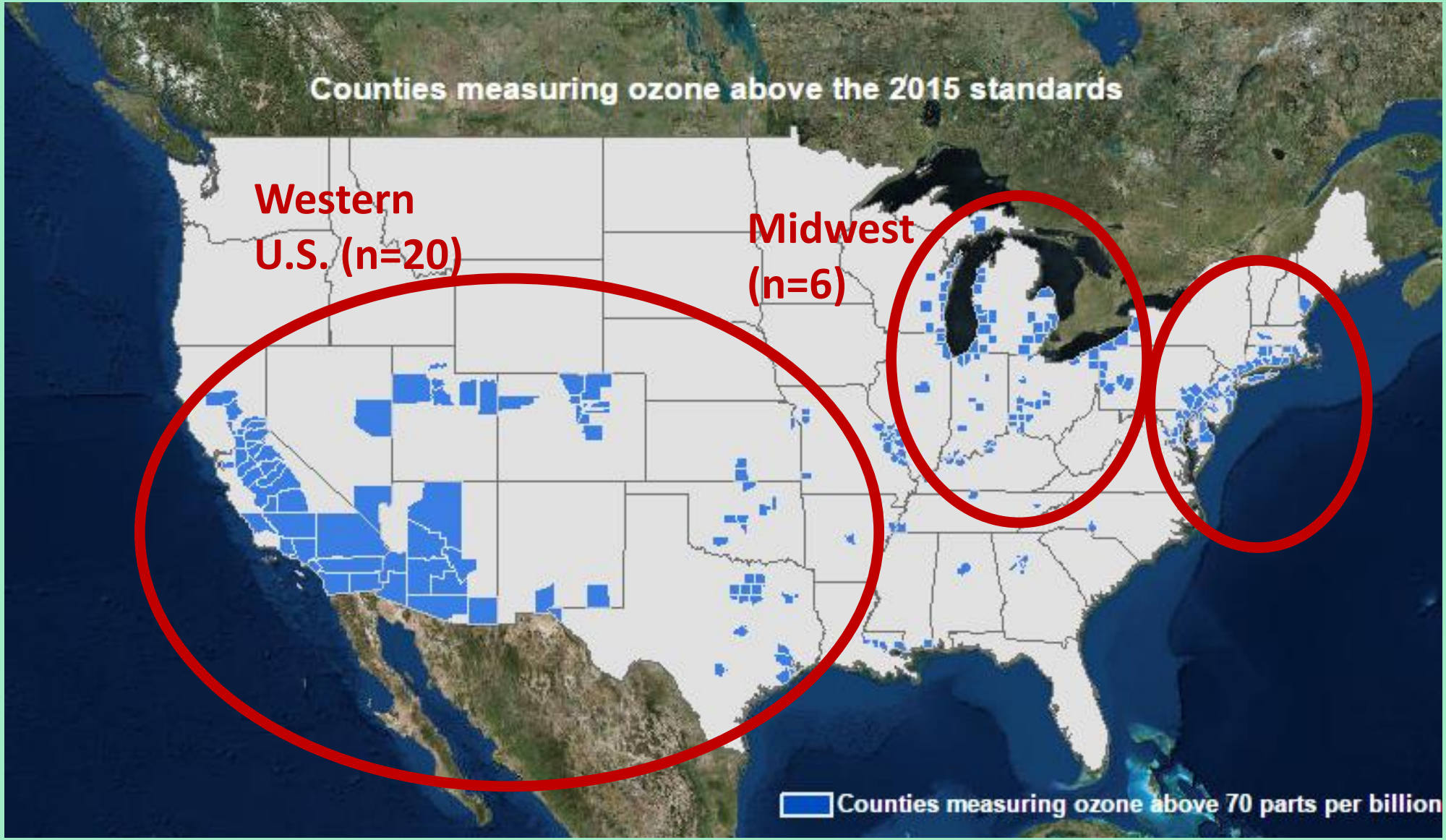
>130 million people are exposed to unhealthy levels of O_3



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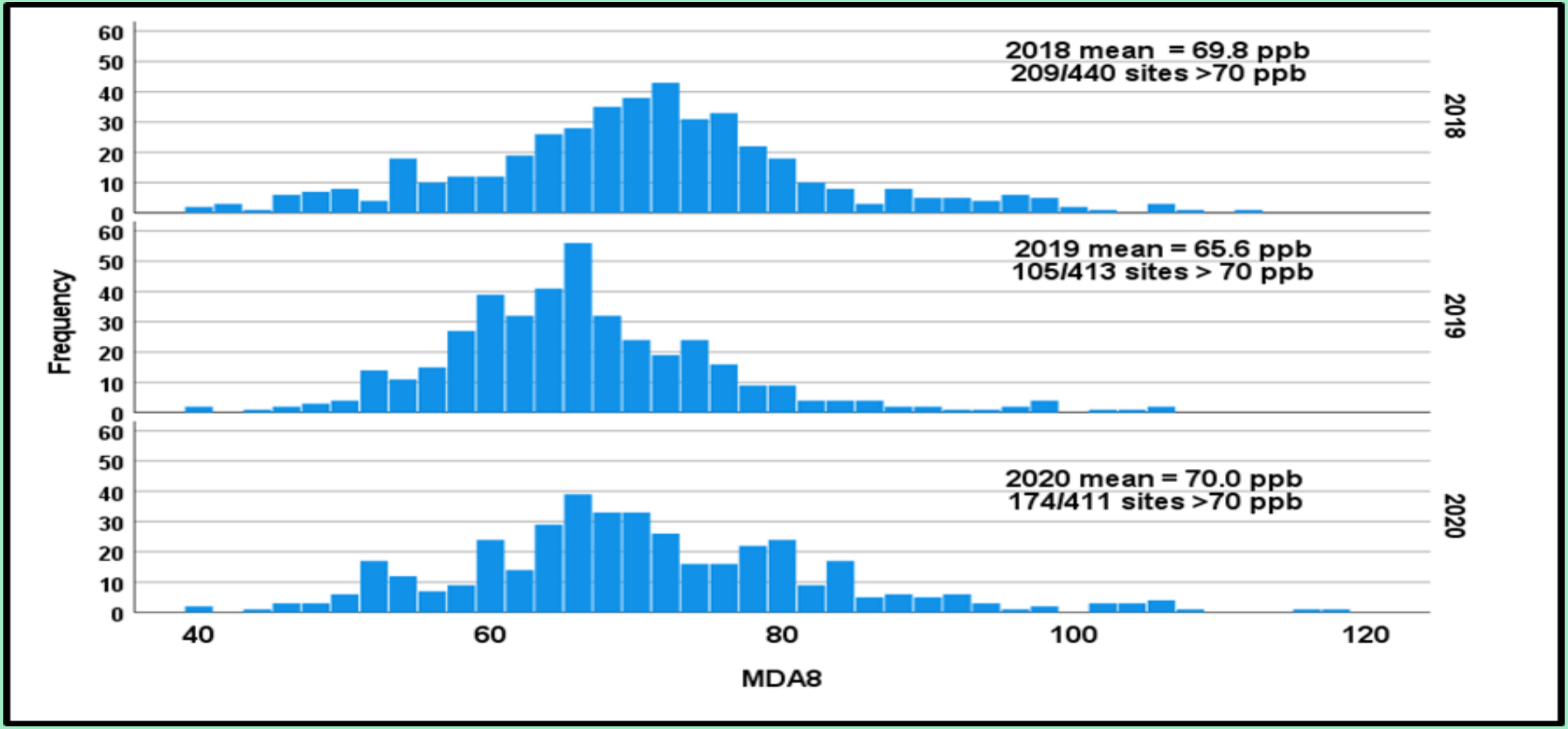
Distribution of fourth highest MDA8, 2018-2020



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