Sensitivity of Ozone Formation To Photons

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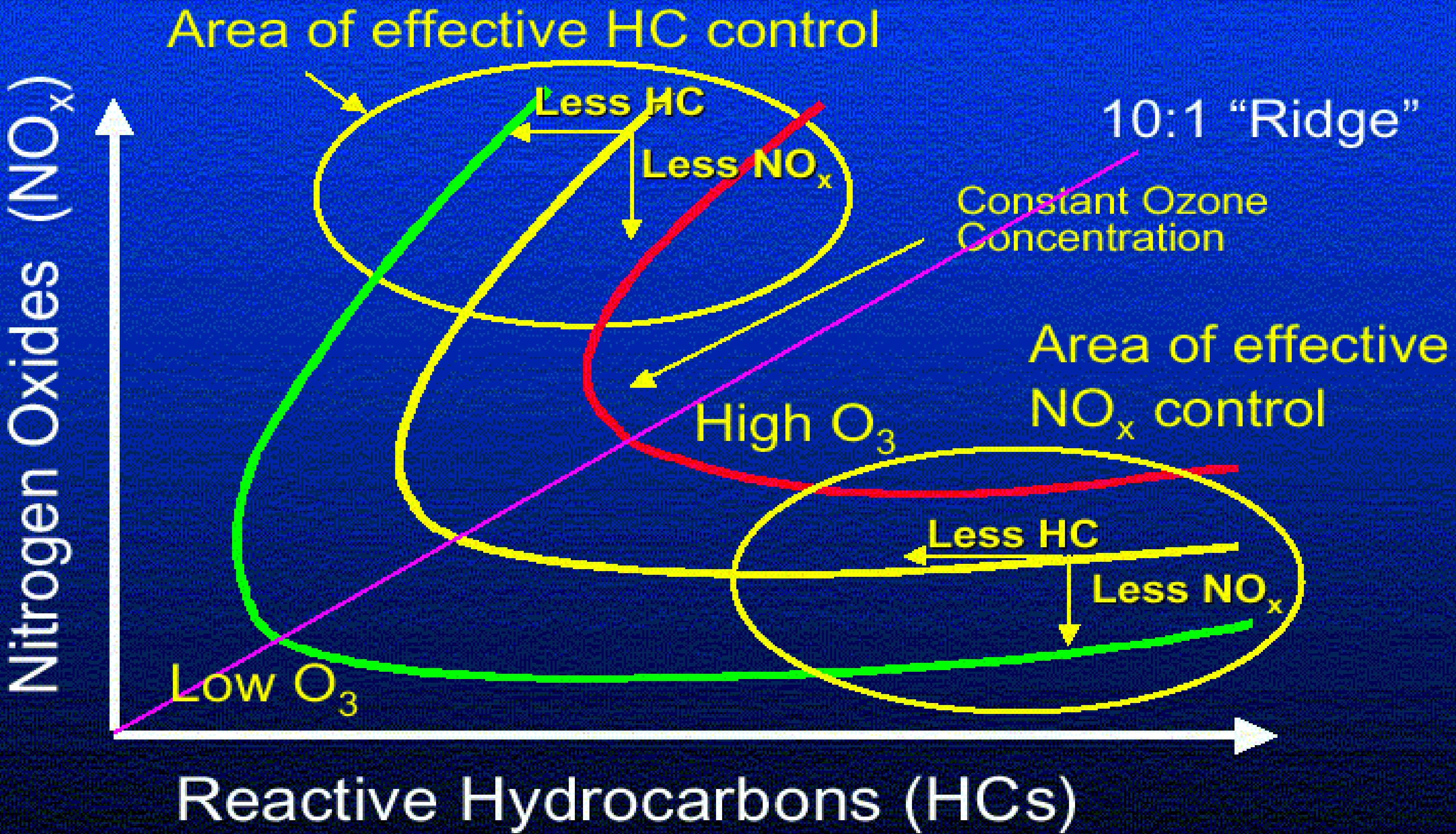
NCAR

Tropospheric Ozone Formation:

Urban ozone is generated when air containing hydrocarbons and nitrogen oxides is exposed to ultraviolet radiation

- Haagen-Smit (1950s)

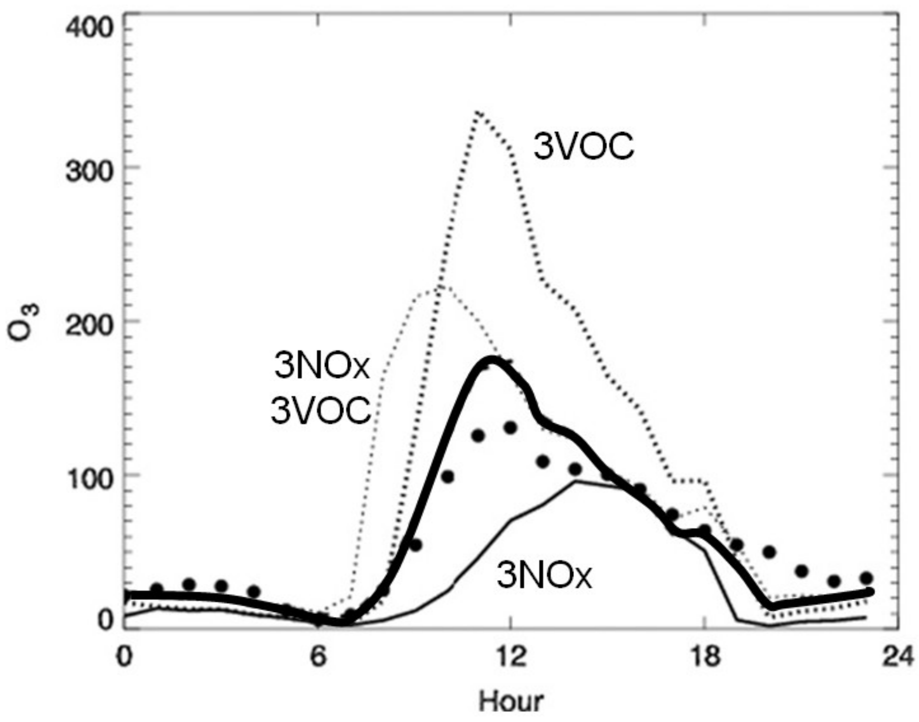
Ozone Isopleth Plot (EKMA Diagram)



CENTER FOR TRANSPORTATION TECHNOLOGIES AND SYSTEMS

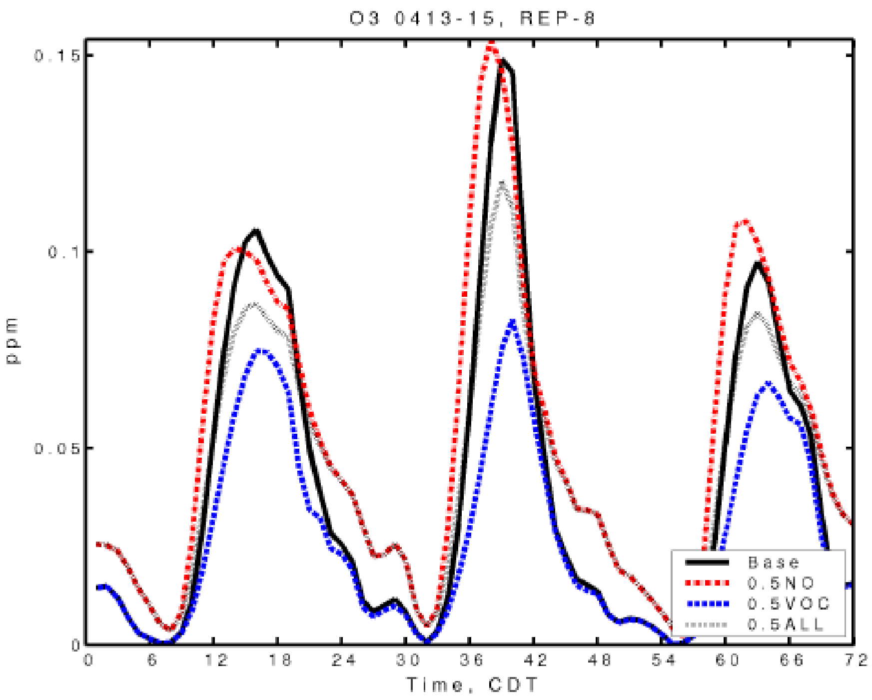
Mexico City's O3 Production is VOC-limited, NOx-inhibited

WRF-Chem --- sensitivity studies
● observations



Tie et al., 2007

CAMx --- sensitivity studies



Lei et al., 2007

NOx-VOC Regimes

NOx-limited

VOC-limited

NOx-inhibited

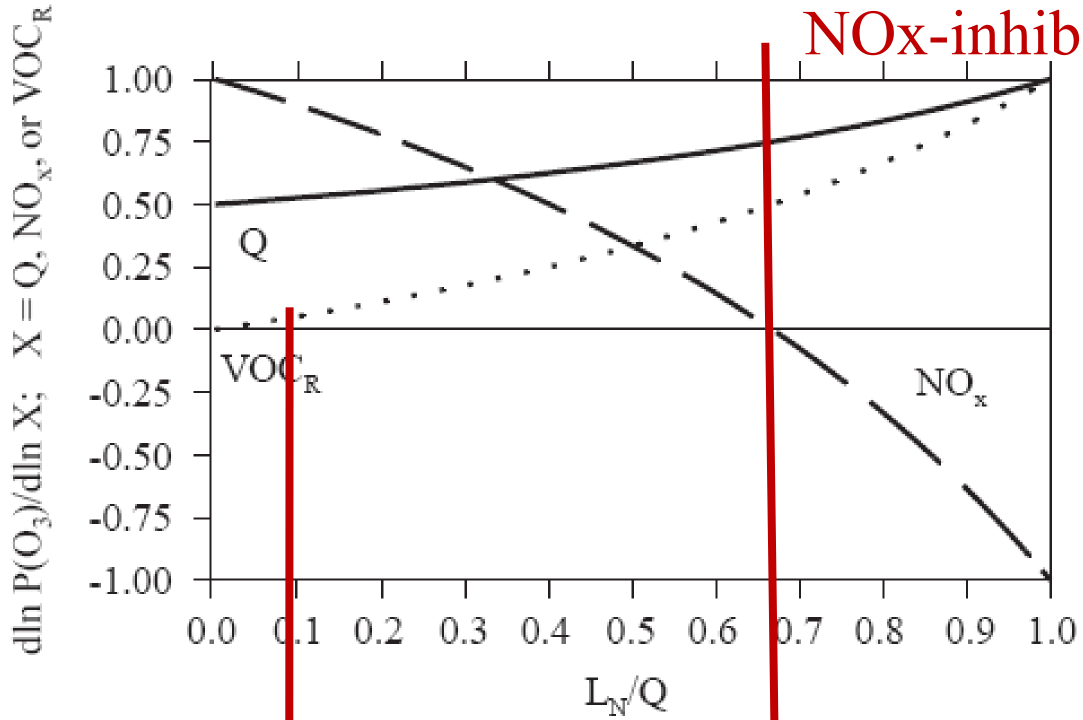


Fig. 1. Relative sensitivity of $P(O_3)$ to radical production rate, Q; NO_x concentration; and VOC reactivity, VOC_R, as a function of the fraction of radicals removed by reaction with NO_x, L_N/Q. Curves are from (7)–(9).

Very low NOx:
O3 ~ J0.5 [NOx]

Very high NOx:
O3 ~ [VOC] / [NOx]

$$\frac{d\ln P(O_3)}{d\ln [NO_x]} = \frac{(1 - 3/2\, L_N/Q)}{(1 - 1/2\, L_N/Q)},$$

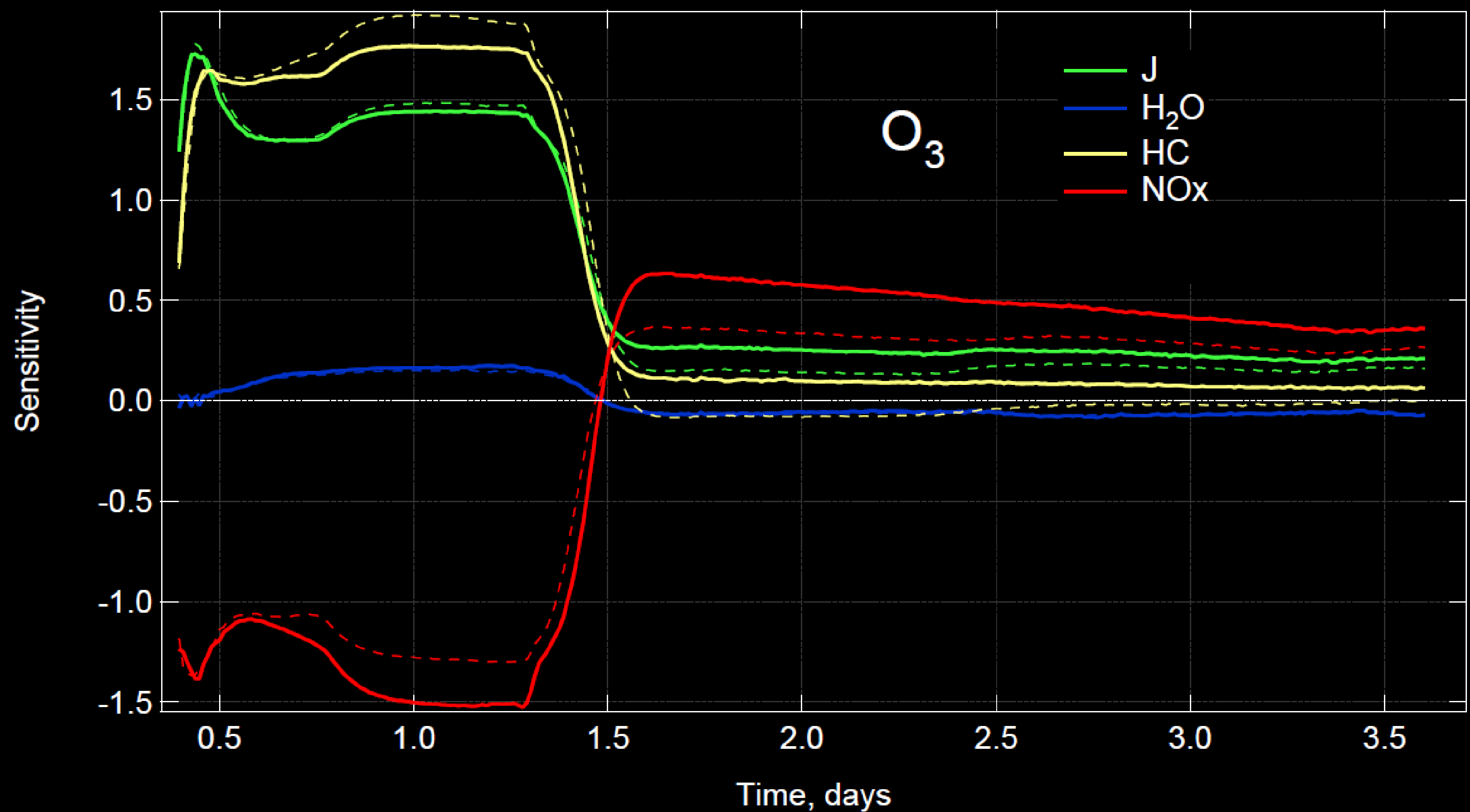
$$\frac{d\ln P(O_3)}{d\ln (VOC_R)} = \frac{1/2\, L_N/Q}{(1 - 1/2\, L_N/Q)}$$

$$d\ln P(O_3)/d\ln Q = (1/2)/(1 - 1/2\, L_N/Q).$$

L.I. Kleinman / Atmospheric Environment 39 (2005) 575–586

Sensitivity (%/%) of O3 in Mexico City

NCAR Master Mechanism box model



Madronich, unpubl..

O3 production is always PHOTON-LIMITED

R
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o
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e

Quantifying Photolysis Processes

Photolysis reaction: AB + hν ü A + B

Photolysis rates:

$$\left.\frac{\mathrm{d[AB]}}{\mathrm{d}t}\right|_{h\nu} = -J[\mathrm{AB}]$$

$$\left.\frac{\mathrm{d[A]}}{\mathrm{d}t}\right|_{h\nu} = \left.\frac{\mathrm{d[B]}}{\mathrm{d}t}\right|_{h\nu} = +J[\mathrm{AB}]$$

Photolysis frequency (s-1) J = ü λF(λ) σ(λ) φ(λ) dλ

(other names: photo-dissociation rate coefficient, J-value)

CALCULATION OF PHOTOLYSIS COEFFICIENTS

J (s-1) = ü $\lambda F(\lambda)\ \sigma(\lambda)\ \phi(\lambda)\ d\lambda$

$F(\lambda)$ = spectral actinic flux, quanta cm-2 s-1 nm-1

ü probability of photon near molecule.

$\sigma(\lambda)$ = absorption cross section, cm2 molec-1

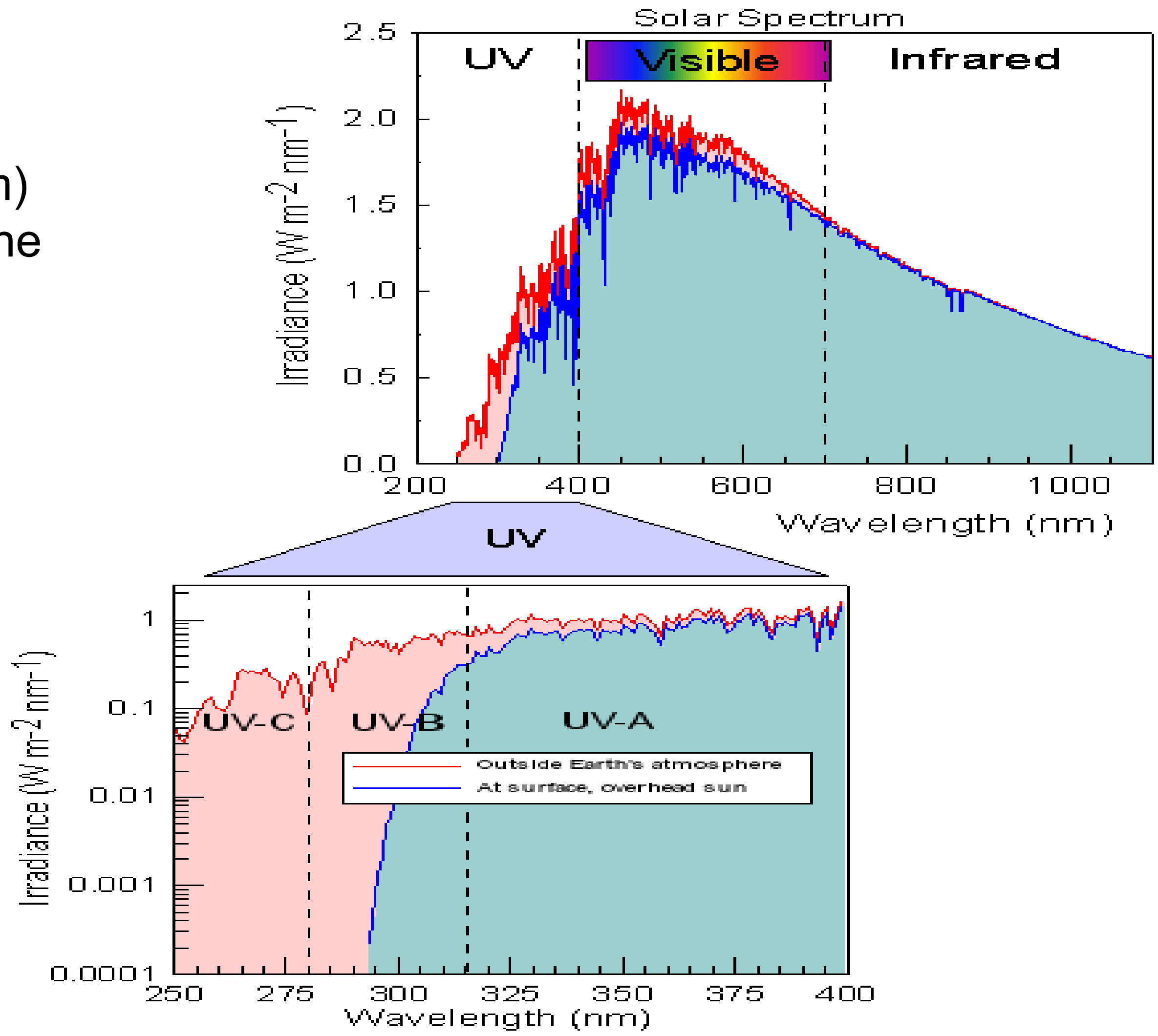
ü probability that photon is absorbed.

$\phi(\lambda)$ = photodissociation quantum yield, molec quanta-1

ü probability that absorbed photon causes dissociation.

Solar Spectrum

O2 and O3 absorb all UV-C (λ<280 nm) before it reaches the troposphere



UNEP, 2002

Spectral Region For Tropospheric Photochemistry

surface, overhead sun

Madronich, unpubl..

Typical Vertical Optical Depths, τ

Direct transmission = exp($-\tau$)
Diffuse transmission can be much larger

Madronich, unpubl..

Effect of Pollutants on UV Irradiance

Model calculations for 21 June, 35 N, noon, pollutants distributed over a 1 km boundary layer

Madronich, unpubl..

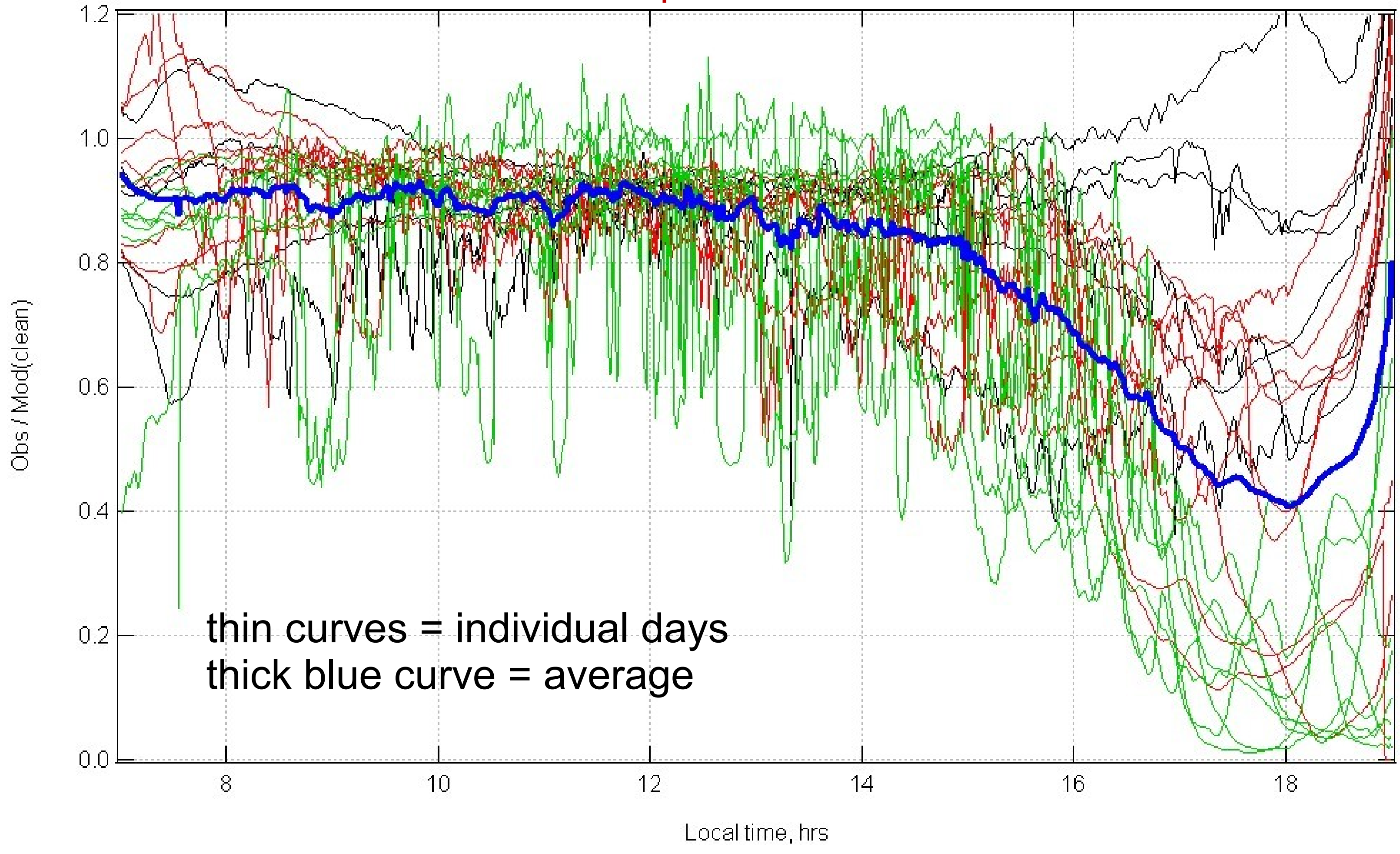
UV Actinic Flux Reduction ü Slower Photochemistry

Mexico City (T1)

Madronich, Shetter, Halls, Lefer, AGU'07

JNO2
Observed/Model_clean

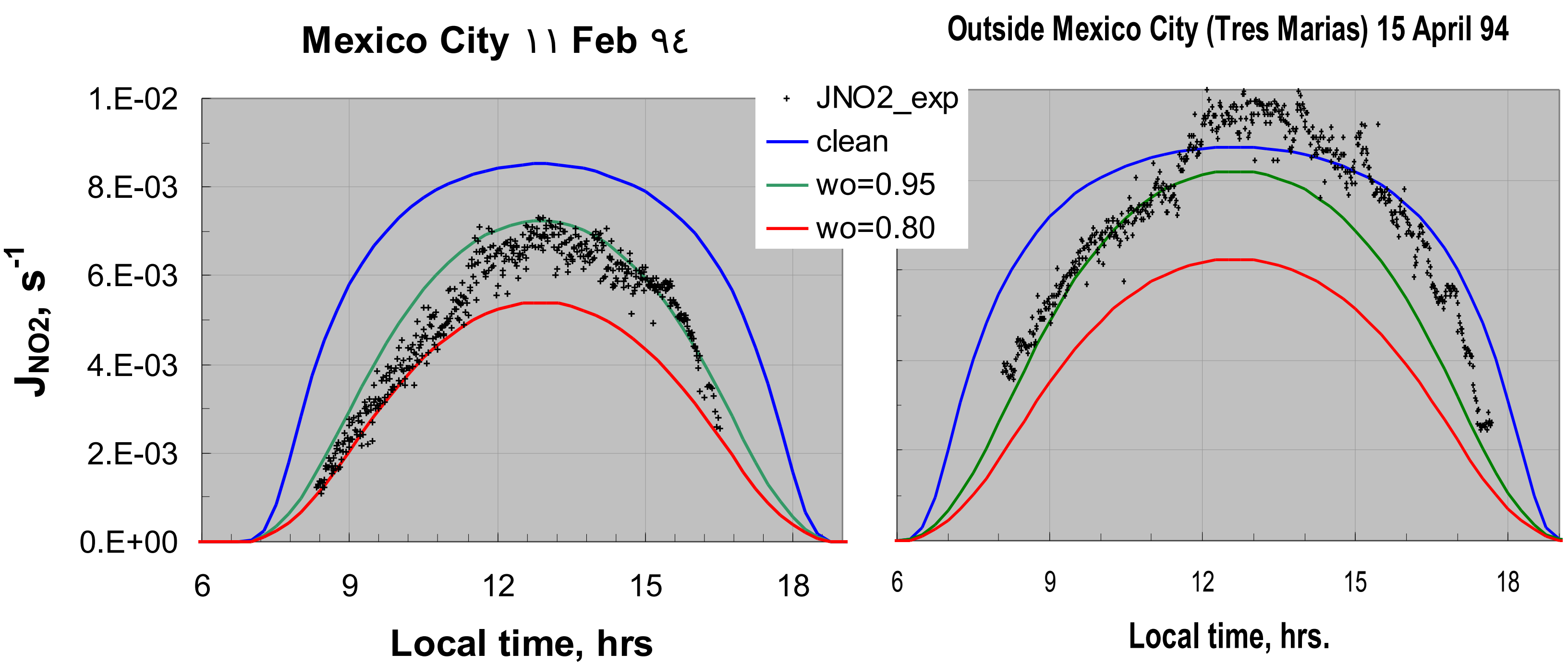
March 2006 T1 supersite



Madronich, unpubl..

Aerosol Impacts on Photochemistry

NO2 + hν ü NO + O (at surface)



Castro et al. 2001

O3 Suppression from Aerosol (Mexico City)

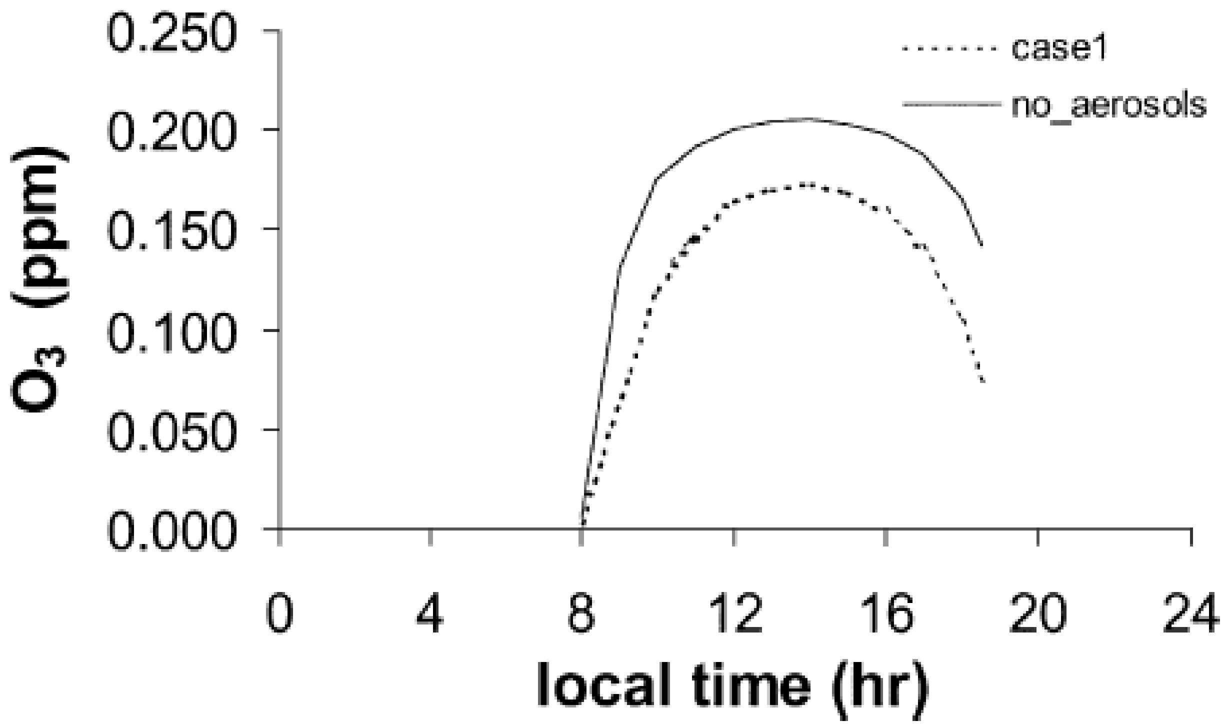


Fig. 8. Ozone concentrations predicted by KINMOD using photolysis rates (NO_2, O_3 and HCHO) computed with no aerosols (thin solid curve) and with Case 1 aerosols (dotted curve).

Castro et al. 2001

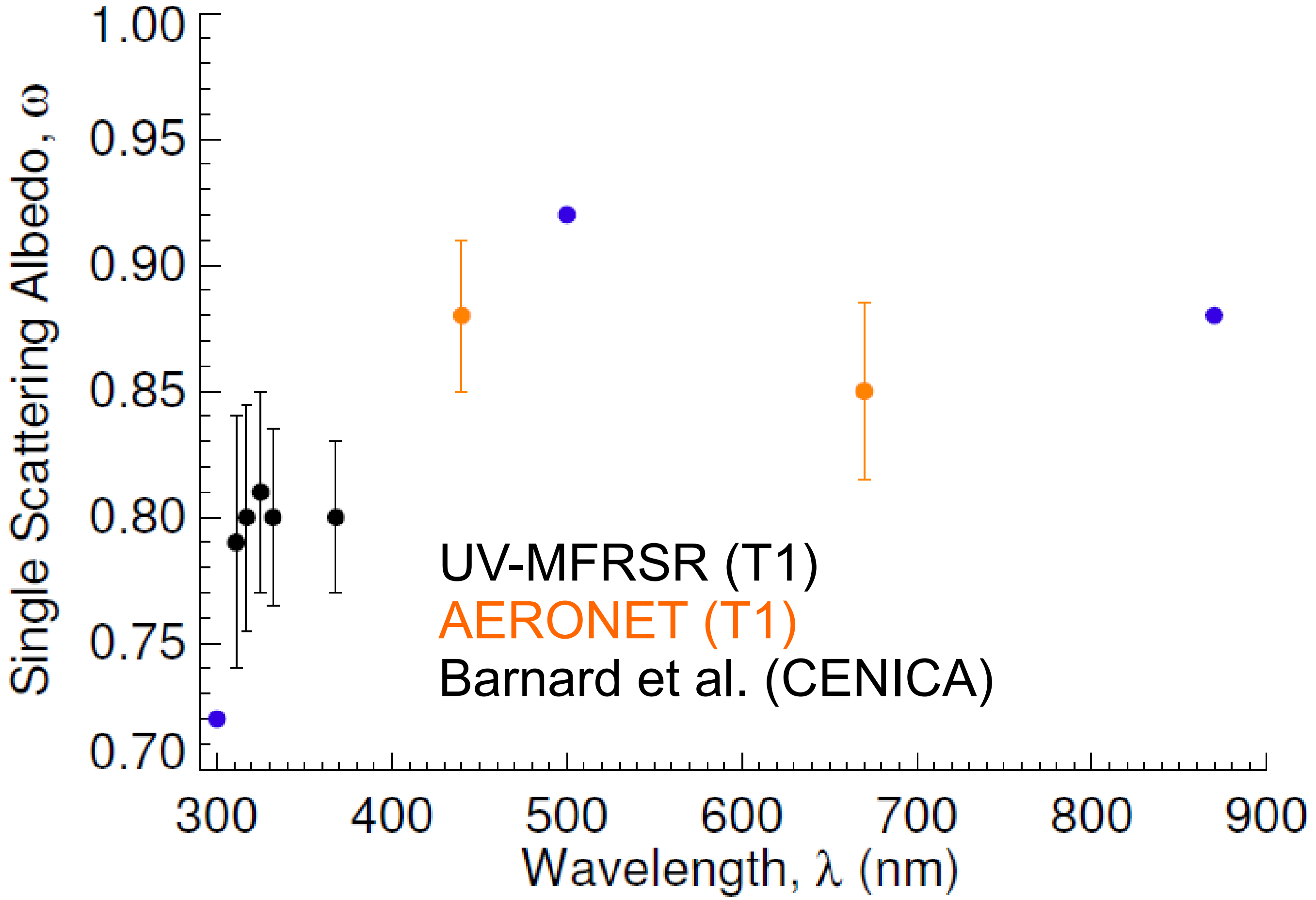
Vertical Structure of Aerosol Effects

NO2 Photolysis Frequency

19N, April, noon, AOD = 1 at 380 nm

Castro et al. 2001

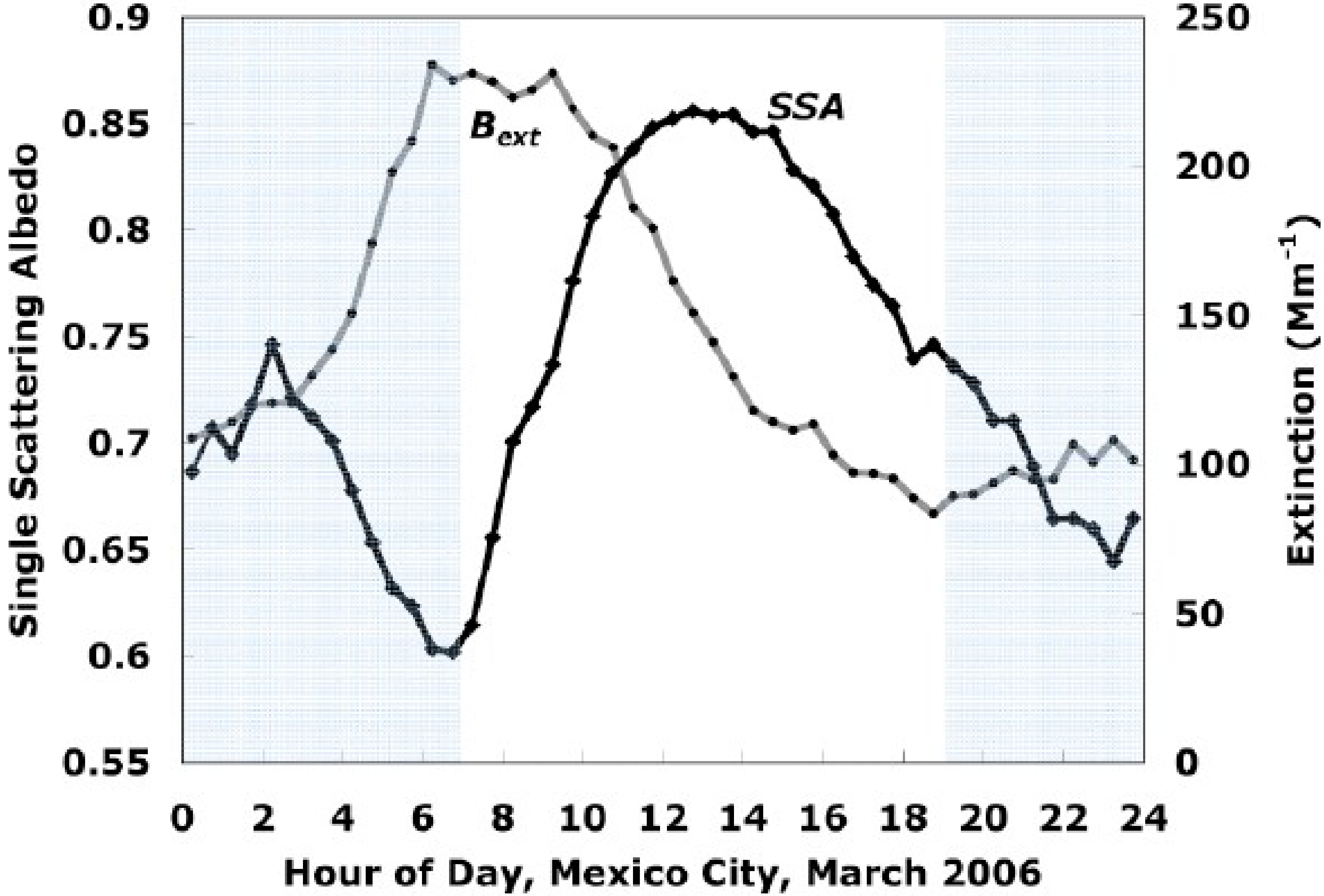
Aerosol Single Scattering Albedo
Mexico City



Corr et al., 2009

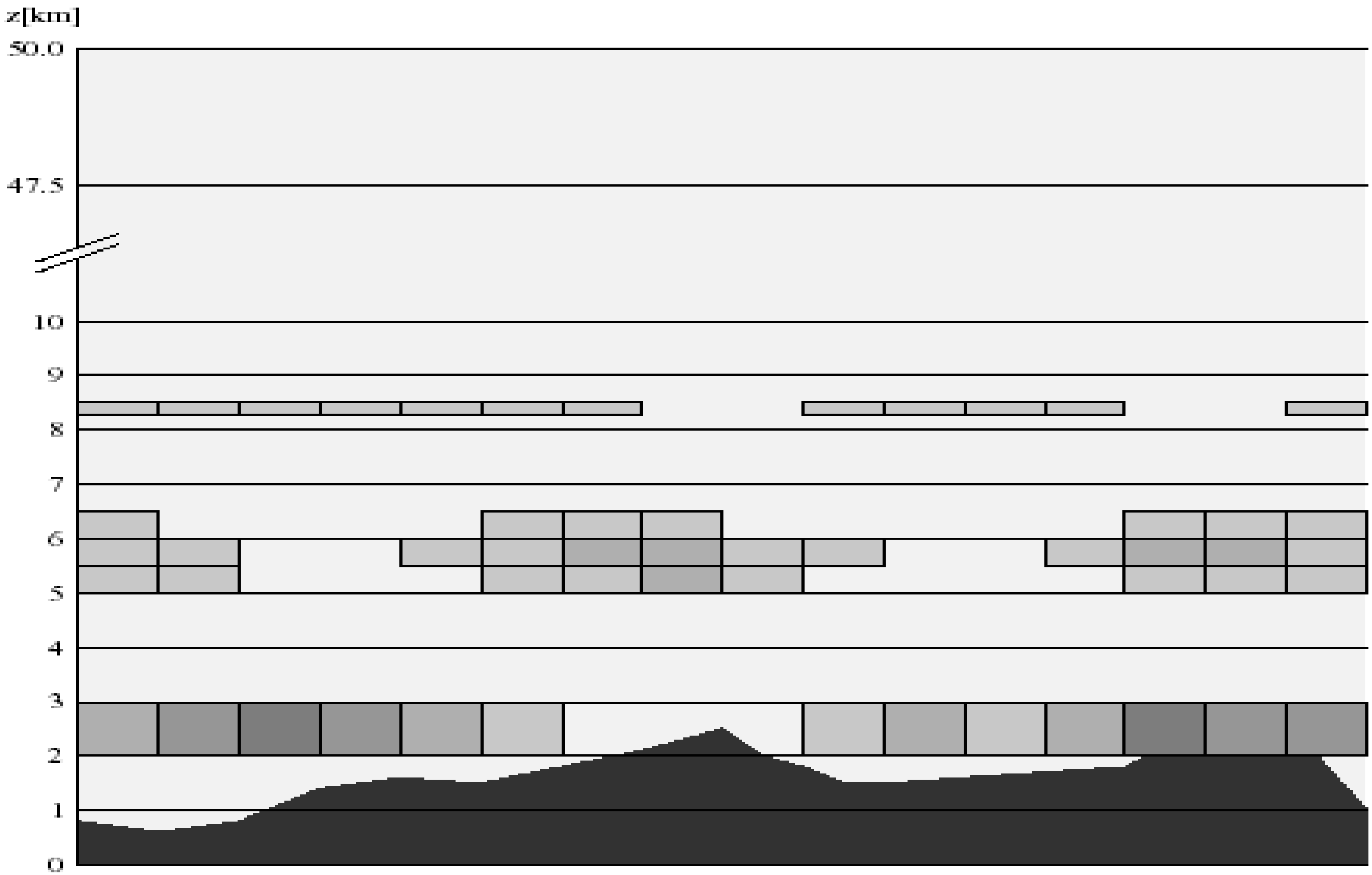
DIURNAL CYCLE OF AEROSOL OPTICS

550 nm



Paredes-Miranda et al., 2008

Clouds



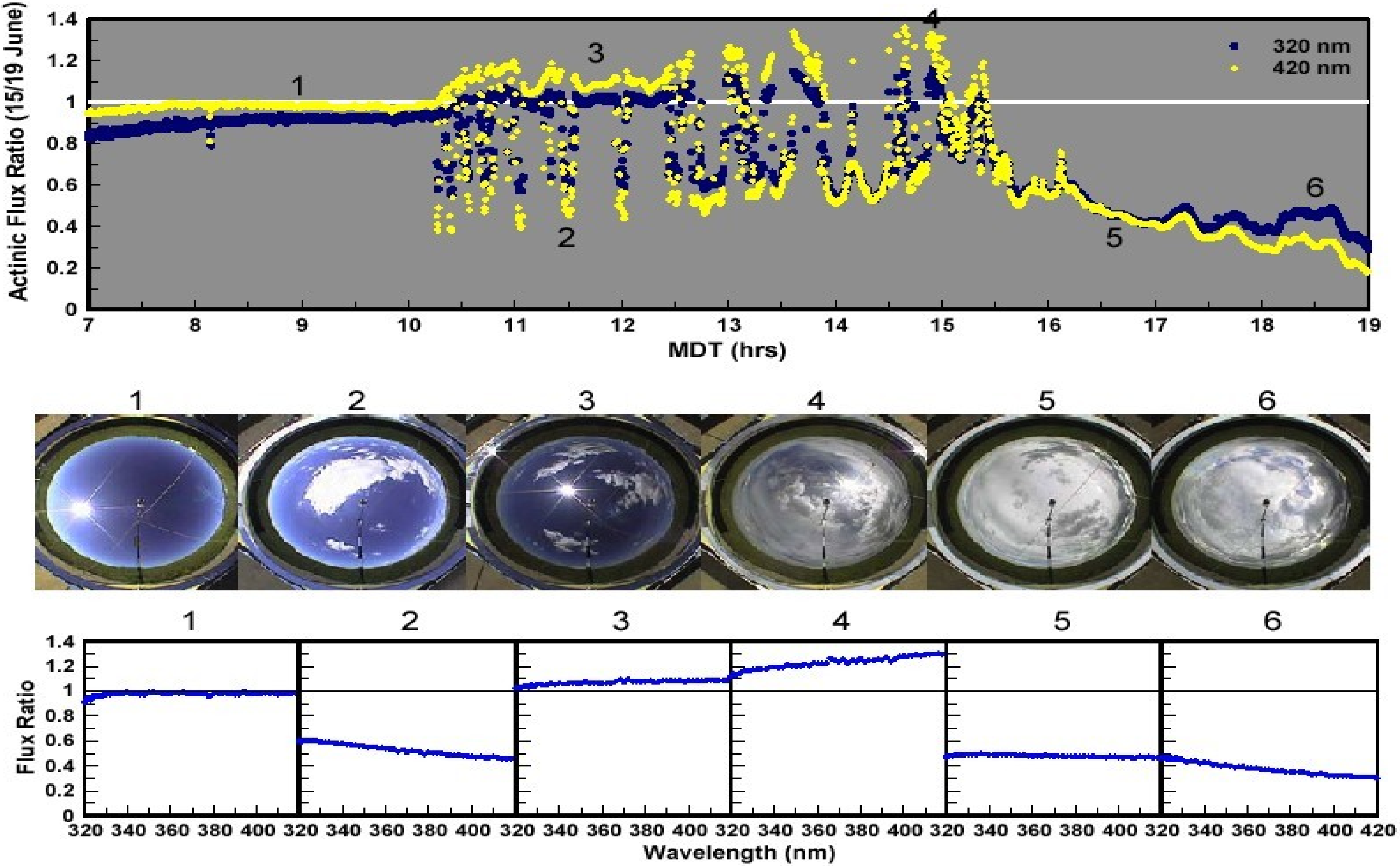
UNIFORM CLOUD LAYER

Above cloud: - hi g

EFFECT OF UNIFORM CLOUDS ON ACTINIC FLUX

Madronich, 1987

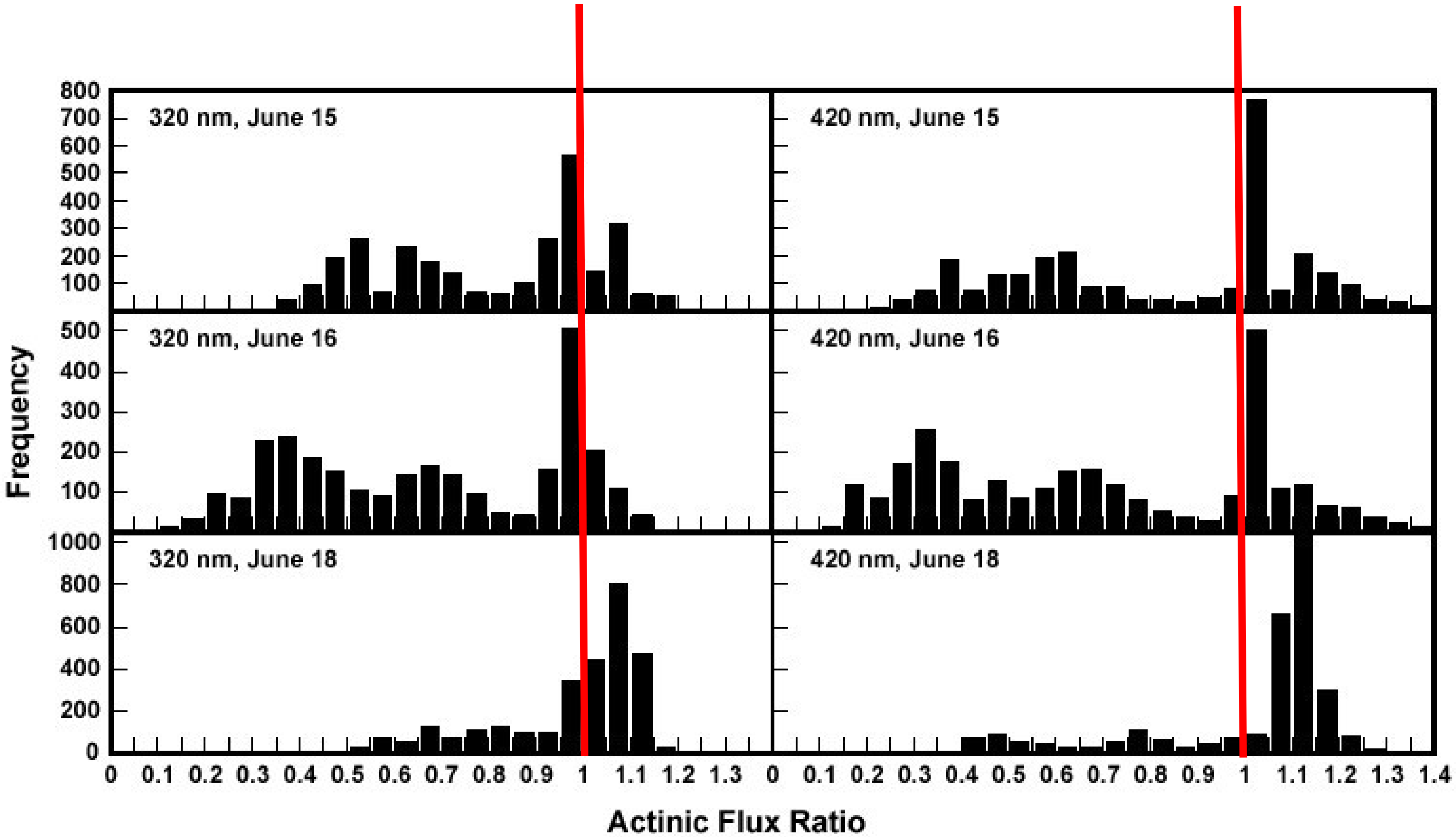
SPECTRAL EFFECTS OF PARTIAL CLOUD COVER



Crafword et al., 2003

PARTIAL CLOUD COVER

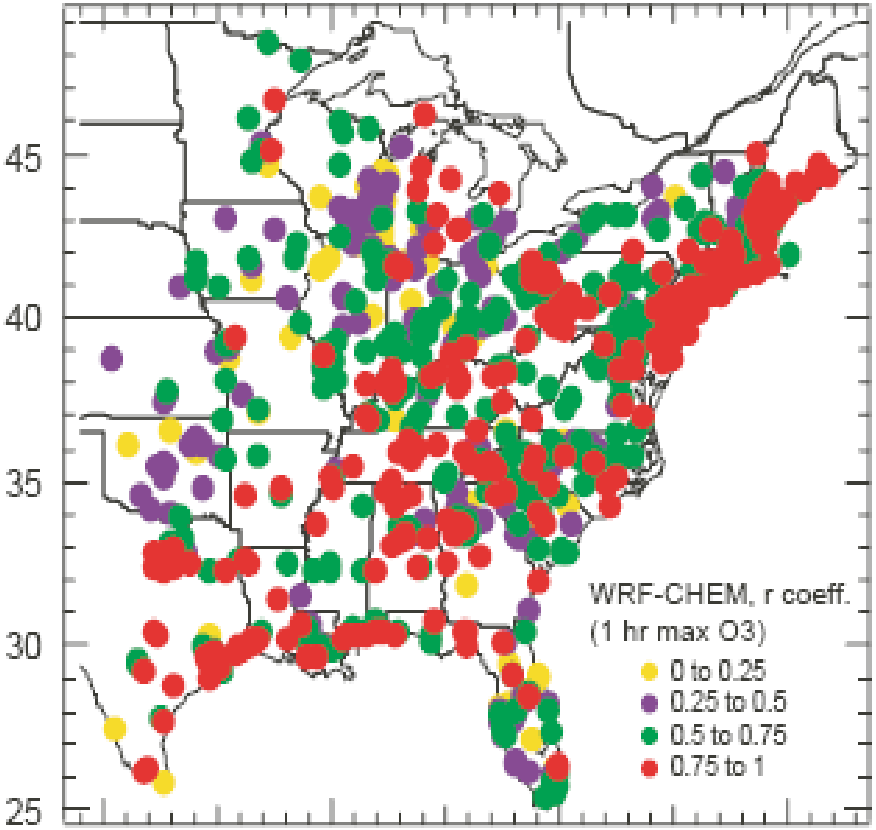
Biomodal distributions

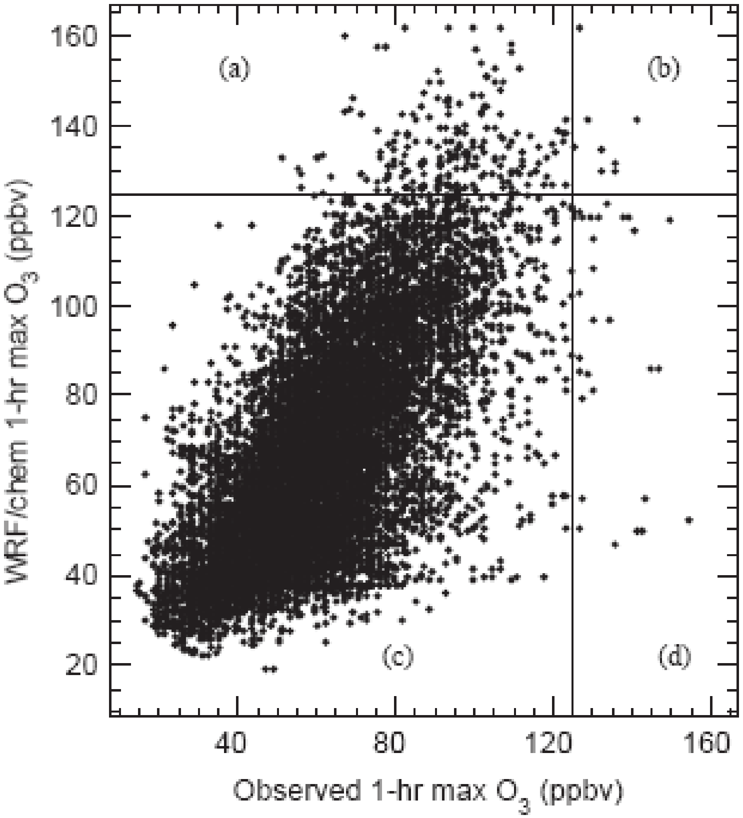


Crafword et al., 2003

WRF-Chem Regional O3 Prediction

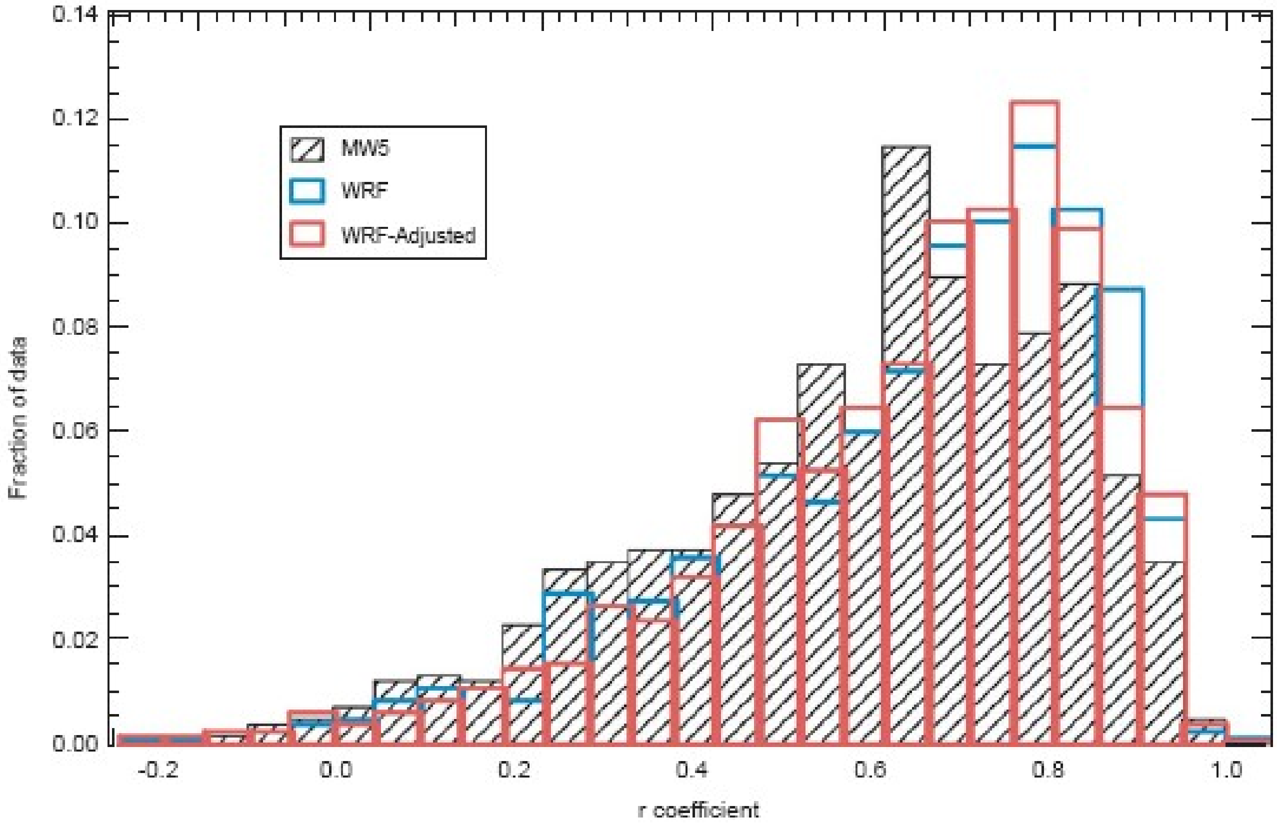
Observed daily 1-h maximum O3 for all EPA AIRNOW surface stations in the model domain, 21 July - 4 August 2002.





G.A. Grell et al. / Atmospheric Environment 39 (2005) 6957–6975

Correlation coefficient - R



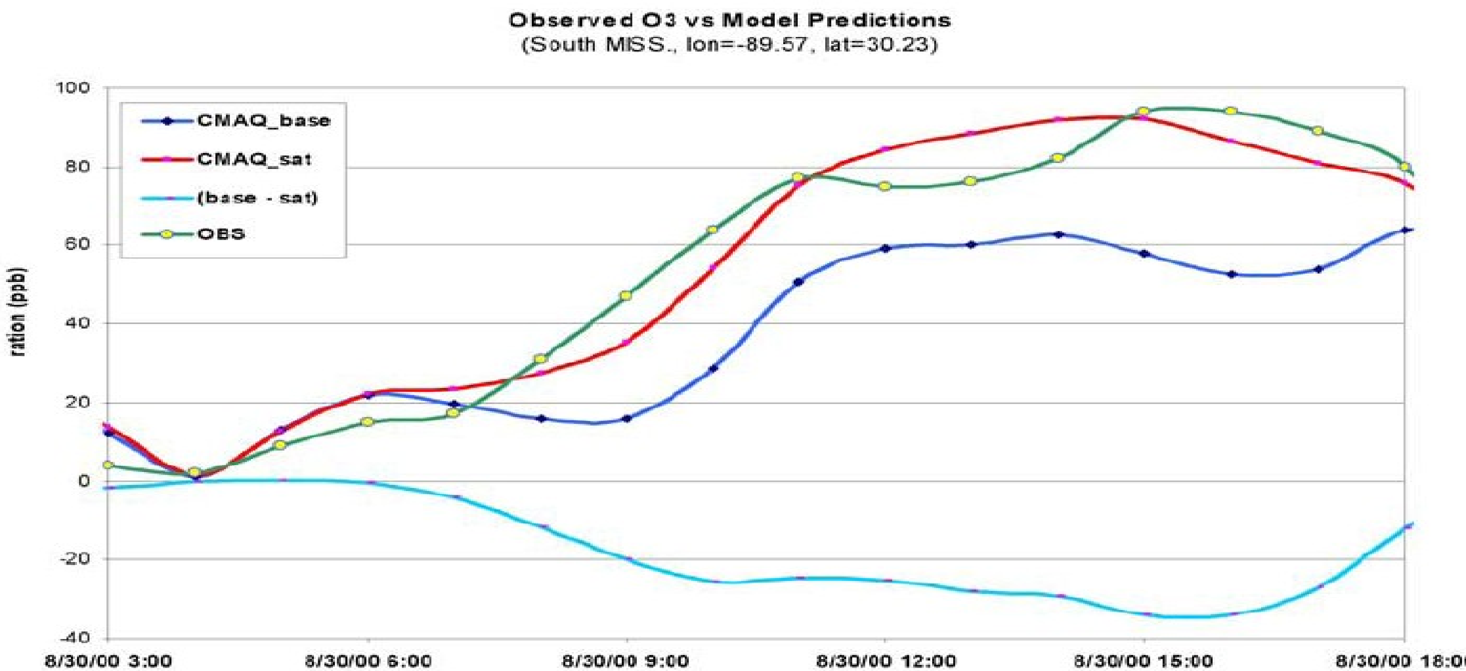
scatter mostly from clouds not modeled correctly !?

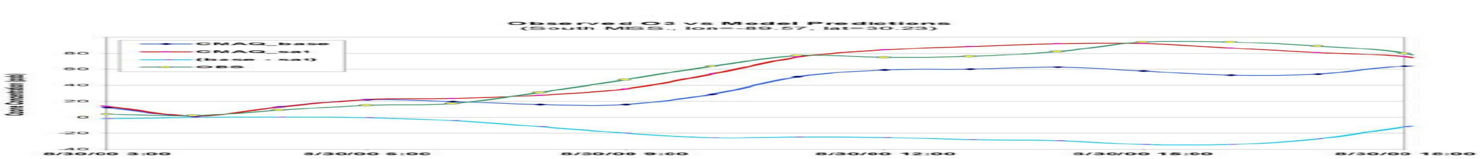
G.A. Grell et al. / Atmospheric Environment 39 (2005) 6957–6975

JOURNAL OF GEOPHYSICAL RESEARCH, VOL. 112, D10302, doi:10.1029/2006JD007422, 2007

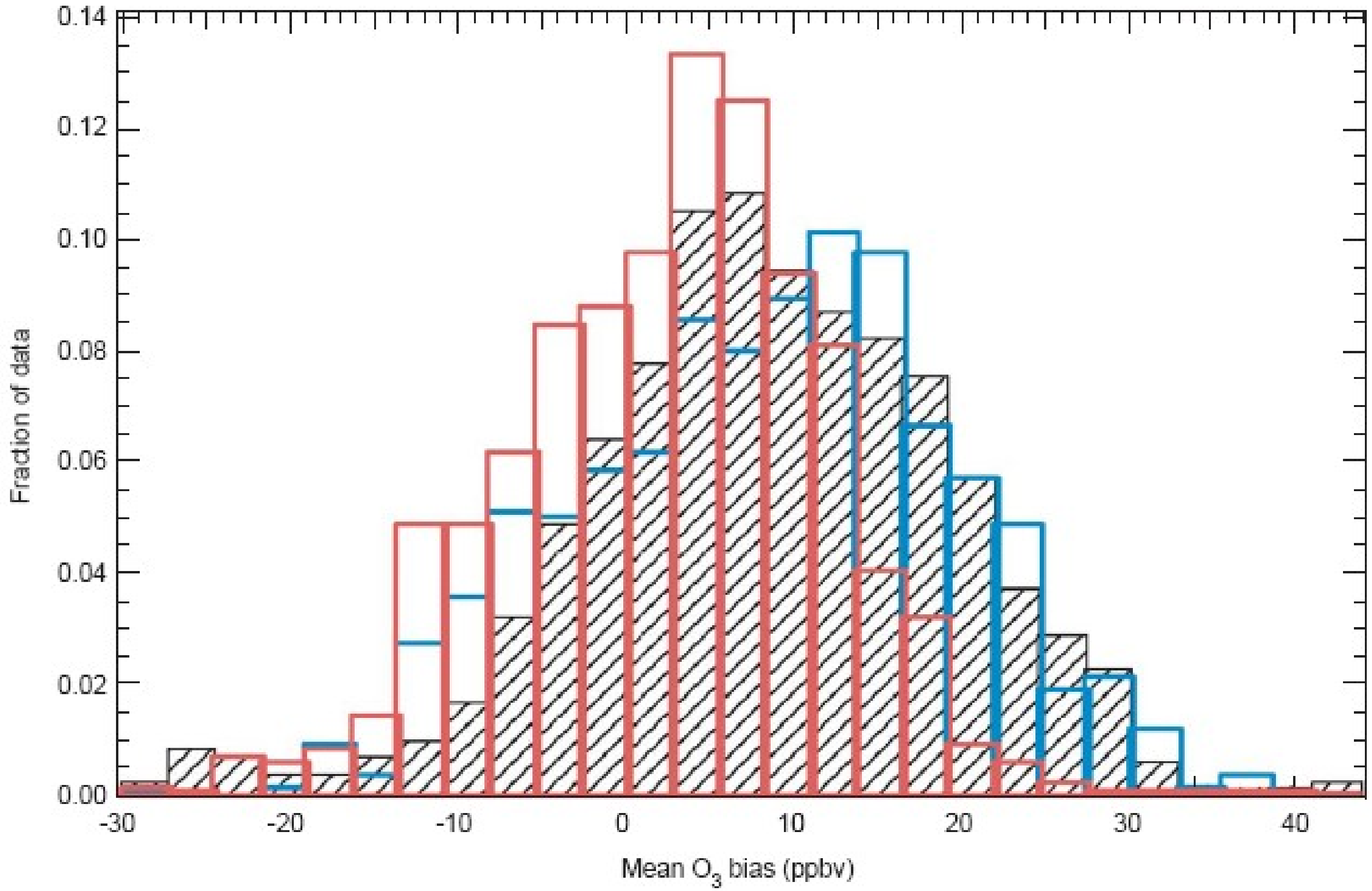
Correcting photolysis rates on the basis of satellite observed clouds

Arastoo Pour-Biazar,[1] Richard T. McNider,[2] Shawn J. Roselle,[3,4] Ron Suggs,[5] Gary Jedlovec,[5] Daewon W. Byun,[6] Soontae Kim,[6] C. J. Lin,[7] Thomas C. Ho,[8] Stephanie Haines,[1] Bright Dornblaser,[9] and Robert Cameron[10]





Mean Bias



bias mostly from aerosols not modeled correctly !?

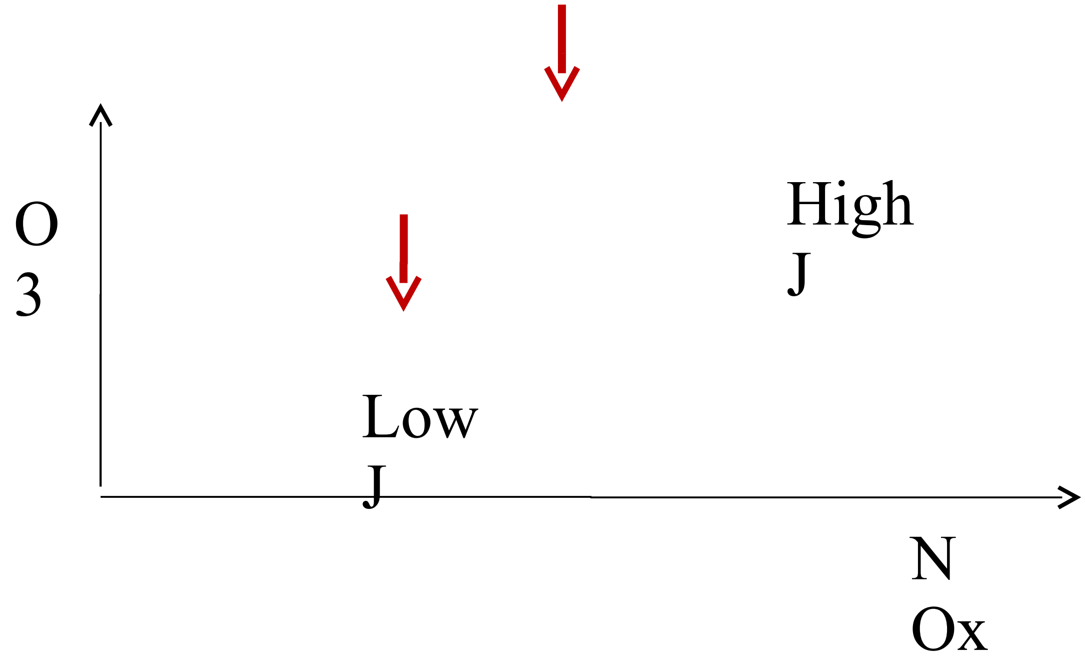
G.A. Grell et al. / Atmospheric Environment 39 (2005) 6957–6975

Problems and Opportunities

- O3 productions is
  - sometimes NOx limited
  - sometimes VOC limited
  - always photon limited
- Pollution affects photon availability (10-30% reductions are not uncommon).
- Aerosols and clouds change the vertical gradient of photochemistry
  - usually brighter above, dimmer below (but not always)

- UV properties of aerosols are poorly known
  - Composition
  - Size distributions
  - Morphologies, mixing states
  - Vertical distribution

- VOC-NOx-photon interactions: Photon availability may change NOx-limited transition point:



- Delay of reactivity: slower urban photochemistry allows more export of precursors for regional oxidants.

- Regional photochemistry may be accelerated by scattering aerosols (Dickerson et al., 1997)

- Clouds: need improved cloud statistics for parameterizing optical properties. Also, how to deal with model vs. real clouds?

- Need evaluation of model J-values with in situ measurements under realistic conditions. Need to demonstrate closure through the vertical extent.