Identifying Sources of Long-Range Ozone Transport Using Aerosols

(Particularly Asian Ozone in Western U.S.)

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Why Track O₃ Transport Events?

• Current “background” ozone in the West is uncomfortably close to the 8-hr NAAQS.
• Exceeding the NAAQS triggers O₃ precursor emission controls.
• In many areas of the West there are not enough ozone precursor sources for regulatory actions to measurably reduce ozone.
• USEPA regulations allow exemptions for “exceptional events”.

40 CFR parts 50 and 51 (50.1, 50.14 and 51.930)
Long-term Monitoring

*Developing a long-term record of transport events:*

- Scientific and Regulatory Interest
- Limited by Operational Constraints
Meeting the Monitoring Challenge

Ozone is relatively easy to measure, but it precursors are not

• Measuring NO$_x$, NO$_y$ (LIF or long-path spec.) & multiple ROG species in situ is very expensive (e.g. Medusa or Perkin Elmer Auto GC)
  – Even more so at remote sites and in widely dispersed networks
• Intermittent integrated collection (PAMS canisters) lacks the temporal resolution to tag individual hours...

• AND – these species carry little source information
Meeting the Monitoring Challenge

What About Aerosols?

- Aerosols are cheap and practical to collect...

But...

- Can we use them to infer remote sites’ ozone sources?
Aerosols as a Monitoring Technology

Aerosol measurements’ advantages:

- Lower cost than gases
- Practical in remote sites
- Tolerant of ambient conditions
- Non-volatile archival samples
- Contain geographic and source markers.
This guy must be nuts!

Ozone is a *gas*, formed from *other gases*.

Why measure aerosols to track a gas?
It’s True That

Ozone is not at all like PM:

• Gas-phase processes (photolysis, NO\textsubscript{x} - ROC cycling)

• Non-linear O\textsubscript{3} production and loss on short and long time scales

• O\textsubscript{3} interacts weakly with aerosols
Aerosols *Accompany* Tropospheric Ozone

- Ozone precursors are co-emitted with aerosols
- Aerosols carry non-volatile markers
- Emissions & transport meteorology repeat in time

➢ Producing recognizable, quasi-repeating downwind chemical mixtures
The $O_3$ – PM Link:

Key Concepts:

• Downwind aged air composition is much less variable than downwind concentration, and

• Characteristic aerosol mixtures are tracers for ozone sources

If these are true, then:

*Aerosols can qualitatively label $O_3$ sources*
Key Concept #1:

*Downwind aged air composition is much less variable than downwind concentration*

- Local Sources are Highly Diverse;
- Distant co-located Sources are Well-mixed
Downwind aged air composition is much less variable than downwind concentration

- Local aerosol mixtures are more diverse than transported ones:
  - Hourly aerosol type composition (sampled aerosols analyzed by PMF) in suburban Sacramento, winter 2009: *only local sources are unmixed.*

![Diagram of PM$_{2.5}$ contributions to BAM-2.5](chart.png)

S.F Bay Area aerosol plume 6-8 hours old 100+ km downwind
Downwind aged air composition is much less variable than downwind concentration

Is there a reliable signature for the Asian pollutant plume – distinct from North American pollutant sources?

- East Asian Dust (loess) is a Global Marker
  - Improve Data ~100k Samples
  - ITCT2K2 - Persistent Asian Tracer
  - Asian signature in Greenland Aerosols
Downwind aged air composition is much less variable than downwind concentration

- Asian dust 1996 seasonal average at Mauna Loa maps with:
  - 36-IMPROVE sites’ mean from April 1998 very large dust storm.
  - Asian profile from 900+ hrs. continuous data, Trinity Alps & Mt. Lassen – ITCT2K2.
Downwind aged air composition is much less variable than downwind concentration

- Asian aerosol composition at Crater Lake and Mt. Lassen is highly correlated for 28 IMPROVE species (600+ samples).
Downwind aged air composition is much less variable than downwind concentration

- Continuous measurements confirm the IMPROVE inferences
  Regional synchrony of Asian transport - Mt. Lassen and Trinity Alps, ITCT2K2
Downwind aged air composition is much less variable than downwind concentration.
Key Concept #2: *Characteristic aerosol mixtures are tracers for ozone sources*

Simple case - Trinidad Head, CA:
Asian intrusion at sea level – gas & aerosol data

Detailed test – Mt. Lassen, CA
Ozone, aerosol and met merged data set; 5 weeks spring ‘06
Characteristic aerosol-gas mixtures are tracers for ozone sources

Simple example:
Natural and anthropogenic gases track with aerosol tracer
The Lassen 3/06 Ozone Transport Events

• Models and experience tell us the upland interior West (and the SW deserts) take the brunt of the transport impact

• 5 weeks at Mt. Lassen in 2006
  – SUPRECIP ’06
    • CASTNET $O_3$
    • RAWS Met T, WS, WD, RH, Solar Radiation
    • RDI – 8 stage, 28 elements, $B_{abs}$; 3-hr continuous data
The Lassen 3/06 Ozone Transport Events

NPS Manzanita Lake RS & Work Ctr.
IMPROVE, CASTNET, RAWS
The Lassen 3/06 Ozone Transport Events

NPS Manzanita Lake RS - Hwy 44 & Hwy 89
The Lassen 3/06 Ozone Transport Events

3-D Perspective View from South

Pacific Ocean  Mt. Shasta  Klamath Basin

Coast Ranges  Modoc Plateau

Sacramento Valley  Mt. Lassen

Data SIO, NOAA, U.S. Navy, NGA, GEBCO
Image ©2012 TerraMetrics
The Lassen 3/06 Ozone Transport Events

Hardware: 8 sizes, 28 elements, aerosol optics, 320+ sample periods unattended.
The Lassen 3/06 Ozone Transport Events

Field operations:
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PMF Aerosol Factors – SUPRECIP’06

F1 - "WET" COMBUSTION
F2 - CLOUD PROCESSED
F3 - LIGHT DUTY VEHICLE
F4 - ASIAN DUST & COMBUSTION
F5 - ROAD SPRAY
F6 - LOW-SULFUR DIESEL
F7 - "DRY" COMBUSTION
F8 - DRY ROAD DUST

R^2 for PMF Linear Model
The Lassen 3/06 Ozone Transport Events

- LAVO Ozone and Asian aerosol factor data
- A Naïve Interpretation of Asian $O_3$ transport
Asian aerosol factor coincides with periods of elevated O$_3$. 

The Lassen 3/06 Ozone Transport Events
The Lassen 3/06 Ozone Transport Event

- Asian aerosol coincides with stronger variability
The Lassen 3/06 Ozone Transport Events

- 4-σ Asian aerosol / $O_3$ co-occurrences; $\sim 8$ ppbv enhancement

![Graph showing ozone (O$_3$) and Asian aerosol factor trends over time.](image)
The Lassen 3/06 Ozone Transport Events

Overall – Asian aerosol tracks with increased O$_3$

Highly significant but very imprecise relationship

![Graph showing relationship between Asian PMF Factor Score and Ozone concentrations.](image)
Combining LAVO Ozone, met, and aerosol factor data in a “less naïve” experiment
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Relevant patterns of aerosols
Relevant meteorological conditions
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- Simple Model:

\[ O_3 \approx \text{Local Natural Background + transported} - \text{sinks} \]

\[ O_3 \approx f \]

- Solar Radiation
- Temperature
- RH
- Dry Combustion
- Wet Combustion
- Asian Mineral - Fly Ash - SO4
- LDV
- Diesel
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Simple Model: results

R² = \(0.48\)

- \(O_3\) FIT
- \(O_3\) OBS
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Simple Model: Significant parameters

![Graph showing significance levels of different parameters.](image-url)

- WET COMBUSTION (FOSSIL & BIOMASS)
- DRY COMBUSTION (FOSSIL & BIOMASS)
- ASIAN DUST AND COMBUSTION
- SOLAR KW-hr/m²
- T degC
- RH pct
Aerosol - $O_3$
co-occurrences:
Pollutant Factor
Curves lag

The Lassen 3/06 Ozone Transport Event
The Lassen 3/06 Ozone Transport Events

Early and late back-trajectories for peak events - Stratospheric enhancement with fronts; Asian transport behind fronts
Implementing the Aerosol Tracer Strategy

• Chews Ridge Experiment
  – UCD/SJVAPCD/MIRA
  – Elevated, very remote site in Central Coastal Ranges
  – Met, Gas, & Aerosol sampling
  – Aircraft transects and soundings
  – Whole season (Spring-Summer) of data
    • 2012 samples in analysis
    • work planned 2013 and...

  – Future
    • Pairing with inland sites
Chews Ridge Site

Off the grid and off the beaten path
MIRA Chews Ridge

Monterey Institute for Research Astronomy

100% Solar Power
1525 m elev. – consistently above marine stratus
Unobstructed flow from Pacific
Remote from any habitation or traffic
Scientific Aviation Mooney M20
END
Observational Evidence for Trans-Pacific Co-transport of Ozone and Aerosols

• History:
  – Asian Dust Signature Recognition
    • Rex, 1969; Dymond et al., 1974; Shaw, 1979; Duce et al., 1980; Shaw, 1980; Parrington et al., 1983; Braaten & Cahill, 1986; Holmes & Zoller, 1996...
    • Many later applications of the Holmes & Zoller profile
  – Anthropogenic Content
    • PEM-West 1991, 1994; Perry, 1999; Yienger et al., 2000; ACE-Asia 2001; Song & Carmichael, 2001...
    • Many follow-on studies
  – Asian Ozone Transport to North America
    • Akimoto et al., 1996; Jaffe et al., 1999; Jacob et al., 1999; Yienger et al., 2000; Fiore et al., 2002...
    • Many more, e.g. Huang et al., 2010