Identification of Ozone Sources in the Western US
Dan Jaffe, University of Washington

Mt. Bachelor Oregon
2.8 km or 9000' above sea level
Acknowledgements
The Challenge:
New O$_3$ Standard in Light of Increasing Background

- Most urban areas in the West have made substantial progress in reducing peak O$_3$ mixing ratios.
- But the new O$_3$ standard presents our greatest challenge yet.
- Springtime background O$_3$ is increasing;
- Wildfires are increasing.
  - Need to improve our understanding of O$_3$ sources.
  - Need to improve our methods to document which O$_3$ is controllable, and which is not, on a day-to-day basis.
Los Angeles, Max Daily 8-hour Average O₃

AQS site # 06-037-0002
## Sources of O$_3$ in the Western US

<table>
<thead>
<tr>
<th><strong>O$_3$ Source</strong></th>
<th><strong>Meteorological Characteristics</strong></th>
<th><strong>Chemical characteristics</strong></th>
<th><strong>Controllable</strong></th>
</tr>
</thead>
<tbody>
<tr>
<td>Local photochemical buildup</td>
<td>Stagnation, high temps.</td>
<td>CO/NOx/VOCs/PM consistent with local sources</td>
<td>Y</td>
</tr>
<tr>
<td>Regional transport (domestic sources)</td>
<td>Regional transport from major source regions (eg Calif) *Currently not well characterized</td>
<td>CO/NOy/VOCs consistent with upwind sources+chemistry</td>
<td>Y</td>
</tr>
<tr>
<td>Upper trop/Lower strat intrusions (UTLS)</td>
<td>Post-cold front Broad spatial distribution (high O$_3$ in non-urban areas)</td>
<td>Very dry air.</td>
<td>N</td>
</tr>
<tr>
<td>Very long-range transport (VLRT)</td>
<td>Important at higher elevation. Subsidence and mixing into the boundary layer can enhance local concentrations.</td>
<td>Dry. Can be hard to distinguish from UTLS without good chemical data.</td>
<td>N</td>
</tr>
<tr>
<td>Wildfire smoke</td>
<td>Warm. Can be stagnant or not. Can be regional or large distant fires.</td>
<td>Chemistry complex and diff from typical urban. O$_3$ enhancements not always seen. O$_3$-PM often poorly correlated. PM/CO/NOy always well correlated and ratios very diff from typ urban.</td>
<td>N</td>
</tr>
</tbody>
</table>
How to id sources of $O_3$ ?

- **Observations:**
  - Spatial relationships;
  - Tracer ratios;
  - Meteorology/trajectories;
  - Satellite observations.

- **Modeling:**
  - Regional Eulerien modeling;
  - Source apportionment modeling (e.g. WRAP-DEASCO3);
  - Statistical modeling.
Mt. Bachelor, Oregon, (MBO) 2.8 km asl

- The only high elevation/free trop research site on west coast of U.S.
- Continuous observations of CO, O$_3$, aerosols and Hg since 2004;
- Frequent detection of Asian pollution and biomass burning plumes;
- More than 2 dozen papers since 2004 on O$_3$, PM, Hg, LRT, wildfires, etc.

**Key goal:** Identify importance of global sources on US air quality.
Diurnal circulation pattern at Mt. Bachelor

Day: upslope flow brings modified BL air to summit. This air is wet and usually low in O$_3$.

Night: downslope flows brings Free Tropospheric (FT) air to the summit. This air is dry and usually high in O$_3$.

ID of Free Tropospheric Air
- Time of day.
- Water vapor mixing ratio
- Chairlift soundings, observations of NOx (Weiss 2006, 2007; Fischer 2009; 2010; Reidmiller 2011)
Max daily 8 hour avg O$_3$ at Mt. Bachelor for 2012-2014
Latest 3-year design value = 79 ppbv
What are causes of high O$_3$ at MBO and how does this influence surface AQ?
Causes of high O$_3$ days at MBO: Strat intrusions, Asian pollution and wildfires

Causes of high O$_3$ in the lower free troposphere over the Pacific Northwest as observed at the Mt. Bachelor Observatory

J.L. Ambrose$^{a, *}$, D.R. Reidmiller$^{b, 1}$, D.A. Jaffe$^{a, b}$

Ozone enhancement in western US wildfire plumes at the Mt. Bachelor Observatory: The role of NO$_x$

P. Baylon$^{a, *}$, D.A. Jaffe$^{a, b}$, N.L. Wigder$^{a}$, H. Gao$^{b}$, J. Hee$^{b}$

Ambrose et al 2011

Baylon et al 2014
Influence of daily variations in baseline ozone on urban air quality in the United States Pacific Northwest

Nicole L. Wigder,1 Daniel A. Jaffe,1,2 Farren L. Herron-Thorpe,3 and Joseph K. Vaughan3
Modeled FT O$_3$ tracer for 4/6/2010 (high O$_3$ day) using CMAQ w/12 km grid

Vertical cross-section

Surface mixing ratio

Wigder et al 2013
Springtime $O_3$ trend at MBO: Gratz et al, 2014

Causes of increasing ozone and decreasing carbon monoxide in springtime at the Mt. Bachelor Observatory from 2004 to 2013

L.E. Gratz $^a$, *, D.A. Jaffe $^a$, $^b$, J.R. Hee $^a$
Changes in Spring $O_3$ at MBO

This is likely due to the build up of Asian emissions (Gratz et al 2014).
Changes in Spring $O_3$ at MBO

This is likely due to the build up of Asian emissions (Gratz et al 2014).
Was high O₃ seen in 2012 at surface monitoring sites?
Importance of spatial correlation in Western US

Selected $O_3$ monitoring sites
<table>
<thead>
<tr>
<th>Location</th>
<th>May 2012 Relative to May 2010-2014 (MDA8, ppbv)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Great Basin NV (2.1 km)</td>
<td>+ 6.1</td>
</tr>
<tr>
<td>Mt Bachelor OR (2.8 km)</td>
<td>+ 5.4</td>
</tr>
<tr>
<td>Boise ID MSA (0.8 km)</td>
<td>+ 4.0</td>
</tr>
<tr>
<td>Reno-Sparks, NV (1.5 km)</td>
<td>+ 4.1</td>
</tr>
<tr>
<td>Salt Lake City, UT (1.4 km)</td>
<td>+ 7.0</td>
</tr>
<tr>
<td>Tehama Cty CA (0.6 km)</td>
<td>+ 3.1</td>
</tr>
<tr>
<td>Portland OR MSA (0.2 km)</td>
<td>+ 2.3</td>
</tr>
<tr>
<td>Lassen N.P. CA (1.8 km)</td>
<td>+ 2.1</td>
</tr>
<tr>
<td>Siskiyou Cty CA (0.8 km)</td>
<td>+ 2.2</td>
</tr>
<tr>
<td>San Joaquin Cty (0.1 km)</td>
<td>+ 5.2</td>
</tr>
</tbody>
</table>

**Higher elevation sites shows greater enhancement.**
Spatial correlation between sites in W. US, Spring 2012
Plotted with 3 day smoothing of MDA8 values

This spatial-temporal correlation tells us that on these dates, high O₃ was not locally generated.
Spatial correlation between Ozone sites in W. US, MDA8 O₃ for Spring 2012 with 3-day Smoothing

Baylon et al 2015
Wildfires

Wolverine Fire, Lake Chelan, Washington
Aug 3, 2015
The last decade has seen a significant increase in the area burned. Approx 70% of these fires are in the Western US.
### Summary of $\Delta O_3/\Delta CO$ from >100 published studies

#### Boreal/ Temperate:

<table>
<thead>
<tr>
<th>Plume Age</th>
<th>Mean $\Delta O_3/\Delta CO$ (ppbv/ppbv) (# plumes)</th>
<th>Range of $\Delta O_3/\Delta CO$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\leq 1-2$ days</td>
<td>0.018 (n=55)</td>
<td>-0.032-0.34</td>
</tr>
<tr>
<td>2-5 days</td>
<td>0.15 (n=39)</td>
<td>-0.07-0.66</td>
</tr>
<tr>
<td>$\geq 5$ days</td>
<td>0.22 (n=29)</td>
<td>-0.42-0.93</td>
</tr>
</tbody>
</table>

#### Tropics/ Subtropics:

<table>
<thead>
<tr>
<th>Plume Age</th>
<th>Mean $\Delta O_3/\Delta CO$ (ppbv/ppbv) (# plumes)</th>
<th>Range of $\Delta O_3/\Delta CO$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\leq 1-2$ days</td>
<td>0.14 (n=59)</td>
<td>-0.06-0.37</td>
</tr>
<tr>
<td>2-5 days</td>
<td>0.35 (n=13)</td>
<td>0.26-0.42</td>
</tr>
<tr>
<td>$\geq 5$ days</td>
<td>0.63 (n=18)</td>
<td>0.19-0.87</td>
</tr>
</tbody>
</table>

Wildfires can make $O_3$ very quickly

Mt. Bachelor observations of the Pole Creek Fire on three successive days. $O_3$ production of 20-50 ppbv in 6 hours. Many other examples of fast $O_3$ production in lit.
Wildfires are responsible for year to year variation in frequency of high O₃ days.
R values between 0.58 and 0.86 for these. Wildfires are partly responsible for year to year variation in frequency of high O$_3$ days (Jaffe et al 2013).
More tools
Observations

- Observations of key tracers and meteorology are critical to understand causes for high $O_3$ days;
- Tracer ratios provide more information than one pollutant alone;
- Most agencies follow EPA specs for $O_3$ and $PM_{2.5}$ and these are done reasonably well;
- Not all regulatory sites have meteorology (!);
- At minimum, need good quality measurements of CO and NOx.
- VOCs and speciated PM are also highly desirable.
- A specific tracer of fires (such as CH$_3$CN) is also very useful.

- Shameless self promotion... my group is working on a simple, transportable “suitcase” method to measure CH$_3$CN.
PM2.5-CO relationship in smoke at some NCORE sites, hourly data


Smoke plume observations at the Mt. Bachelor Observatory, Sept 9, 2014 using Picarro G2302

Smoke plume observations at the Mt. Bachelor Observatory, Sept 25, 2009 using Thermo 48C TLE.

Our observations show that fire plumes have $\Delta PM/\Delta CO$ ratios of 0.1-0.4 $\mu g/m^3$ per ppb.
### Fires vs typical urban emissions

<table>
<thead>
<tr>
<th></th>
<th>NOy/CO molar</th>
<th>PM2.5/CO μg/m³ per ppb</th>
</tr>
</thead>
<tbody>
<tr>
<td>Typical urban obs</td>
<td></td>
<td></td>
</tr>
<tr>
<td>EPA emission inventory</td>
<td>0.123</td>
<td>0.06</td>
</tr>
<tr>
<td>Fire emission inventory (Akagi 2011)</td>
<td>0.026 to .009</td>
<td>0.12-0.16</td>
</tr>
<tr>
<td>Fire plume observations</td>
<td>0.01 to 0.005</td>
<td>0.1-0.4</td>
</tr>
</tbody>
</table>

Observations of CO, PM2.5 and NOy can distinguish source of pollutants on high O₃ days.
Eularian modeling vs Statistical modeling

Eularian modeling:
- Gridded emissions, meteorology, solar fluxes (J values).
- Use known photochemistry and transport to model mixing ratios.
- For wildfires significant challenges with emissions, plume rise, aerosols and the chemistry, which can be very different from typical urban photochemistry.
- Modeled concentrations may differ significantly from observations making quantitative attribution difficult.

Statistical modeling:
- Examines the relationship between the observed mixing ratios and other factors.
- Possible factors to include are temp, wind speed, RH, solar flux, etc.
- Outliers (high residuals) represent an additional O₃ source and are candidates for further investigation.

\[ O₃ = A*\text{temp} + B*\text{winds} + C*\text{DOY} \ldots + \text{residual} \]

(Jaffe et al 2004; 2013; Camalier et al 2007; CARB 2011; EPA 2015)
SLC MDA8 vs Daily max T (SLC airport)

$R^2 = 0.45$
SLC MDA8 vs DOY

$R^2 = 0.28$
Statistical model for SLC: $R^2 = 0.60$

<table>
<thead>
<tr>
<th>SLC Model</th>
<th>Unstandardized Coefficients</th>
<th>Standardized Coefficients</th>
<th>t</th>
<th>Sig.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>B</td>
<td>Std. Error</td>
<td>Beta</td>
<td></td>
</tr>
<tr>
<td>Constant</td>
<td>829.8</td>
<td>96.62</td>
<td>8.59</td>
<td>.000</td>
</tr>
<tr>
<td>T-max2</td>
<td>.0243</td>
<td>.0006</td>
<td>.683</td>
<td>40.7</td>
</tr>
<tr>
<td>Daily Avg Wnd Spd</td>
<td>-2.38</td>
<td>.138</td>
<td>-.286</td>
<td>-17.2</td>
</tr>
<tr>
<td>Yr</td>
<td>-.389</td>
<td>.048</td>
<td>-.132</td>
<td>-8.08</td>
</tr>
<tr>
<td>DOY$^2$</td>
<td>-.000177</td>
<td>.000</td>
<td>-.233</td>
<td>-14.1</td>
</tr>
</tbody>
</table>

Parameter inclusion requires:
1. Statistical significance
2. Reasonable physical interpretation
Why use Statistical Models?

1. Give important information on meteorology impacts on AQ in your area;
2. Give information on usual relationship between met variables and AQ;
3. Provides quantitative information on unusual conditions; e.g. exceptional events.

In Jaffe et al 2013 (EST) we compared statistical model with two Eulerien models for wildfire O₃ impacts in SLC, Reno and Boise.
EPA 2015:
Guidance on the Preparation of Exceptional Events Demonstrations for Wildfire Events that May Influence Ozone Concentrations

AirNow MetData

MetDat

Sites & Parameters

Surface Air Site
UT - SALT_LAKE_CITY_INT'L_ARPT (KSLC)

Corresponding Upper-Air Site
UT - SALT_LAKE_CITY_INT'L_ARPT (KSLC)

Parameters

Suggested Subset
- DT700 (degK)*
- T850 (degK)*
- TDELTA (degK)*
- TMAX (degK)*
- VAVG (m/s)*
- WSAVGAM (m/s)*
- WSAVGPM (m/s)*

Date Selection

Range of Years
- 2007 through 2011

Range of Months
- January through December

Run Query

Results

January through December data for 2007 to 2011.

KSLC_20072011_JanDec_unpivoted.CSV
Comparison of my original statistical model with AirNow statistical model

<table>
<thead>
<tr>
<th></th>
<th>My model (Jaffe et al 2014-EST)</th>
<th>AirNow model</th>
</tr>
</thead>
<tbody>
<tr>
<td>Location</td>
<td>Salt Lake City, UT</td>
<td>Salt Lake City, UT</td>
</tr>
<tr>
<td>Time period</td>
<td>2000-2012</td>
<td>2008-2011</td>
</tr>
<tr>
<td>% variance explained</td>
<td>0.60 (60%)</td>
<td>0.59 (59%)</td>
</tr>
<tr>
<td>Key met variables</td>
<td>Maxtemp, WS, DOY, 700 mb zonal wind, etc.</td>
<td>Maxtemp, WS, 850 mb temp, etc.</td>
</tr>
<tr>
<td>How long to construct</td>
<td>~ 1 month</td>
<td>~ 1 hour</td>
</tr>
</tbody>
</table>
Comparison of residuals in my original statistical model with AirNow statistical model

\[ y = 0.84x + 0.58 \]

\[ R^2 = 0.75 \]
AirNow MetData

MetDat

Sites & Parameters

Surface Air Site
UT - SALT_LAKE_CITY_INT'L_ARPT (KSLC)

Corresponding Upper-Air Site
UT - SALT_LAKE_CITY_INT'L_ARPT (KSLC)

Parameters

Select all
7 selected

Suggested Subset

- DT700 (degK)*
- T850 (degK)*
- TDELTA (degK)*
- TMAX (degK)*
- VAVG (m/s)*
- WSAVGAM (m/s)*
- WSAVGPM (m/s)*

Date Selection

Range of Years
2007 through 2011

Range of Months
January through December

Run Query

Results

January through December data for 2007 to 2011.
KSLC_20072011_JanDec_unpivoted.CSV
Final area designations due Fall 2017 - based on 2014-2016 final DVs (120-day letters by June 2017)

Early-certified 2017 data may also be relevant to final designations.

We expect state designation recommendations to be based on 2013-2015 and preliminary 2016 data, including any exceptional event considerations.

Exceptional event demonstration submission deadlines: October 1, 2016 for 2014-2015 events

May 31, 2017 for 2016 events
Preliminary stakeholder discussion questions:

- From the stakeholder perspective, what additional data elements and/or model improvements are needed to better characterize background O3 levels across the U.S.?
- From the stakeholder perspective, has EPA properly characterized the various CAA provisions under consideration for areas influenced by background O3?
- Are there sufficient technical tools and data available to make the demonstrations necessary to invoke relevant CAA provisions?
More on process and timeline-tentative

- EPA plans to convene state agency/stakeholders meeting in Phoenix in late Feb (last week?) to discuss implementation;
- AWMA will convene a second webinar on $O_3$ implementation in spring (April or May?)
- Need a continuous dialogue.
Summary

1. The new O$_3$ standard will be a major challenge for the western US. While O$_3$ is improving in many urban areas the standards are now approaching background concentrations;

2. Stratospheric intrusions (UTLS) and very long-range transport can be identified from tracer ratios, met and spatial correlations;

3. Wildfires are becoming increasingly important. While the PM and health effects are obvious, there are many uncertainties around secondary aerosol and O$_3$ production;

4. Need to develop and use all the tools available to us. This includes better observations, tracer ratios, spatial-temporal correlations and statistical modeling;

5. Need to push EPA to improve these tools.