Today:

Discuss two critical aspects of urban $\text{O}_3$:

- In general, most of the $\text{O}_3$ in an urban area is transported in from the outside, not produced locally.
- On average, the dominant effect of local emissions in an urban area is to destroy, not produce, $\text{O}_3$.

(Regulatory Question: Are NOx controls beneficial for local urban $\text{O}_3$ control?)
Urban-Rural Interactions in $O_3$ Distributions

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(Regulatory Question: Are NOx controls beneficial for local urban $O_3$ control?)
In general, most of the O$_3$ in an urban area is transported in from the outside, not produced locally.

Three flights from TexAQS 2000

Regional background can exceed 8-hr std.

DFW adds substantial amounts of O$_3$, but most is transported in from outside
In general, most of the $O_3$ in an urban area is transported in from the outside, not produced locally.

Urban $O_3$ violations have strong regional component.

At least in DFW, the highest exceedances are still dominated by local production.

(June-Sept., 2002 APCA Calculations G. Yarwood et al.)
In general, most of the O₃ in an urban area is transported in from the outside, not produced locally.

Urban O₃ violations have strong regional component.

At least in DFW, the highest exceedances are still dominated by local production.

(Aircraft Data: TexAQS 2000 TexAQS 2006)

(DFW Ozone Contribution (ppbv)

DFW Maximum 8-hr Average Ozone (ppbv)

y = 1.19x + 41.49
R² = 0.88

Local production dominates
Regional transport dominates

DFW Ozone Concentration (ppbv)

NAAQS (June-Sept., 2002 APCA Calculations G. Yarwood et al.)
On average, the dominant effect of local emissions in an urban area is to destroy, not produce, $O_3$.

Consider 3 areas:

- Marine Inflow
- Urban
- Far Downwind

(Channel Islands are not strongly affected by L.A. area emissions)
On average, the dominant effect of local emissions in an urban area is to destroy, not produce, $O_3$.

Average $O_3$ in marine background higher than in urban L.A. area, even during $O_3$ season.

Strong Weekend $O_3$ Effect: average max 1-hr avg. $O_3 \approx 30$ ppbv higher on Sunday than weekday.

(The average is not an exceedance; regulatory considerations should focus on exceedances.)

On average, the dominant effect of local emissions in an urban area is to destroy, not produce, $O_3$.

In far downwind areas the weekend effect is reversed.

Far downwind average $O_3$ higher than in urban areas, but maxima are lower and exceedances are less common.

On average, the dominant effect of local emissions in an urban area is to destroy, not produce, O₃.

Average O₃ on weekday in L.A. is comparable to marine background during summer; but higher on weekends.

Strong Weekend O₃ Effect

*(June-August data)*

- **WE <O₃> = 44**
- **WD <O₃> = 35**

Azusa, 1995

Channel Is. <O₃> = 33

(The weekend, but not weekday, average is an exceedance.)

On average, the dominant effect of local emissions in an urban area is to destroy, not produce, O$_3$.

Average O$_3$ on weekday in L.A. is comparable to marine background during summer; but higher on weekends.

Strong Weekend O$_3$ Effect

Weekend NO$_2$ lower: counterintuitive?

On average, the dominant effect of local emissions in an urban area is to destroy, not produce, O₃.

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Strong Weekend O₃ Effect

Weekend NO₂ lower: counterintuitive?

Ox = NO₂ + O₃ similar through week

Primary cause of Weekend O₃ Effect is titration of O₃ by local NO emissions

The Weekend $O_3$ Effect is primarily due to less local emissions, and hence less $O_3$ destruction, on weekends.

Consider 8 sites in southern California

Color-coded by longitude
The Weekend O$_3$ Effect is primarily due to less local emissions, and hence less O$_3$ destruction, on weekends.

Consider 8 sites in southern California

Color-coded by longitude

$\Delta$ indicates (weekend-weekday)

Throughout L.A. Basin: $\Delta$O$_3 \approx - \Delta$NO$_2$

Primary cause of Weekend O$_3$ Effect is titration of O$_3$ by local NO emissions

Data from Qin et al., (2004) Weekend/weekday differences of ozone, NO$_x$, CO, VOCs, PM10 and the light scatter during the ozone season in southern California, Atmos. Environ., 38:3069-3087.
What about Northern California?

Consider 2 areas:

Urban Area:
Sacramento Valley

Downwind:
Mountain Counties

In Sacramento Valley (urban) exceedances more likely on weekends.

In Mountain Counties (downwind) the effect is reversed.

More exceedances downwind than in urban area.

Primary cause of Weekend O$_3$ Effect is titration of O$_3$ by local NO emissions.

O₃ Weekend Effect: Does it have regulatory implications?

- In many areas average O₃ is higher on weekends
- Caused by lower NOx emissions on weekends

Therefore, do not implement NOx controls!

Is this a valid argument?
O₃ Weekend Effect: Does it have regulatory implications?

- In many areas average O₃ is higher on weekends
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Therefore, do not implement NOx controls!

Is this a valid argument?

Maybe, if VOC limited chemistry were the primary cause

NOx inhibits O₃ production: \( NO_2 + OH \rightarrow HNO_3 \)

But titration is the primary cause

Titration \( NO + O_3 \rightarrow NO_2 + O_2 \)

Titration moves O₃ production downwind, which contributes to O₃ transported into urban area

Further analysis must focus on exceedances; treat titration and transport
In general, most of the O$_3$ in an urban area is transported in from the outside, not produced locally.

For reliable results, photochemical models must accurately reproduce long-range transport, including boundary conditions.

On average, the dominant effect of local emissions in an urban area is to destroy, not produce, O$_3$.

For reliable results, photochemical models must accurately reproduce boundary layer evolution, which strongly affects the effect of NO + O$_3$ titration.

Both of these are difficult for models; box models certainly cannot
Does $O_3$ in Marine Inflow Vary up Coast?

Channel Islands - 1997-2004 - 39 ppbv
Point Reyes - 1988-1992 - 32 ppbv
Redwood NP - 1988-1995 - 31 ppbv

(March-October data)
What about Northern California?

Consider 3 areas:

- Marine Background
- Urban
- Downwind

Mountain Counties

Pt. Reyes

Blodgett Forest

T Street Sacramento
In Sacramento Valley (urban) exceedances more likely on weekends.

In Mountain Counties (downwind) the effect is reversed.

More exceedances downwind than in urban area.

**O$_3$ Weekend Effect**

Average max Weekend O$_3$ Effect $\approx 7$ ppbv in urban area

Downwind average O$_3$ higher than in urban areas.

Pacific marine background is nearly 50% of maximum urban and downwind values.

**O₃ Weekend Effect**

Oₓ = O₃ + NO₂ nearly constant over week

**Primary cause of Weekend O₃**
Effect is titration of O₃ by local NO emissions