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*Today:*

Discuss two critical aspects of urban O<sub>3</sub>:

- In general, most of the O<sub>3</sub> 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, O<sub>3</sub>.

*(Regulatory Question:*

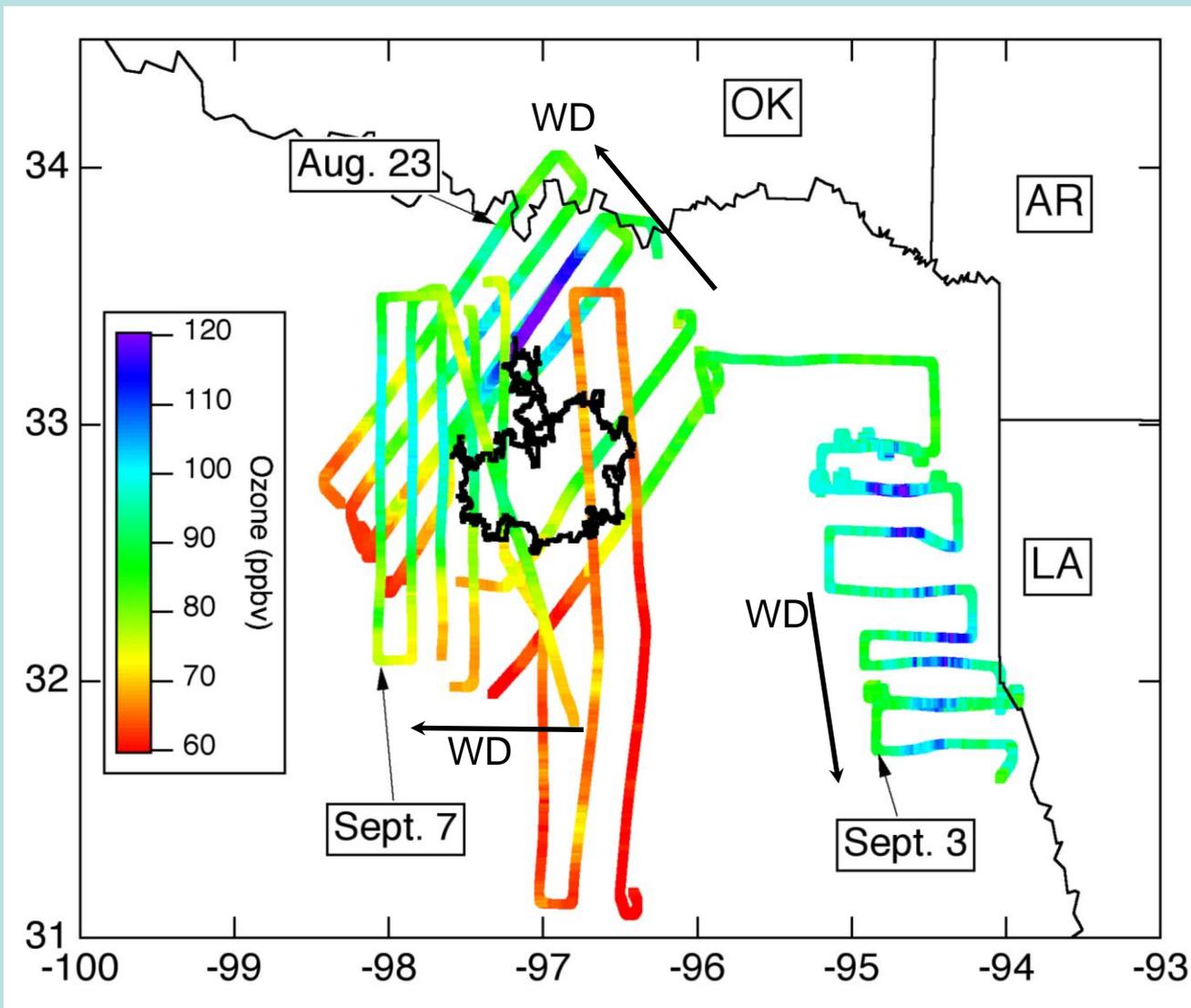
Are NO<sub>x</sub> controls beneficial for local urban O<sub>3</sub> control? )

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Three flights from  
TexAQS 2000

Regional background can  
exceed 8-hr std.

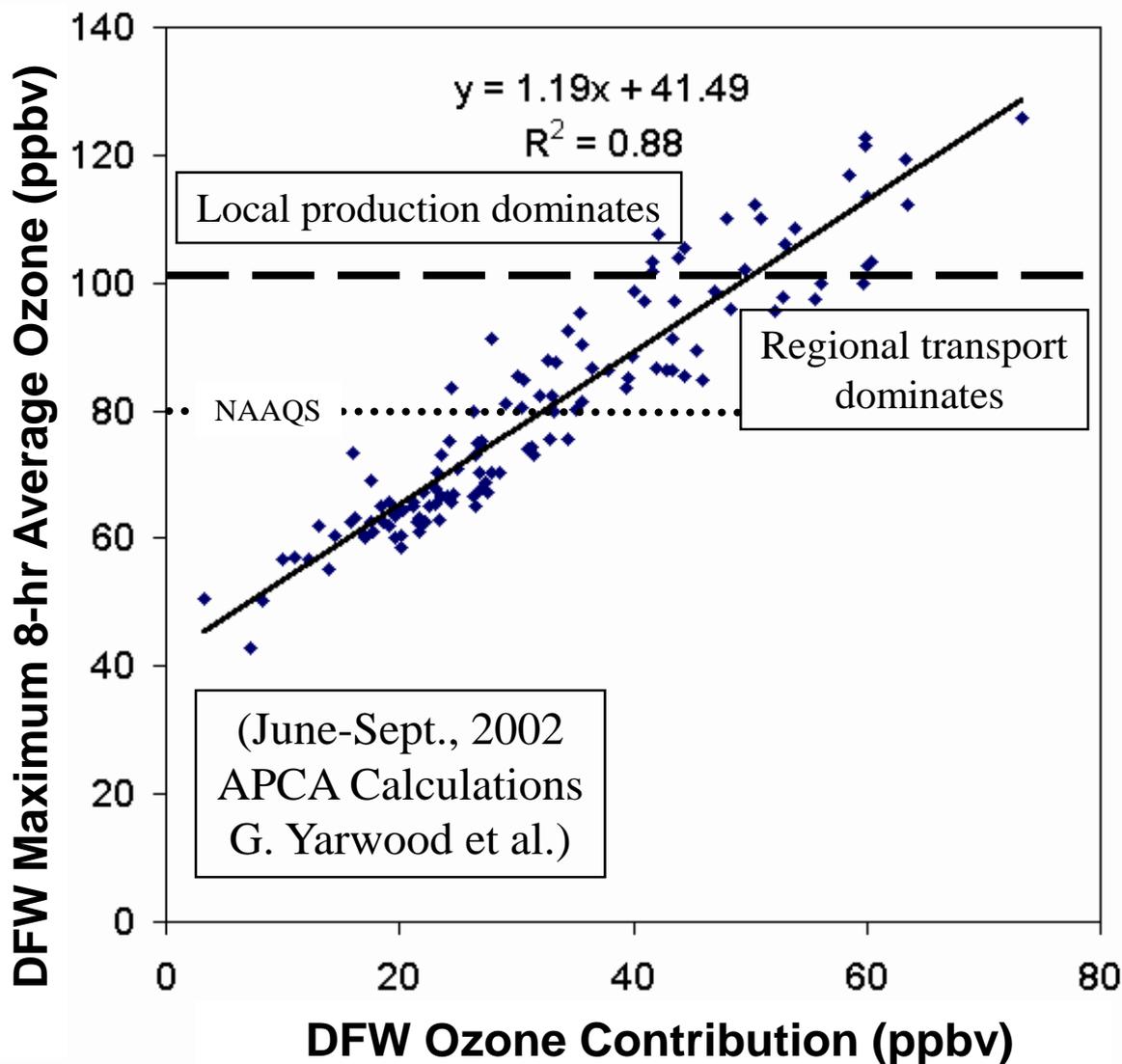
DFW adds substantial  
amounts of  $O_3$ , but most  
is transported in from  
outside



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Urban O<sub>3</sub> violations have strong regional component.

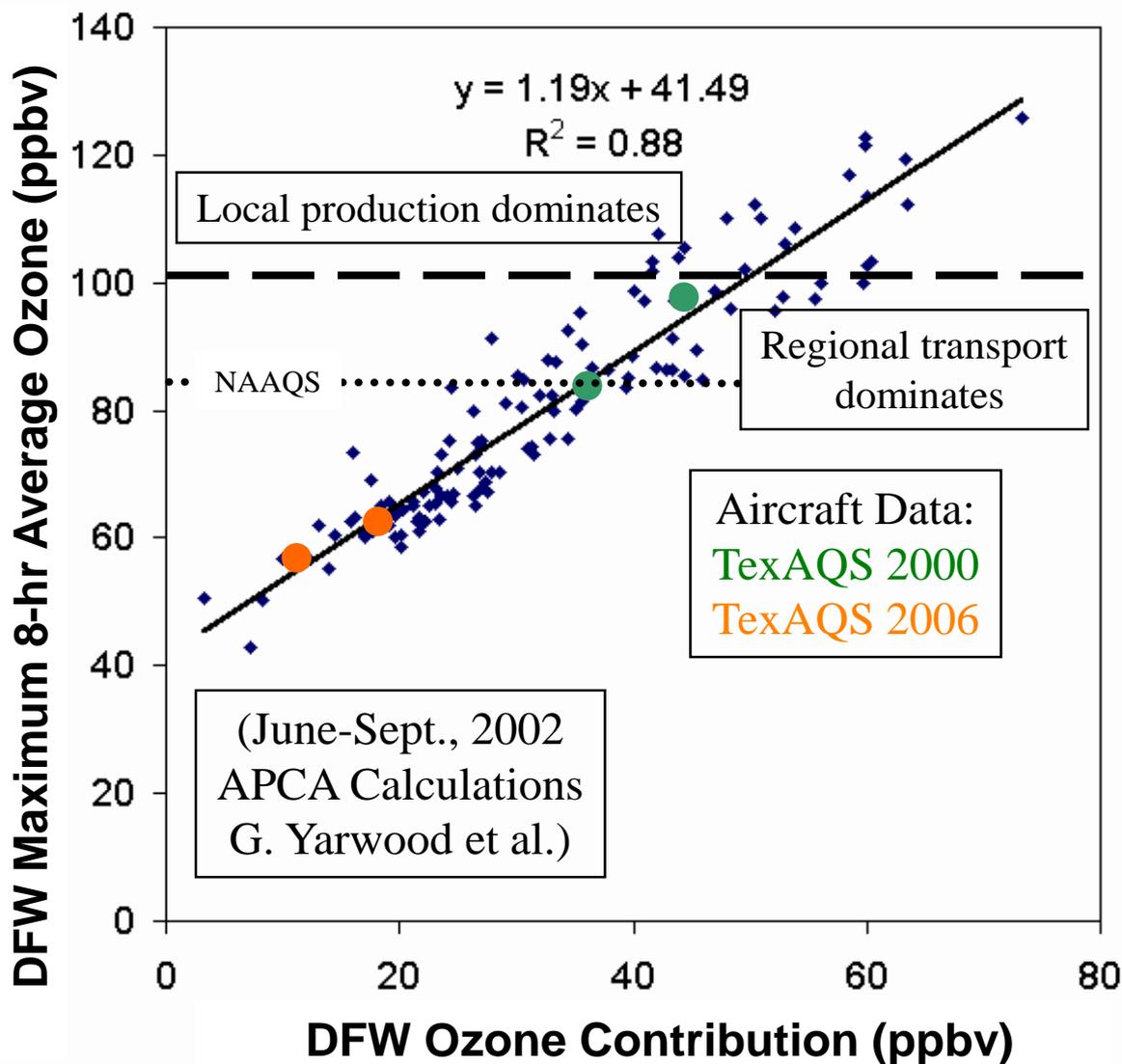
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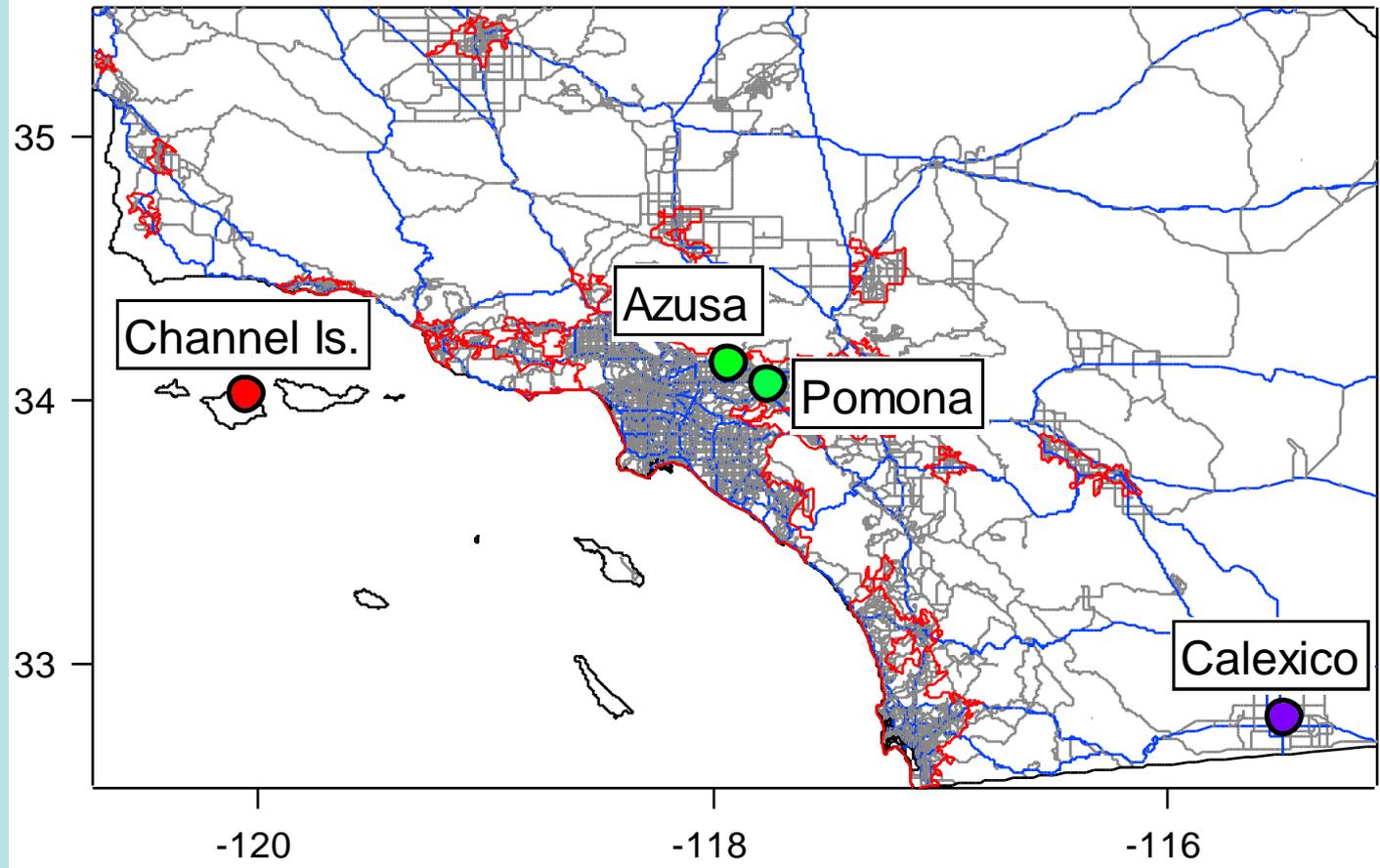
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Consider 3 areas:

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.)

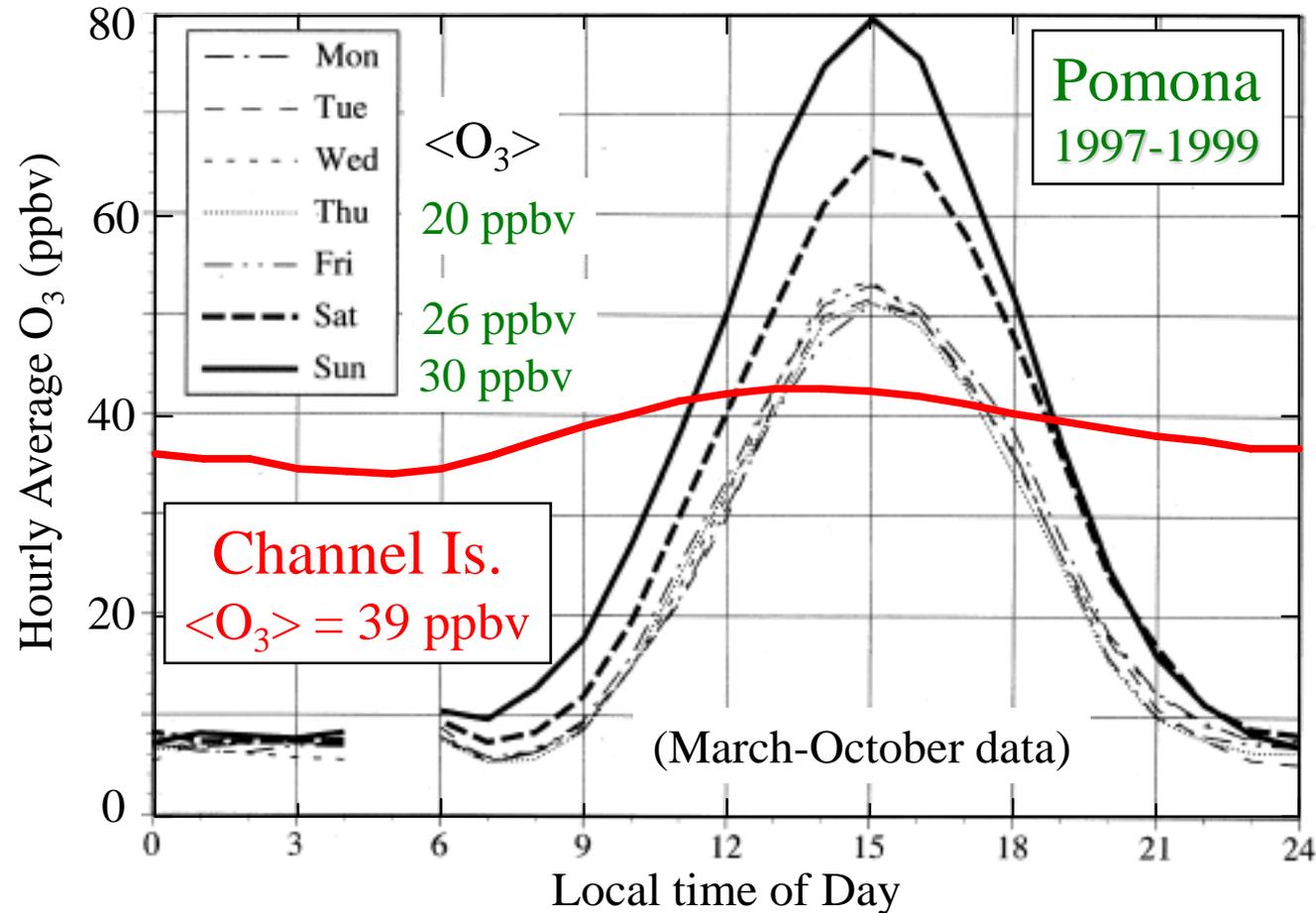


Figure from Huess et al., (2003) Weekday/Weekend Ozone Differences: What Can We Learn from Them?, *J. Air & Waste Manage. Assoc.*, **53**:772-788.

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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.

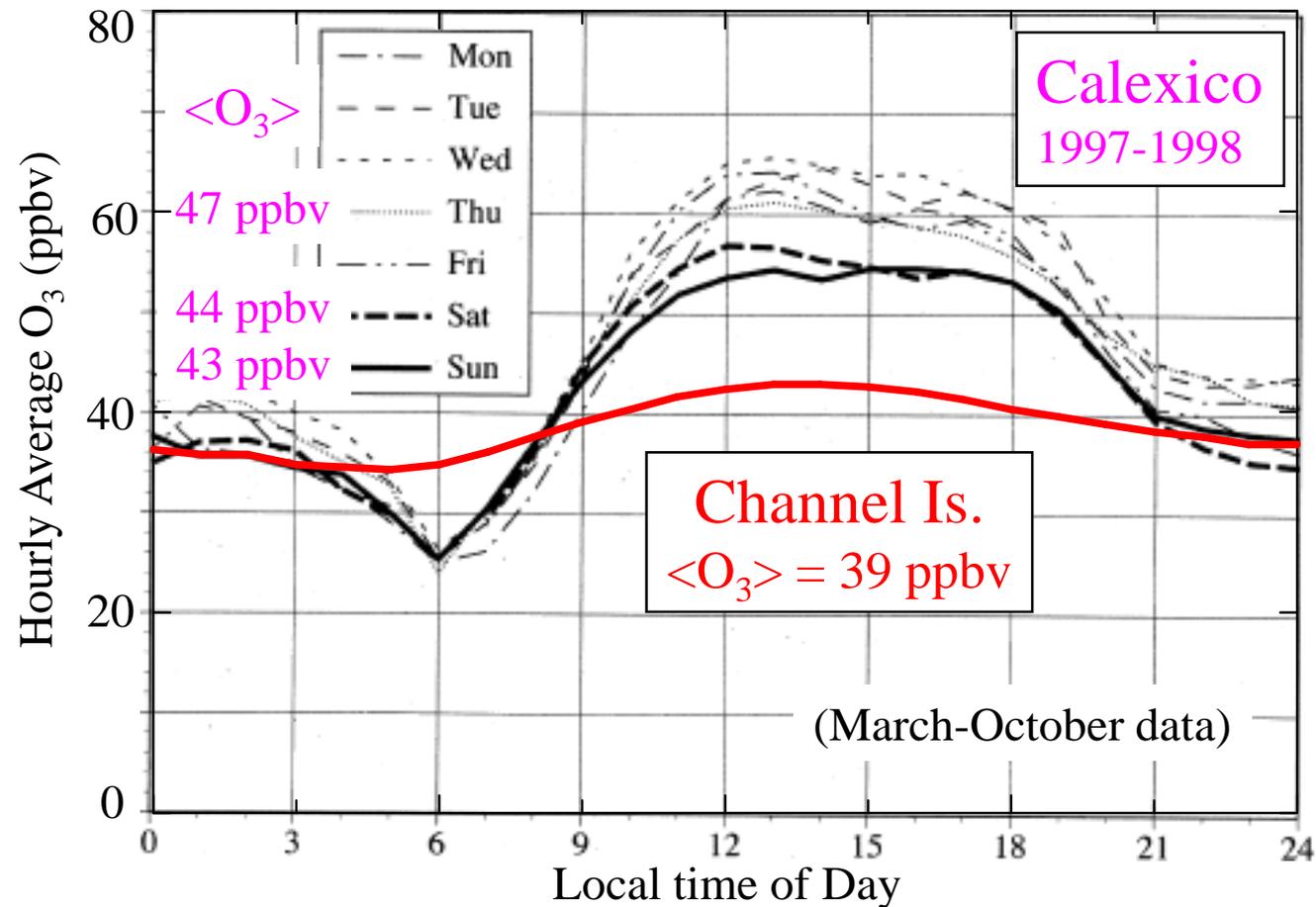


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On average, the dominant effect of local emissions in an urban area is to destroy, not produce,  $O_3$ .

Average  $O_3$  on weekday in L.A. is comparable to marine background during summer; but higher on weekends.

Strong Weekend  $O_3$   
Effect

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

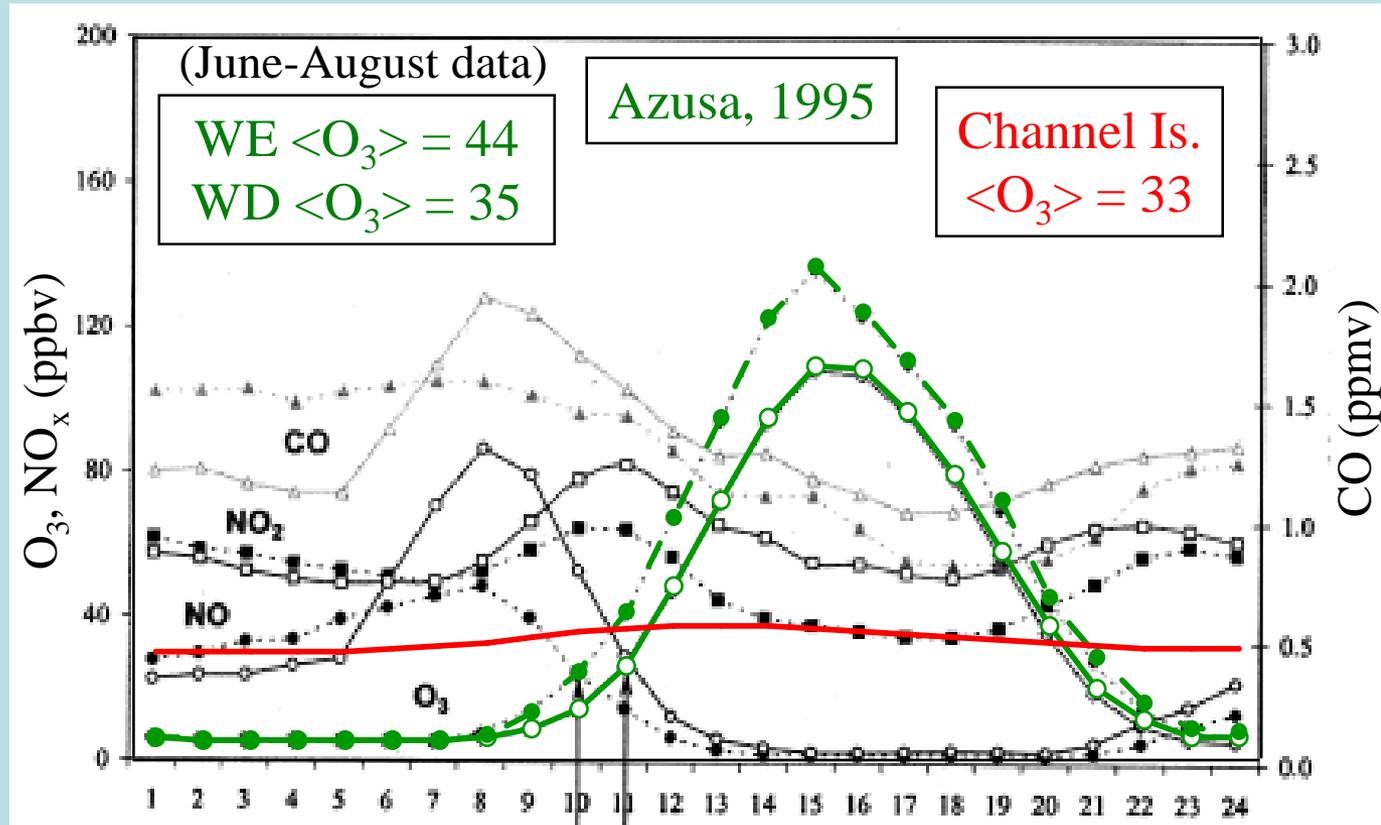


Figure from Fujita et al., (2003) Evolution of the Magnitude and Spatial Extent of the Weekend Ozone Effect in California's South Coast Air Basin, 1981-2000, *J. Air & Waste Manage. Assoc.*, **53**:802-815.

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Weekend  $NO_2$  lower:  
counterintuitive?

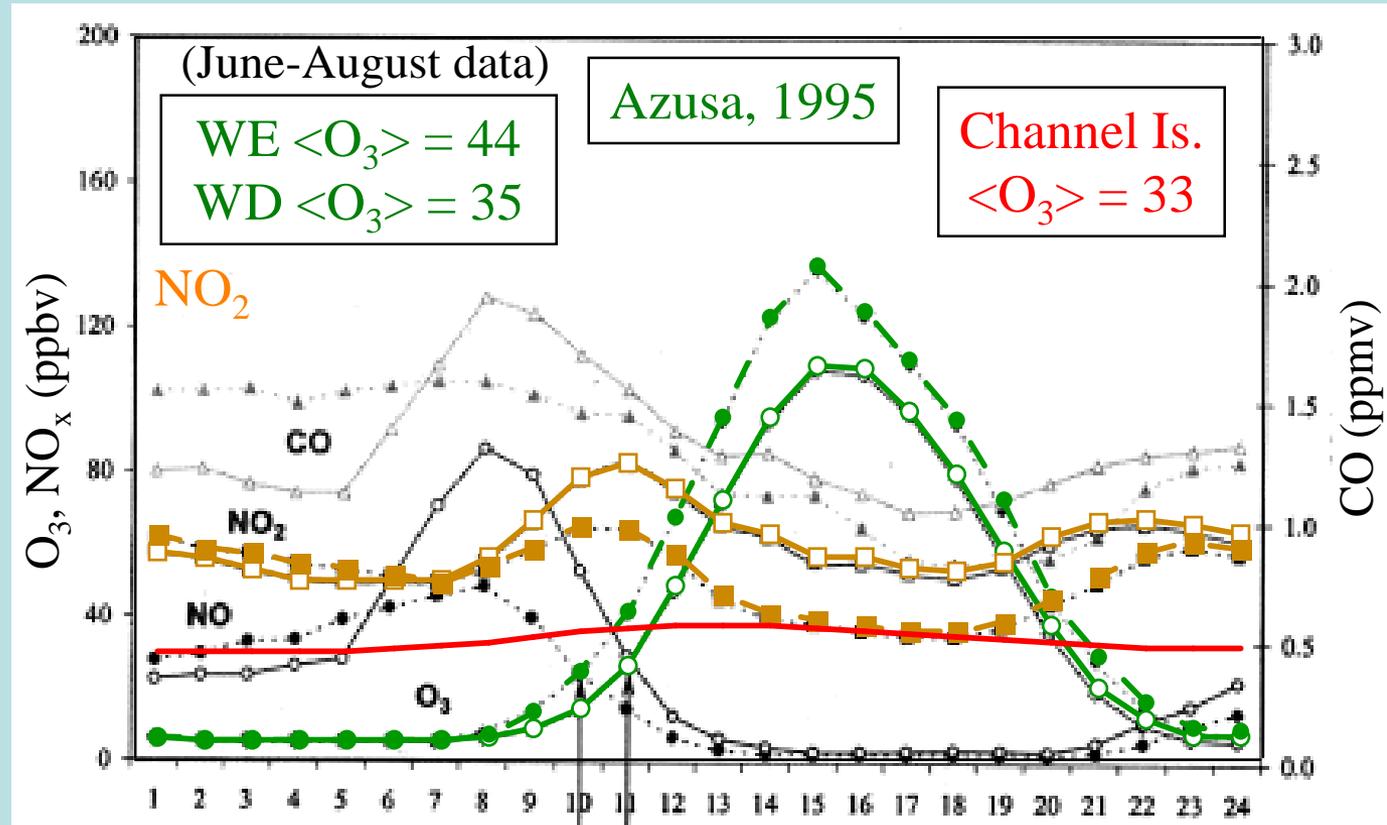


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Effect

Weekend  $NO_2$  lower:  
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$O_x = NO_2 + O_3$  similar  
through week

Primary cause of  
Weekend  $O_3$   
Effect is titration  
of  $O_3$  by local  
 $NO$  emissions

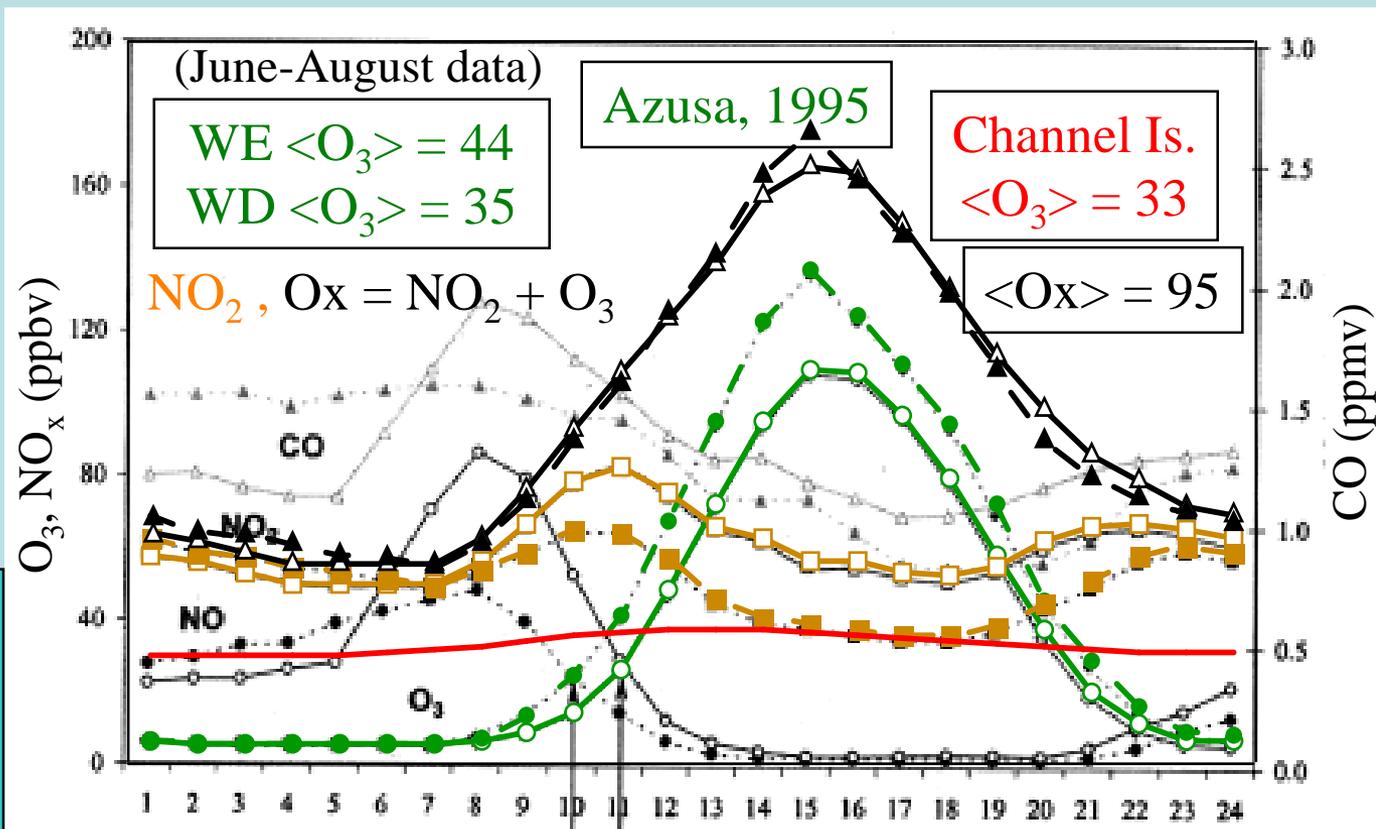
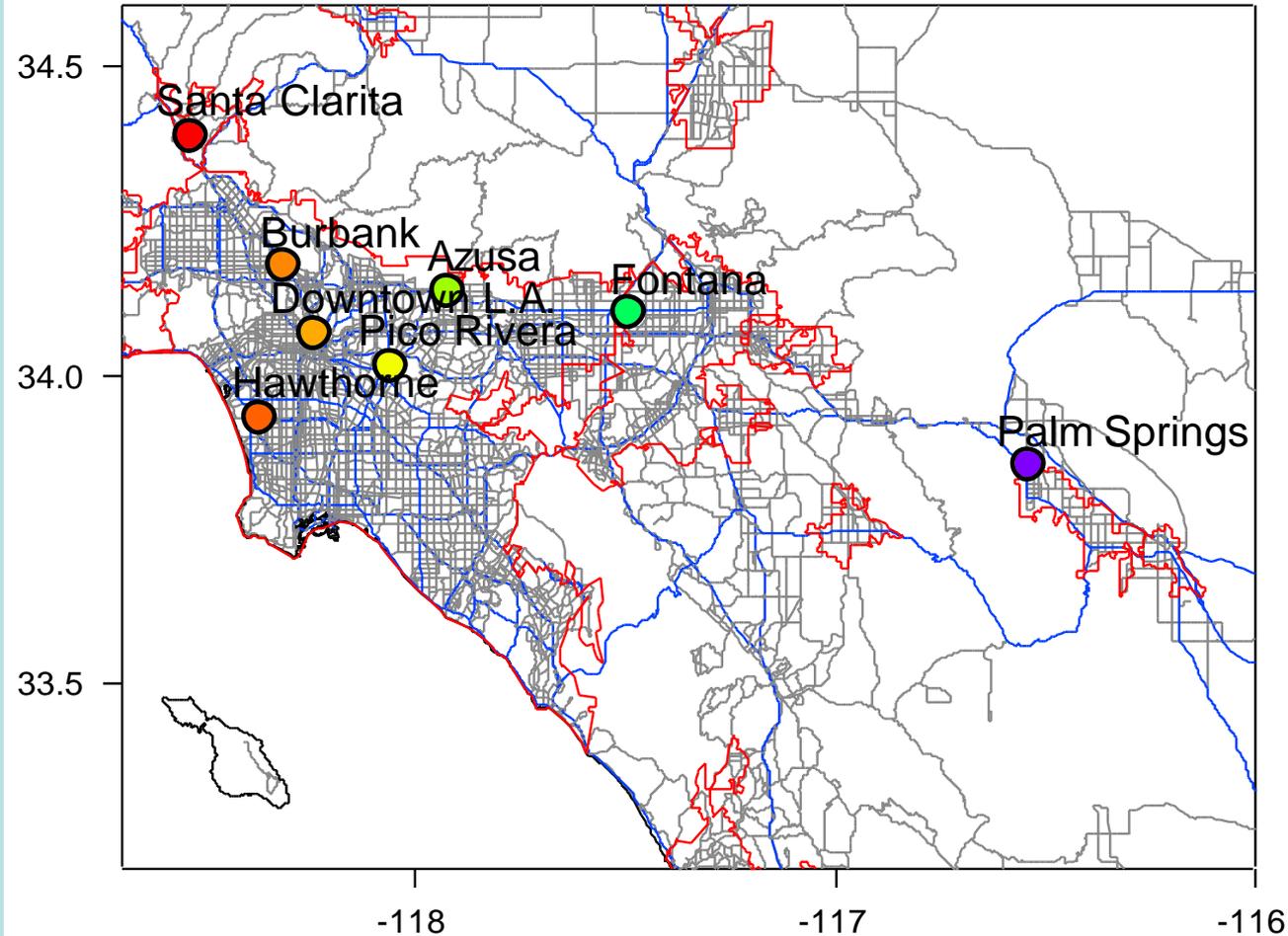


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The Weekend O<sub>3</sub> Effect is primarily due to less local emissions, and hence less O<sub>3</sub> destruction, on weekends.

Consider 8 sites in southern California

Color-coded by longitude



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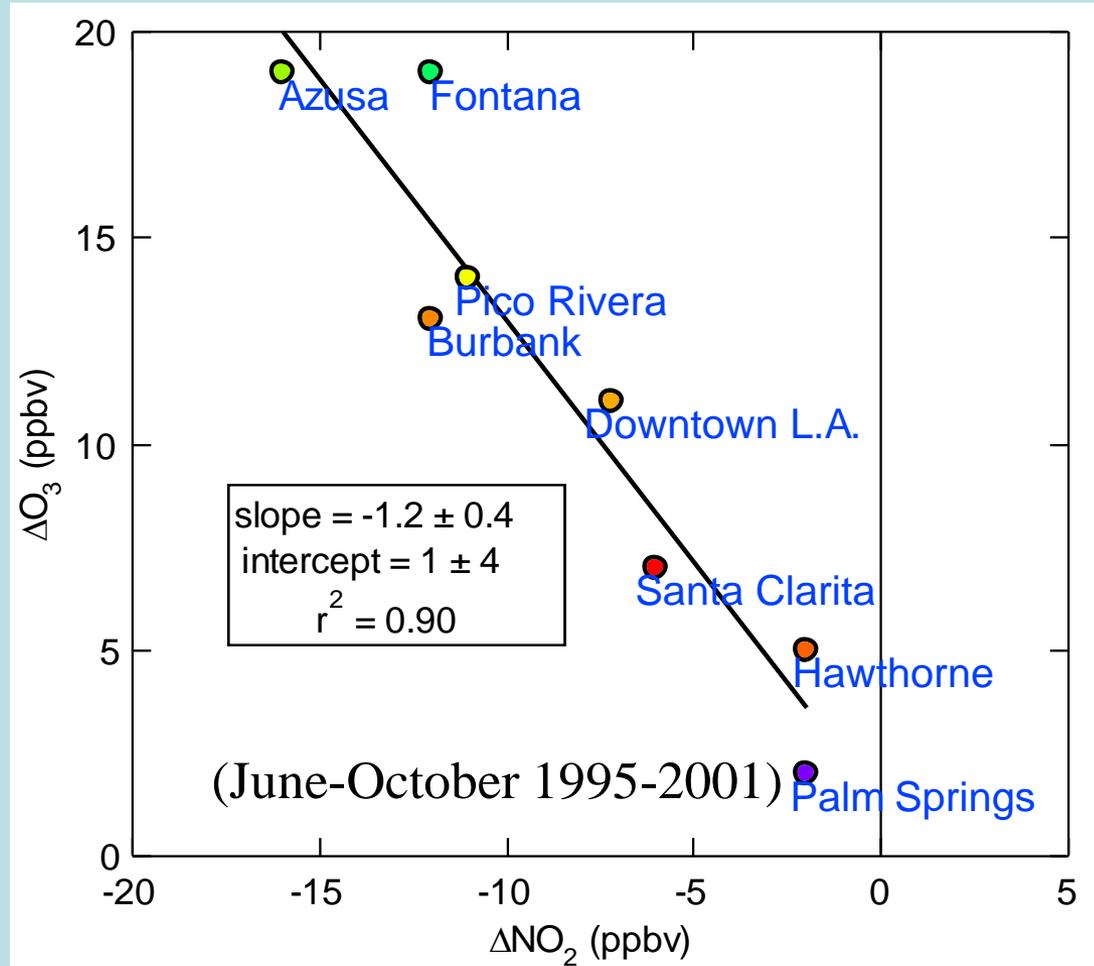
Color-coded by longitude

$\Delta$  indicates (weekend-weekday)

Throughout L.A. Basin:

$$\Delta O_3 \approx - \Delta NO_2$$

Primary cause of Weekend O<sub>3</sub> Effect is titration of O<sub>3</sub> by local NO emissions



Data from Qin et al., (2004) Weekend/weekday differences of ozone, NO<sub>x</sub>, CO, VOCs, PM<sub>10</sub> and the light scatter during the ozone season in southern California, *Atmos. Environ.*, **38**:3069-3087.

## O<sub>3</sub> Weekend Effect: Does it have regulatory implications?

- In many areas **average** O<sub>3</sub> is higher on weekends
- Caused by lower NO<sub>x</sub> emissions on weekends

**Therefore, do not implement NO<sub>x</sub> controls!**

Is this a valid argument?

Maybe, if VOC limited chemistry were the primary cause

NO<sub>x</sub> inhibits O<sub>3</sub> production:  $NO_2 + OH \Rightarrow HNO_3$

But titration is the primary cause

Titration  $NO + O_3 \Rightarrow NO_2 + O_2$

Titration moves O<sub>3</sub> production downwind, which contributes to O<sub>3</sub> transported into urban area

Further analysis must focus on **exceedances**; treat titration and transport

# Urban-Rural Interactions in O<sub>3</sub> Distributions: Implications

In general, most of the O<sub>3</sub> 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<sub>3</sub>.

For reliable results, photochemical models must accurately reproduce boundary layer evolution, which strongly affects the effect of NO + O<sub>3</sub> titration.

Both of these are difficult for models;  
box models certainly cannot