8-hr Ozone National Ambient Air Quality Standard (NAAQS) Implementation

EPA

July 2, 2002

Pilat Edited

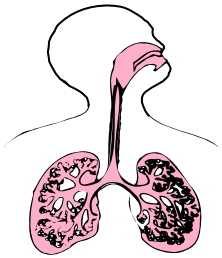
Different Considerations Used in Setting and Achieving NAAQS

Setting the Standards

- Health Effects
- Environmental Effects

Achieving the Standards

- Costs
- Time to attain the standards



Ozone-Related Health Effects of Concern

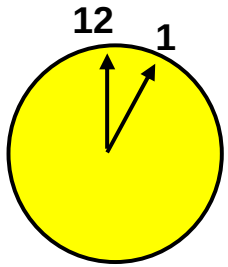
- Difficulty in breathing, shortness of breath
- Aggravated/prolonged coughing and chest pain
- Increased aggravation of asthma, susceptibility to respiratory infection resulting in increased hospital admissions and emergency room visits
- Repeated exposures could result in chronic inflammation and irreversible structural changes in the lungs, that can lead to premature aging of the lungs and illness such as bronchitis and emphysema
- Growing evidence suggests association with premature death

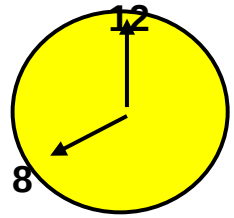
What is the New 8-Hour Ozone NAAQS?

The *New Ozone NAAQS* is an 8-hour standard at the *level* of *0.08 ppm* (parts per million by gaseous volume) with a *form* based on the *3-year average of the annual 4th highest daily maximum 8-hour average Ozone concentrations* measured at each ozone monitor within a geographical area.

Pilat Comment: Note that if there are no ozone monitoring instruments, Ozone NAAQS will not be exceeded. Hence some regions avoid installing ozone monitors.

O_3 NAAQS





Averaging Time	1-hr NAAQS	8-hr NAAQS
Avg time	1-hour	8-hour
Level	0.12 ppm	0.08 ppm
Form	exceedance-based	concentration-based
Air Quality Indicator	daily max 1-hr conc within day	daily max 8-hr conc starting within day
NAAQS Statistic	annual estimated exceedances	annual 4th high 8-hr daily max conc
Rounding	0.125 ppm--smallest number greater than the 0.12 ppm NAAQS level	0.085 ppm--smallest number greater than 0.08 ppm NAAQS level
Compliance period	three consecutive years	three consecutive years
Attainment Test	avg expected exceed'c rate <= 1.0	avg annual 4th high daily max 8-hour conc <= 0.08 ppm

Background

- EPA revised ozone standard July 1997; added 8-hr standard; indicated phase-out of 1-hr standard eventually.
- Initially announced implementation of 8-hr standard under less prescriptive "subpart 1" requirements of Clean Air Act, rather than the more prescriptive "subpart 2" requirements.
- Sued by a number of litigants in U.S. Court of Appeals for DC Circuit over the standard itself and EPA's implementation approach.
- In May 1999, Court ruled Clean Air Act contained an "unconstitutional delegation of authority" to EPA and also ruled EPA's implementation approach under subpart 1 was improper.
- EPA appealed to the Supreme Court.

More from the Supreme Court decision …

Background (continued)

- **In February 2001, Supreme Court upheld constitutionality of the standard-setting process in the Clean Air Act, but ruled that EPA's implementation approach was unlawful and that EPA could not ignore subpart 2 when implementing the 8-hr standard.**

- **Supreme Court recognized gaps in the subpart 2 scheme, however, and left it to EPA to develop a reasonable resolution of the roles of subparts 1 and 2 in implementing a revised ozone standard.**

- **Court said …"It may well be ... that some provisions of Subpart 2 are ill fitted to implementation of the revised standard."**

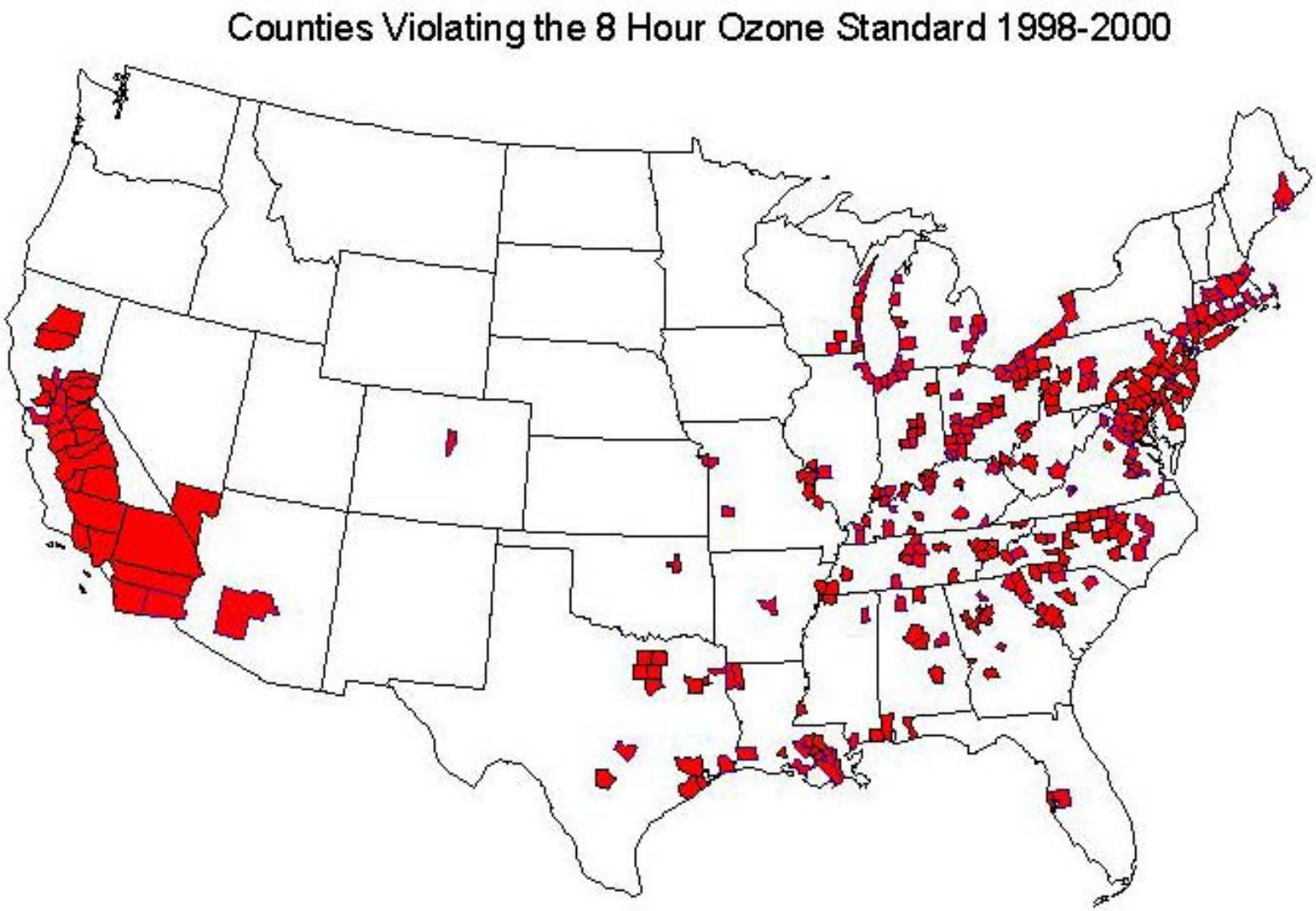
Background (continued)

Currently revising options for addressing Supreme Court ruling and for other implementation issues.

Taking input from stakeholders and the public at large from public meetings & written comments.

(Note these slides presented in July 2002)

what areas of the country exceed the 8-hr standards?

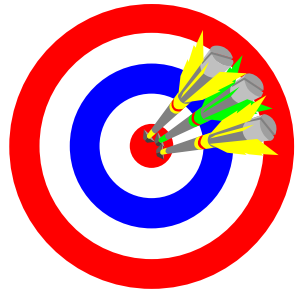


Principles Guiding EPA When Developing Approach to Meet O_3 NAAQS

Provide incentives for expeditious attainment of O_3 8-hour standard … avoid incentives for delay to protect public health.

- **Provide reasonable attainment deadlines.**
- **Have a basic, straightforward structure that can be communicated easily.**
- **Consistent with Clean Air Act and US Supreme Court decision, provide flexibility to states and EPA on implementation approaches and control measures**
- **Emphasize national and regional measures to help areas come into attainment and, where possible, reduce the need for more expensive local controls.**
- **Provide a smooth transition from 1-hr O_3 NAAQS to 8-hr O_3 NAAQS implementation**

Schedule



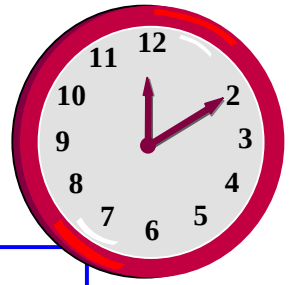
- **Propose rulemaking on the implementation approach in summer of 2002 … finalize the rule in mid-2003.**

- **During 2003 …. ask State/Tribes to update recommended designations … promulgate air quality designations in mid-2004.**

- **State implementation plans (SIPs) …. likely be due in the 2007 and 2008 time frame, with attainment dates ranging from 2007 to 2019 or longer.**

- **No plans for EPA to issue final designations of nonattainment areas until EPA issues a final implementation strategy for the O_3 standard.**

Potential Schedule for Implementing the 8-Hour Ozone NAAQS and Related Actions



Under Subpart 1	Under Subpart 2	Action
2003	Same	Final rule on implementation of 8-hour ozone NAAQS
2004	Same	Designation of 8-hour nonattainment areas Reinstate the NOx SIP call with respect to the 8-hour ozone NAAQS
2005	Same	Complete new modeling for additional "coarse grid" states. Make additional SIP calls as results dictate.
2007	2007/2008	8-hour ozone NAAQS SIP attainment demonstration submission date
2007-2008	Same	Compliance with full NOx SIP call budgets for 19 States (assumes EGU at 0.15 lbs/mm BTU) EGU compliance for any "newly added coarse grid" States
2007	Same	Assess impact of reductions from NOx SIP Call
	2007*	Part D/Subpart 2 attainment date - marginal areas (3 years after designation)**
2009*		Part D/Subpart 1 default attainment date**
	2010*	Part D/Subpart 2 attainment date - moderate areas (6 years after designation)**
	2013*	Part D/Subpart 2 attainment date - serious areas (9 years after designation)**
2014*		Potential 5-year attainment date extension**,***
	2019-2021*	Part D/Subpart 2 attainment date - severe areas (15-17 years after designation)**

* Two, 1-year extensions are possible.

**All potential attainment dates are "as expeditiously as practicable, but no later than" the dates presented.

***Based on severity of nonattainment & feasibility of control measures

Where EPA Is (July 2002)

- **Assessing comments from the public meetings & written comments**
- **Revising some options, considering new ones**
- **Starting to develop Federal Register proposed rule notice—planning to propose several alternative approaches**

Information on the Web including comments received ….

Office of
Air Quality Planning
and Standards

http://www.epa.gov/ttn/rto/ozonetech/o3imp8hr/o3imp8hr.htm

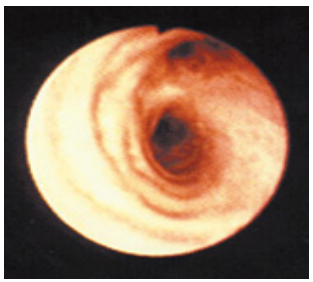
- **Photochemical smog**
  - **How it forms, key ingredients**
- **Photolysis**
  - **Photolytic cycle**
- **Role of reactive organics RO_2**
- **Control of smog**
- **EKMA or Empirical Kinetic Modeling Approach (note an EKMA graph enables the estimation of the NOx and VOC emission reduction needed to meet O_3 air quality standard)**

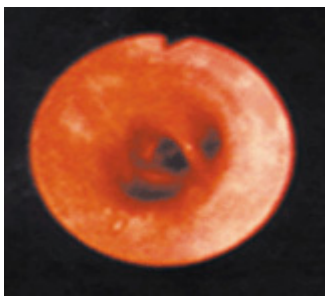
- **What are the essential ingredients for creating photochemical smog?**

Nitrogen oxides NOx , sun, reactive organics RO_2

Health effects

- **Reduce lung function**
- **irritate the respiratory system**
- **aggravate asthma**
- **Inflame & damage the linings of lung airways**





The top photo shows a healthy lung air way and the bottom photo an inflamed lung air way. Ozone can inflame the lung's lining, and repeated episodes of inflammation may cause permanent changes in the lung.

Photolysis

- **Energy for reaction comes from an absorbed photon**
  - **Only certain species photolyze**
  - **In troposphere, photolysis is initiated for light of 280–730 nm wavelengths**
- **Example: NO_2 dissociation**
  - **$NO_2 + h\nu \rightarrow NO + O^*$ ($k_{max} = 0.5\ min^{-1}$)**
  - **h = Planck's constant (6.63×10^{-34} J s)**
  - **ν = frequency of photon ($=c/\lambda$, where $c = 3 \times 10^8$ m/s)**
  - **Dissociation only occurs if photon possesses enough energy to break molecular bonds, $\lambda < 430$ nm for NO_2**

Primary photolytic Cycle

- **Which of the following is part of the photolytic cycle?**
  - **a. $NO + h\nu \rightarrow N + O$**
  - **b. $O + NO \rightarrow NO_2$**
  - **c. $O_3 + NO \rightarrow NO_2 + O_2$**

$$NO_2 + h\nu \xrightarrow{1} O(3P)^* + NO$$

$$O(3P)^* + O_2 + M \xrightarrow{2} O_3 + M$$

Main source of ozone in troposphere

$$O_3 + NO \xrightarrow{3} NO_2 + O_2$$

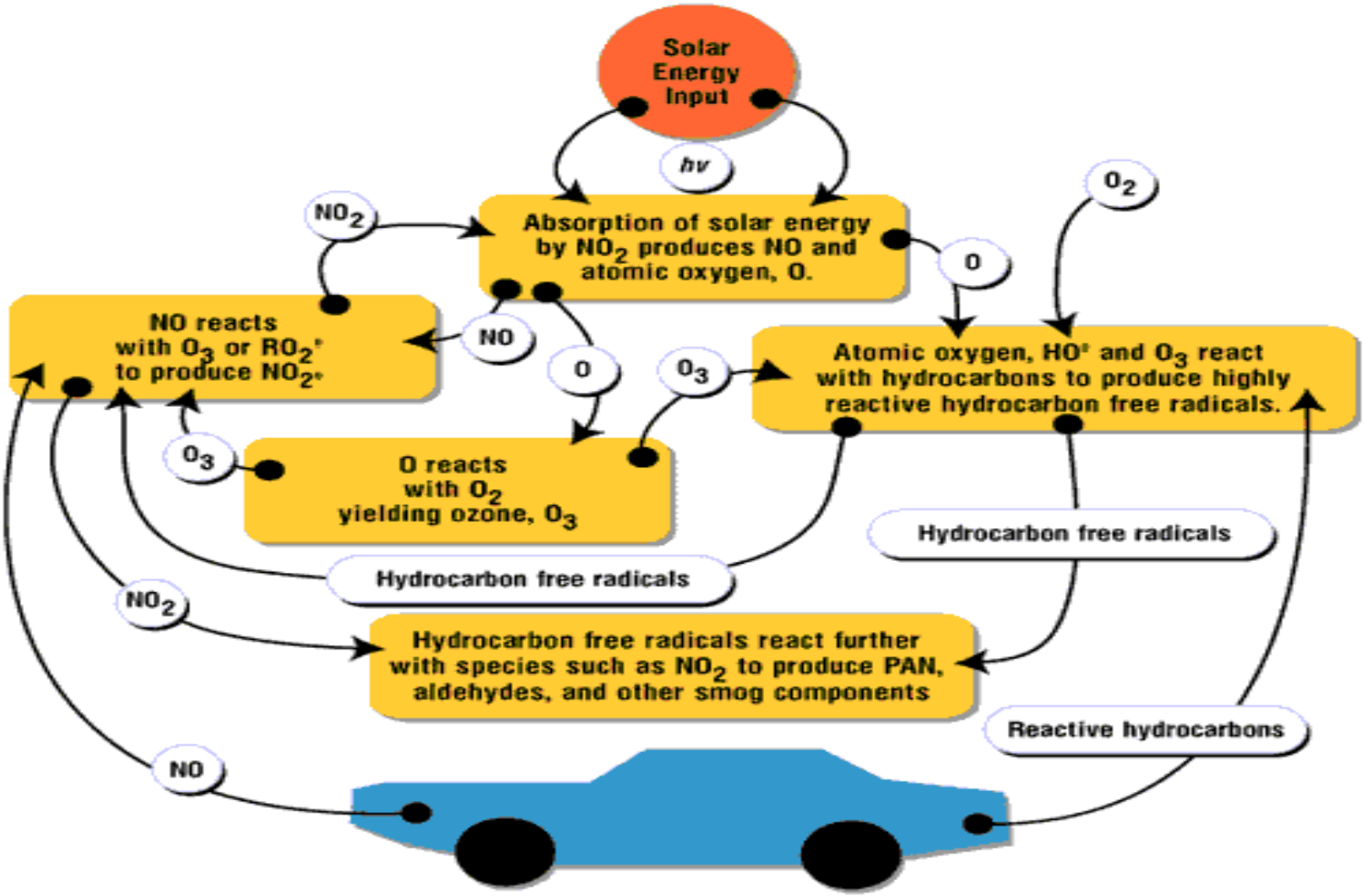
Ozone is higher than photolytic reactions predict!

- **Assuming photostationary state for O and O_3, then we can derive equation for O_3 formation:**

$$[O_3] = \frac{k_1[NO_2]}{k_3[NO]}$$

- **When NO_2 ~ NO, ozone is predicted by above to be around 20 ppb**
- **But in reality ozone concentration is much higher by as much as an order of magnitude -**

- **Hydrocarbons are source of radicals that convert NO to NO_2**
  - **Increase rate at which O_3 is produced by increasing NO_2**
  - **Decrease rate at which O_3 is scavenged by decreasing NO**



Reactive organics RO_2 provides a shortcut to NO_2 production that does not consume ozone - so ozone accumulates

Control of Ozone Smog

- **Ozone smog is a Secondary air pollutant**
- **Must control primary emissions of O_3 precursors to control smog: HCs, NOx**
  - **source of HCs: solvents, cars, trucks, industrial sources**
  - **source of NOx: cars, trucks, all combustion, power plants,**
  - **Analyze system using EPA's EKMA or Empirical Kinetic Modeling Approach**
  - **Relates changes in HCs and NOx emissions to changes in maximum ozone concentration**
  - **EKMA diagram can be used to estimate reductions in HCs and NOx concentrations in air needed to reduce ozone air concentrations to NAAQS.**

Weekend/Weekday Ozone Observations in the South Coast Air Basin

Sponsored by

National Renewable Energy Laboratory and Coordinating Research Council

Eric Fujita, Robert Keislar, and William Stockwell
Desert Research Institute
University and Community College System of Nevada
Reno, Nevada

Paul Roberts, Hilary Main, and Lyle Chinkin
Sonoma Technology, Inc.
Petaluma, CA

Weekend/Weekday Ozone Effect Workshop
Sacramento, CA
November 16, 1999

What do we know about the weekend/weekday ozone effect in the South Coast Air Basin?

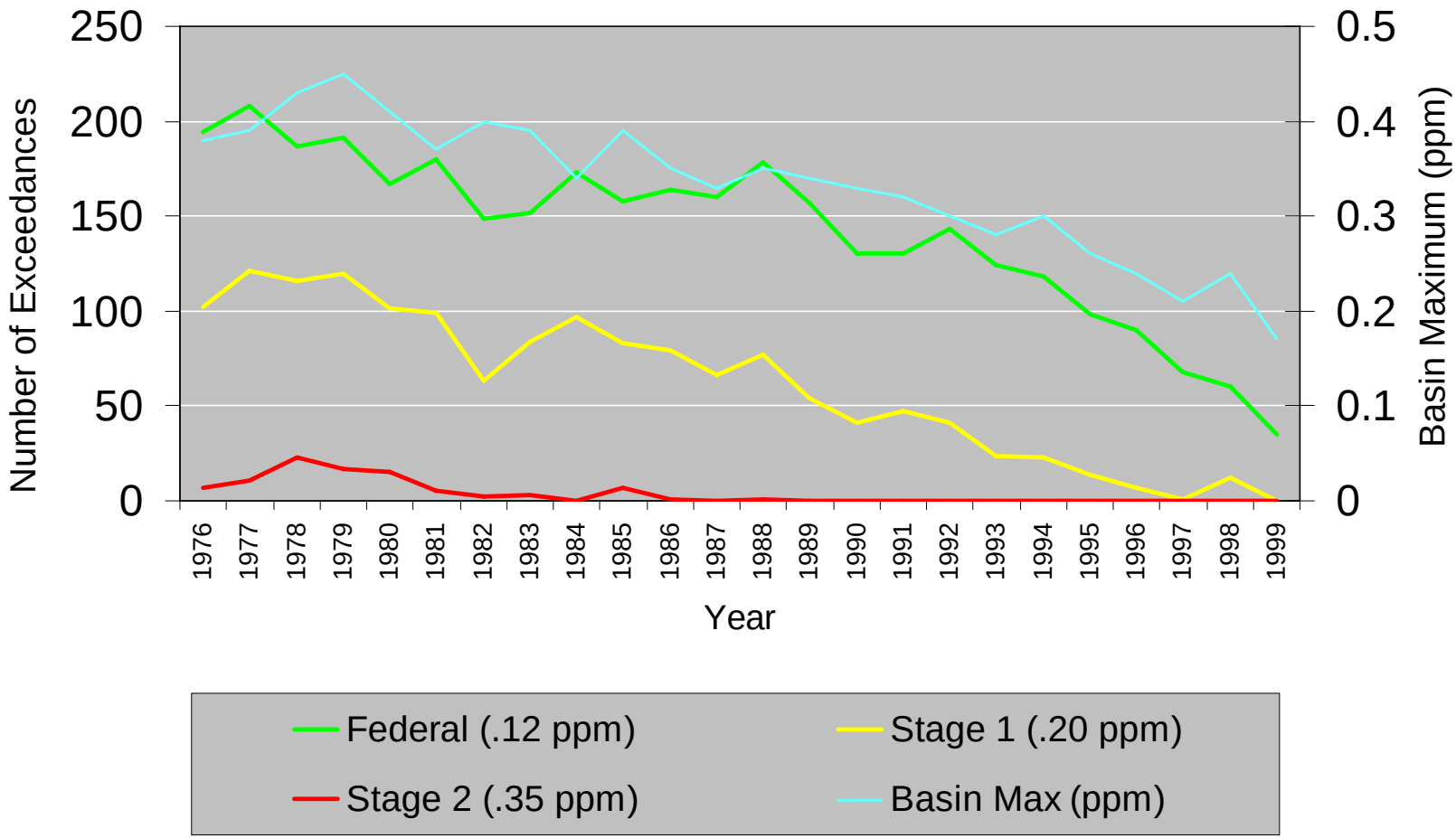
- **During 1986-93, ozone episodes occurred significantly more often on Saturdays than on Sundays through Wednesdays**
- **During 1992-94, large increases in ozone from Friday to Saturday (~30%) in many sites in central So C Air Basin, no change or slight decrease from Saturday to Sunday (Austin and Tran, 1999).**
- **Many sites show a "Sunday effect" in the 1996-98 period**
- **Weekend effect is least pronounced at transport sites further downwind (e.g., Lake Gregory, Banning, Perris, & Santa Clarita).**
- **Decreases in peak ozone levels from the mid-1980 to mid-1990 were greatest in western and central portions of the SoCAirBasin. Greater reductions on weekdays than on weekends & hence the differences in Week Day vs. Week End ozone maxima are larger now than the 1980s**
- **Similar WeekEnd/WeekDay effect in San Francisco Bay Area and cities in northeastern U.S., no effect in Sacramento, reserve effect in Atlanta**

What do we know about the weekend/weekday differences in VOC, NOx and PM in the South Coast Air Basin?

- **VOC, NOx and PM are all higher during weekdays.**
- **During 1986-93, average early morning NO_2 and NOx were lower by 20-25% and 30-50%, respectively on weekend days in the Coastal/Metropolitan region of the SoCAB. (Blier and Winer, 1996)**
  - **Morning NOx is highest on weekdays, followed by Sat and lowest on Sunday.**
  - **Sat afternoon levels are comparable to or slightly lower than weekday levels.**
  - **Saturday evening levels tend to be lower than on Friday and roughly equal to or higher than the mean weekday evening levels.**
  - **NOx mixing ratios are lower on Sunday than other days for all hours except at midnight to 4 a.m. when they are comparable to weekdays.**
- **The reactivity of the ambient hydrocarbon mixture has dropped between 1995 and 1996. Reactivity appears slightly lower on weekends (Franzwa and Pasek, 1999).**
- **6 to 9 a.m.VOC/NOx ratios have decreased from 8 to 10 in 1987 (SCAQS) to 4 to 7 in 1997.**

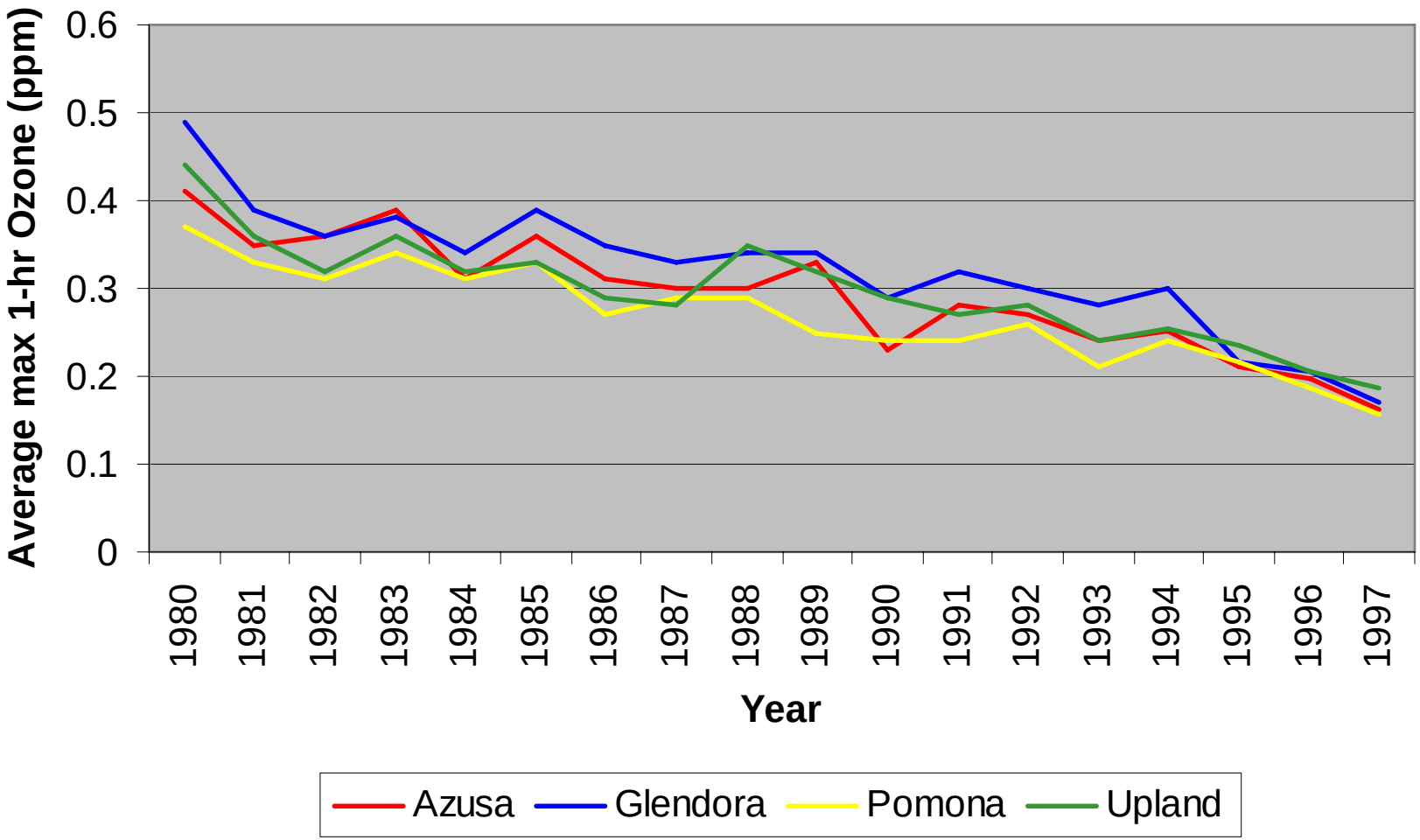
Historic Ozone Air Quality Trends

South Coast Air Basin (1976-1999)

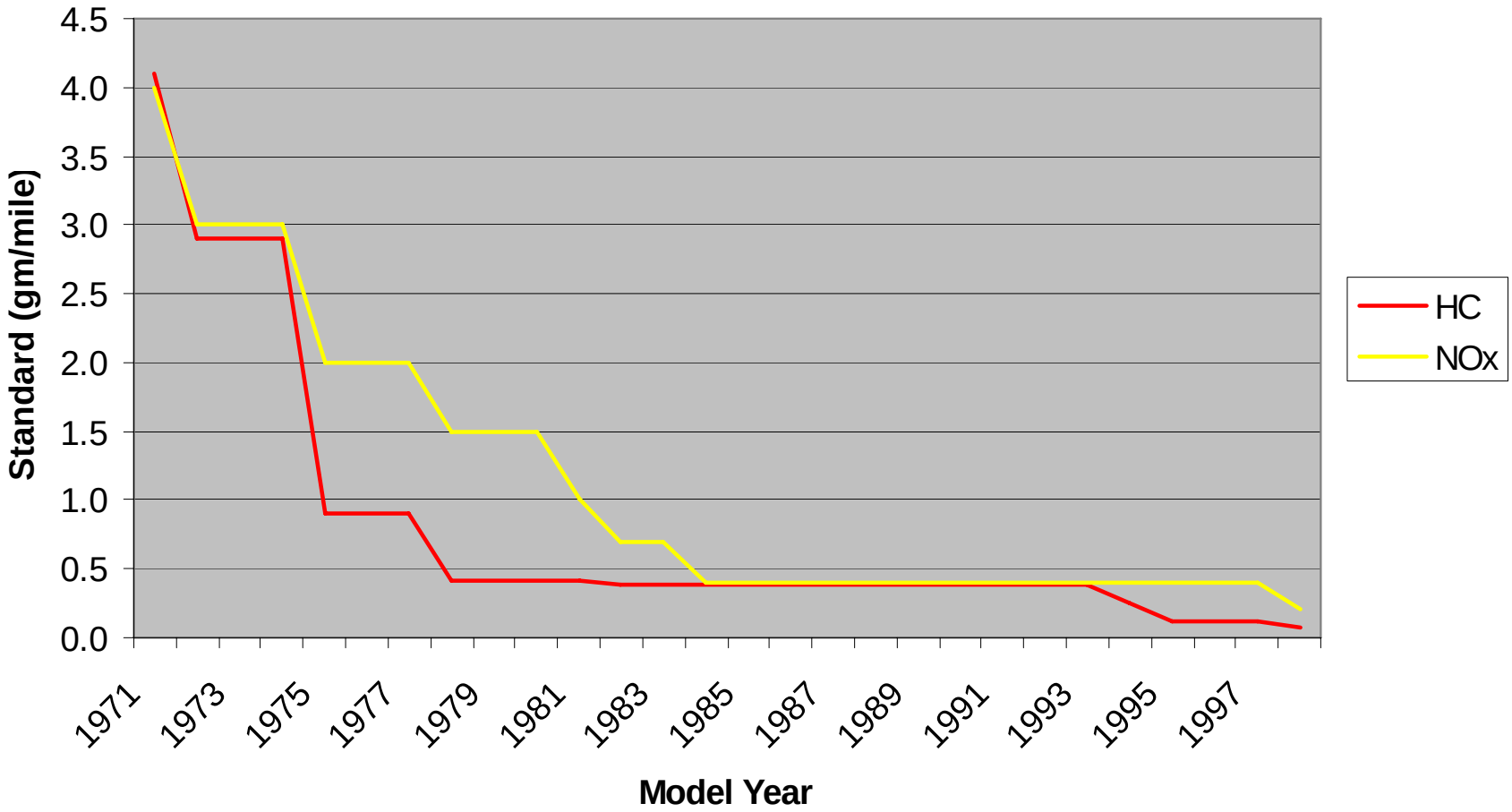


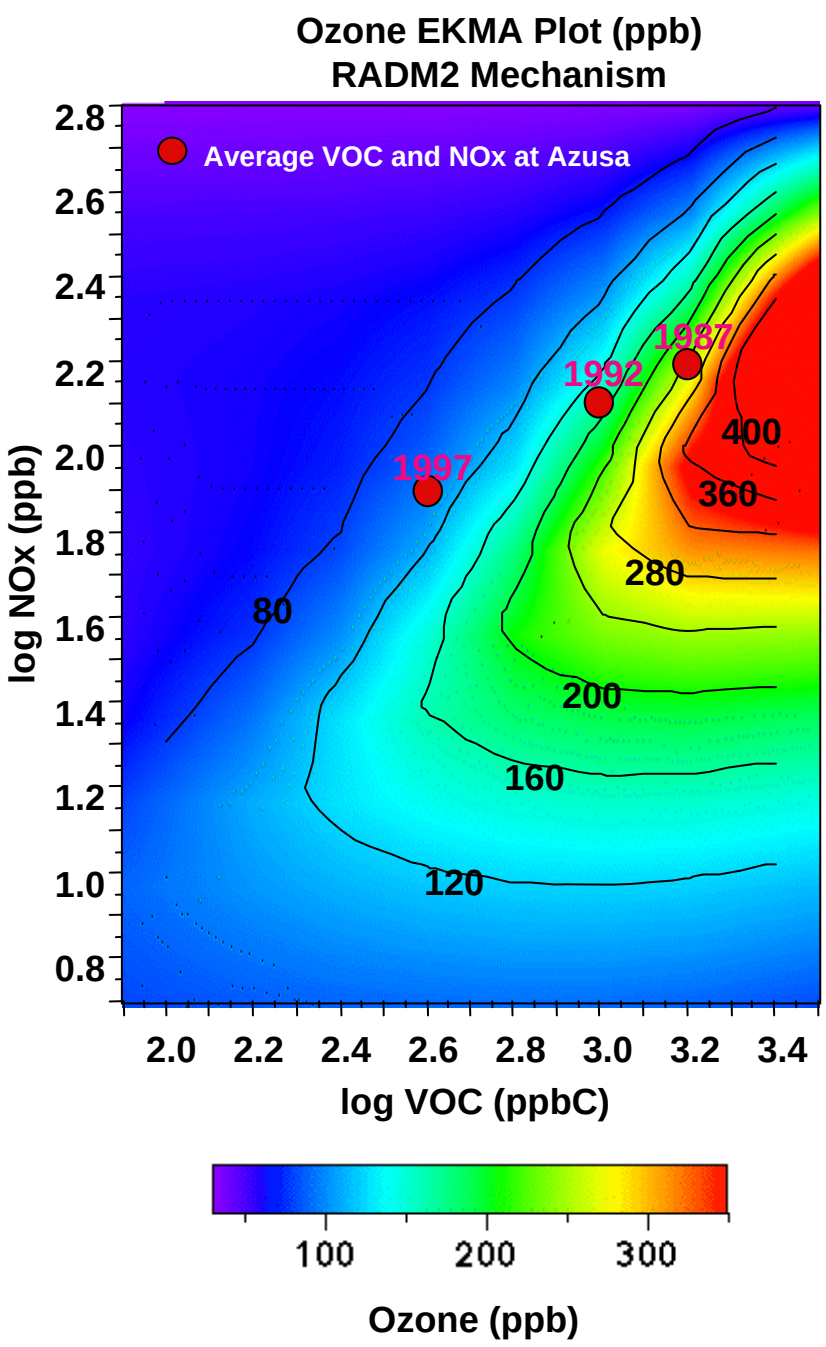
Historic Ozone Air Quality Trends

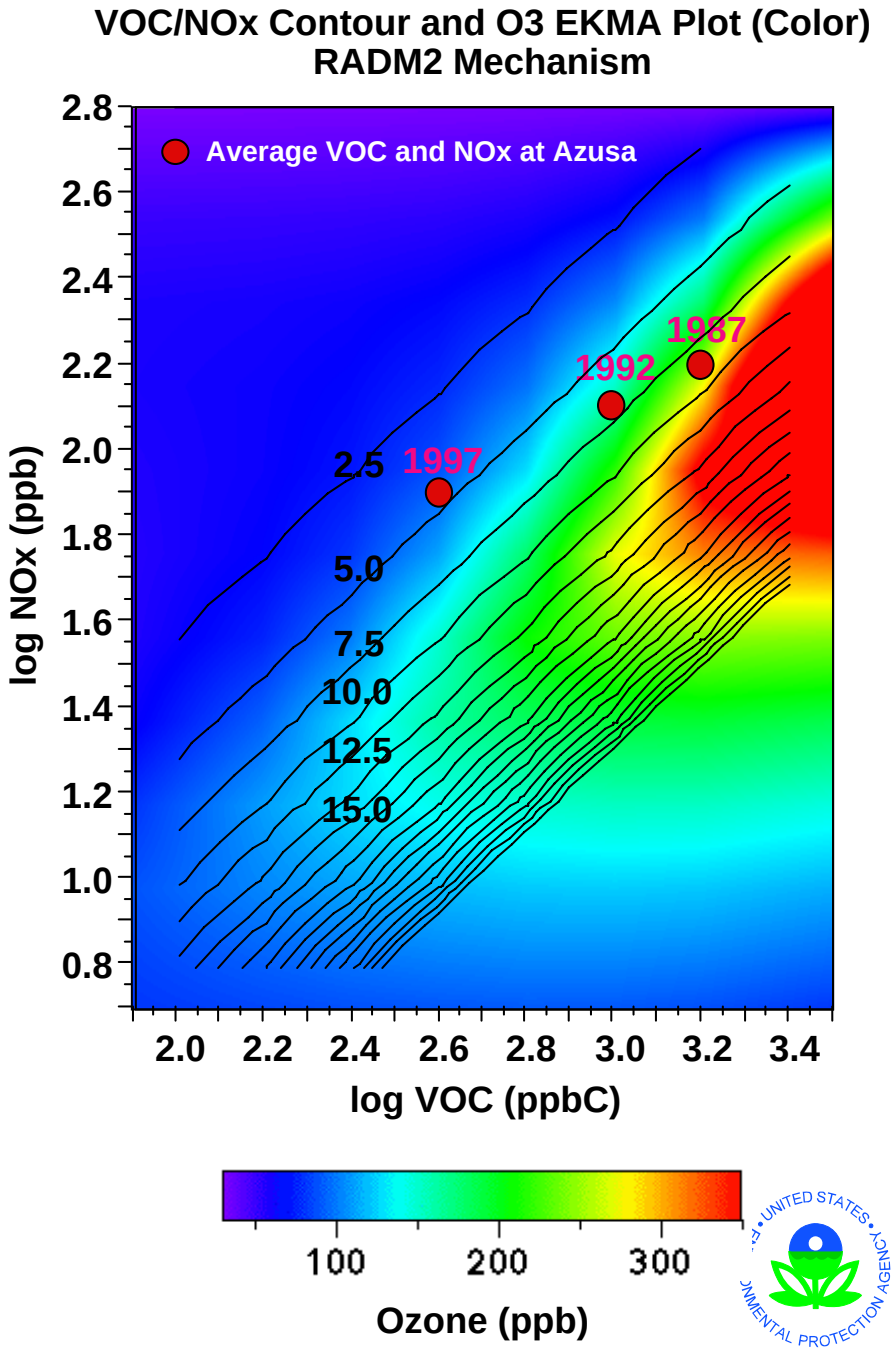
South Coast Air Basin (1980-1997) - CENTRAL



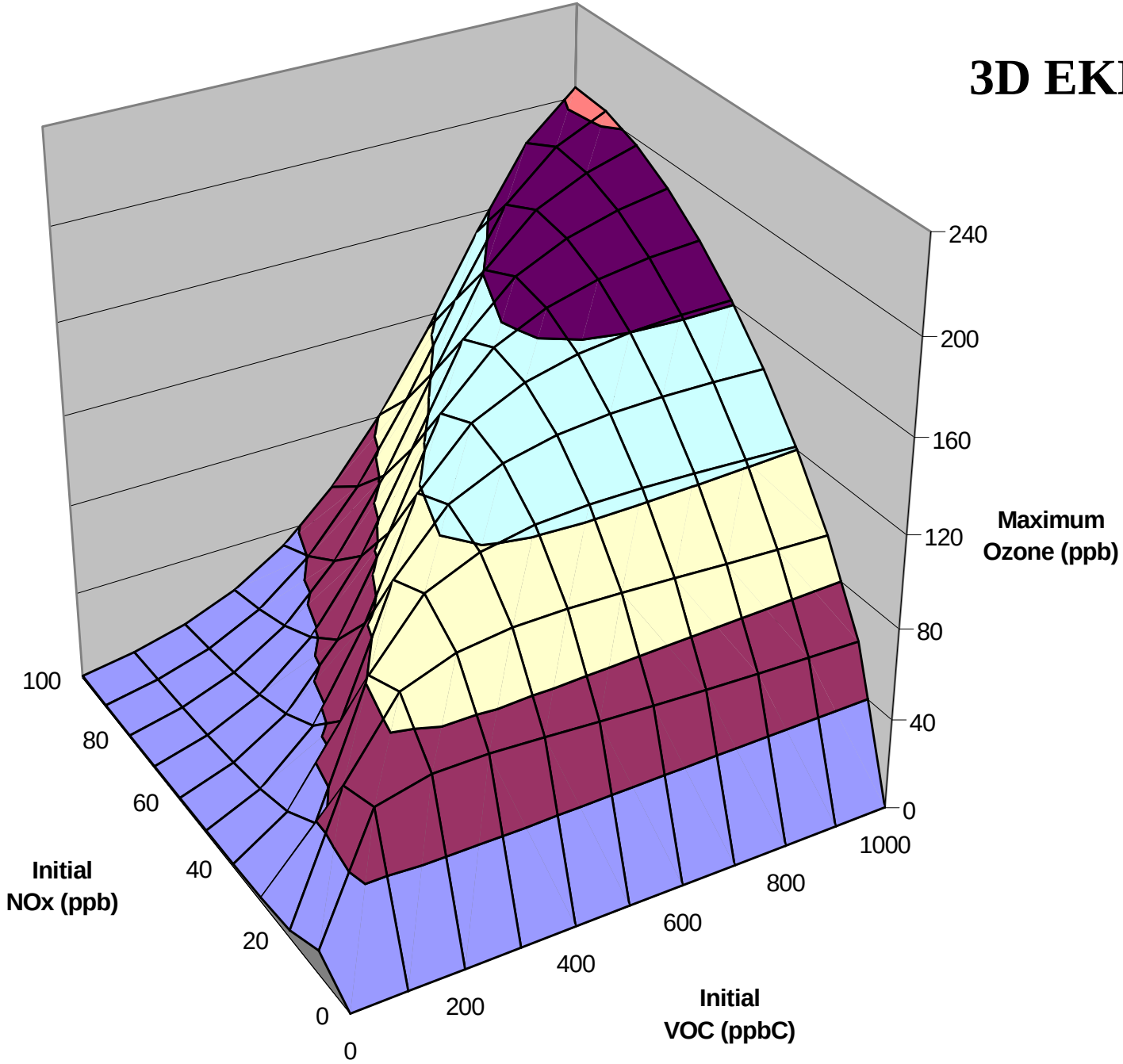
History of Light-Duty Vehicle Exhaust Emission Standards




Ozone EKMA Plot (ppb)
RADM2 Mechanism
Average VOC and NOx at Azusa
1997
1992
1987
80
120
160
200
280
360
400
log NOx (ppb)
log VOC (ppbC)
2.0 2.2 2.4 2.6 2.8 3.0 3.2 3.4
0.8 1.0 1.2 1.4 1.6 1.8 2.0 2.2 2.4 2.6 2.8
100 200 300
Ozone (ppb)


VOC/NOx Contour and O3 EKMA Plot (Color)
RADM2 Mechanism
Average VOC and NOx at Azusa
1997
1992
1987
2.5
5.0
7.5
10.0
12.5
15.0
log NOx (ppb)
log VOC (ppbC)
2.0 2.2 2.4 2.6 2.8 3.0 3.2 3.4
0.8 1.0 1.2 1.4 1.6 1.8 2.0 2.2 2.4 2.6 2.8
100 200 300
Ozone (ppb)

3D EKMA


240
200
160
120
80
40
0
Maximum
Ozone (ppb)
100
80
60
40
20
0
Initial
NOx (ppb)
0
200
400
600
800
1000
Initial
VOC (ppbC)

Factors Affecting the Magnitude and Spatial Extent of the Week End/Week Day Ozone Effect

- **Ozone formation depends on VOC, NOx and VOC/NOx ratios .**
  - **For VOC/NOx < 5.5, OH reacts more with NO_2, removing radicals and NOx to retard O_3 formation. Under these conditions, a decrease in NOx favors O_3 formation.**
  - **At low NOx mixing ratios, or sufficiently high VOC/NOx, decrease in NOx favors peroxy-peroxy reactions, which retard O_3 formation by removing free radicals from the system.**
  - **At a given level of VOC, there exists an optimum VOC/NOx ratio at which a maximum amount of ozone is produced. For ratios less than this optimum ratio, increasing NOx decreases ozone. This situation occurs more commonly in urban centers and is the case for most of the central SoCAB.**
- **Week End/Week Day differences in VOC and NOx emissions patterns (Diurnal and Spatial Distribution).**
- **Transport and**
  - **Increasing mixing height due to surface heating reduces [VOC] and [NOx].**
  - **Horizontal transport increases VOC/NOx ratios due to more rapid removal of NOx than VOC.**

The observed "weekend effect" in the South Coast Air Basin arises from differences in ozone forming potential due to day-of-the-week changes in ROG and NOx emissions. Variations in meteorology affect the magnitude

and spatial extent of the WE/WD ozone effect within the basin.

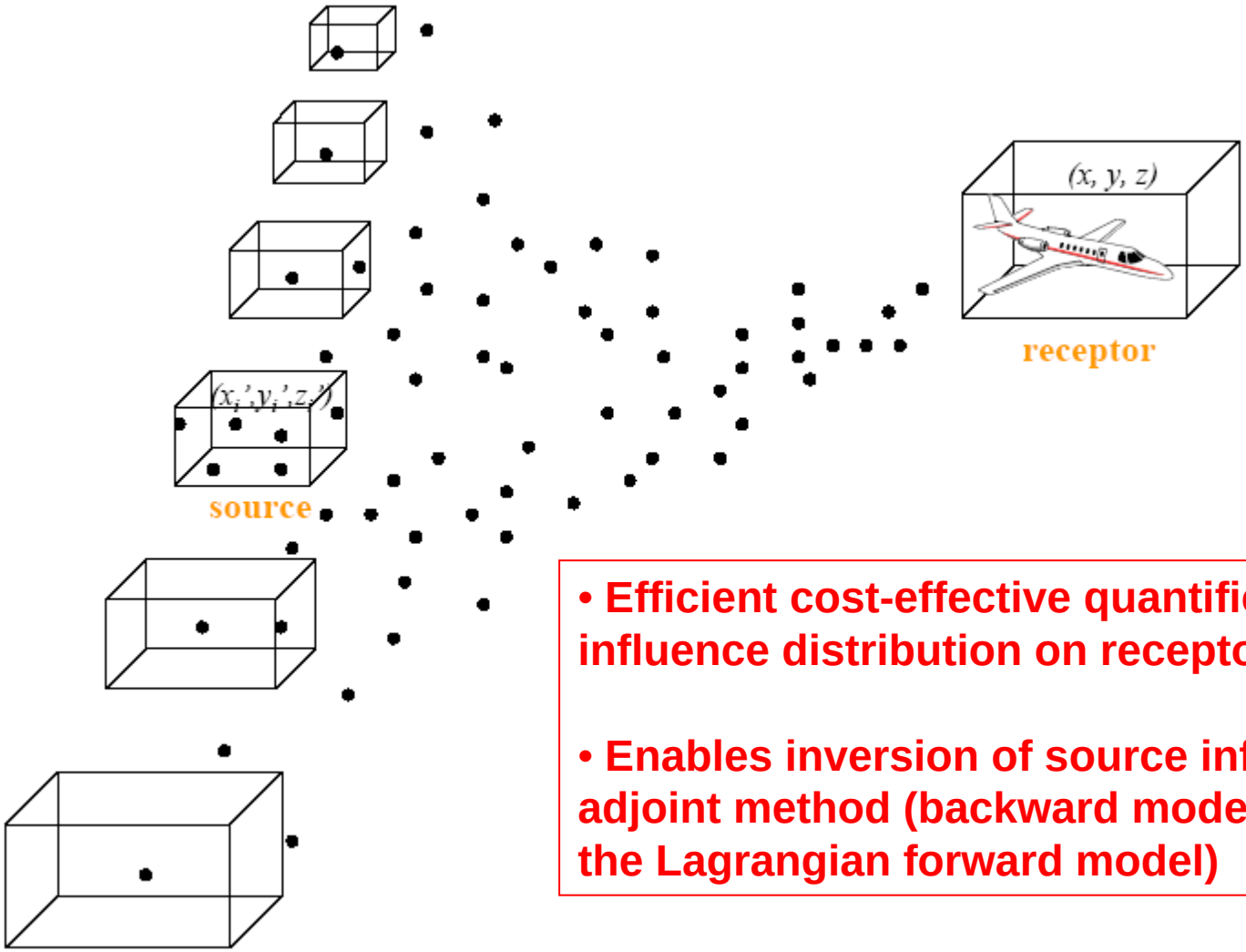
Preliminary Hypotheses

1. **Ozone formation in SoCalif Air Basin, particularly the western & central portions of the basin, is VOC-sensitive with respect to O_3 formation. VOC/NOx ratios are higher on weekends due to Week End/Week Day changes in emissions resulting in greater O_3 forming potential despite lower [VOC] and [NOx] on weekends.**
   - **The weekend effect is greater where $\Delta [O_3]_{max}/\Delta$[VOC] is greater during weekdays than during weekend days.**
   - **Week End/Week Day effect is most pronounced in area of the basin with the greatest NOx disbenefit (i.e., most VOC-limited on weekdays).**
2. **The magnitude of the weekend effect is a function of the O_3 forming potential and the time available for O_3 formation before dilution offsets O_3 formation.**
3. **The "weekend effect" is less pronounced in the eastern portion of the SoCAirB where Week End/Week Day differences in VOC and NOx emissions are masked by emission transport. Transport causes higher VOC/NOx ratios due to more rapid removal of NOx versus VOC as the emissions are transported toward the eastern side of the Basin.**
4. **Overnight carry-over of O_3, VOC and NOx from Friday and Saturday nights are greater than during other days of the week. Increased carryover is greater for VOC than for NOx. This affects the O_3 forming potential of the ambient air.**

Global Models Of Atmospheric Composition

LAGRANGIAN RECEPTOR-ORIENTED MODELING

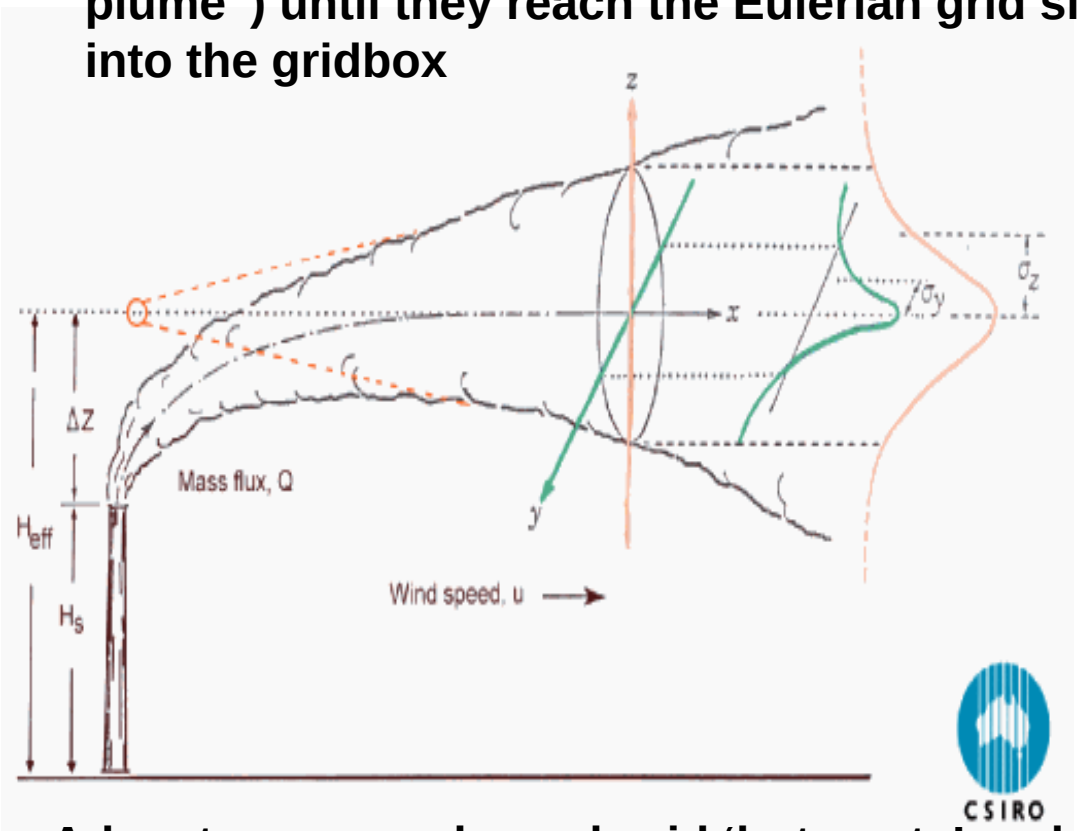
Run Lagrangian model backward from receptor location, with points released at receptor location only (Lagrangian follows the flow of a fluid parcel whereas Eulerian looks at fluid flow at a fixed location)



- **Efficient cost-effective quantification of source influence distribution on receptor ("footprint")**
- **Enables inversion of source influences by the adjoint method (backward model is the adjoint of the Lagrangian forward model)**

Embedding Lagrangian Plumes in Eulerian Models

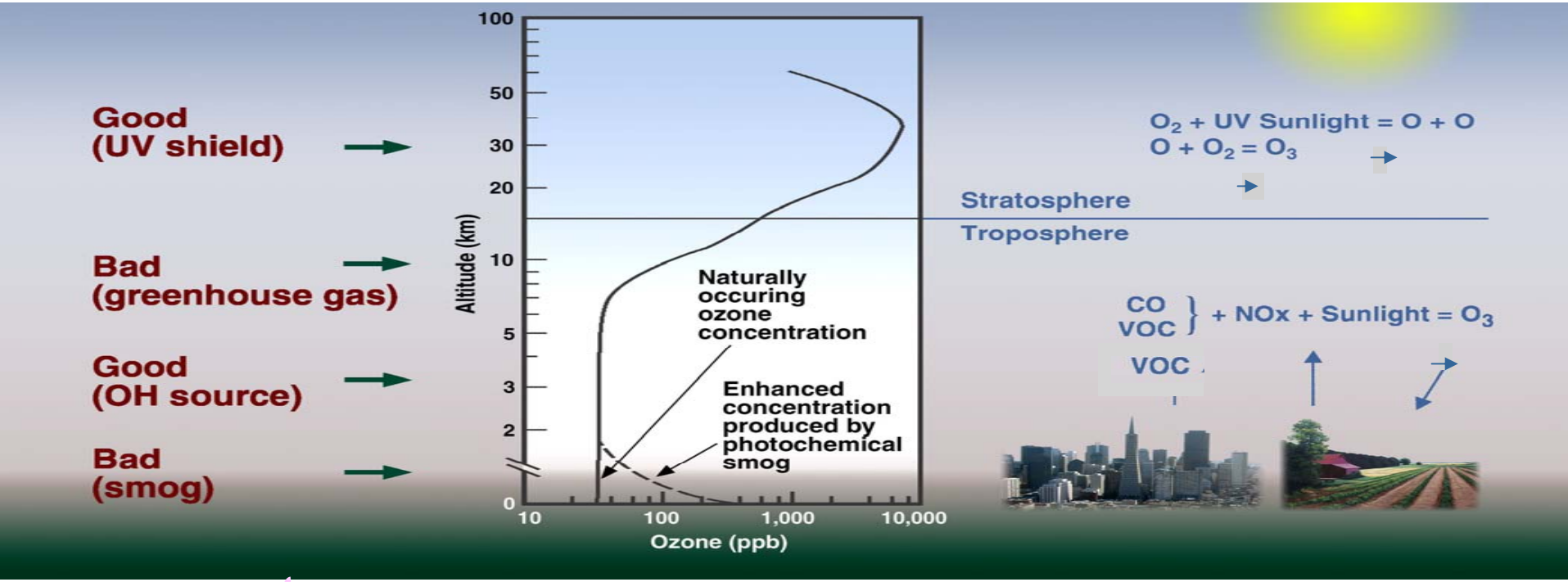
Release puffs from point sources and transport them along trajectories, allowing them to gradually dilute by turbulent mixing ("Gaussian plume") until they reach the Eulerian grid size at which point they mix into the gridbox



S. California fire plumes, Oct. 25 2004

- **Advantages: resolve subgrid 'hot spots' and associated nonlinear processes (chemistry, aerosol growth) within plume**
- **Difference with Lagrangian approach is that (1) puff has volume as well as mass, (2) turbulence is deterministic (Gaussian spread) rather than stochastic**

OzoneE: “Good Up High, Bad Nearby (Low)”

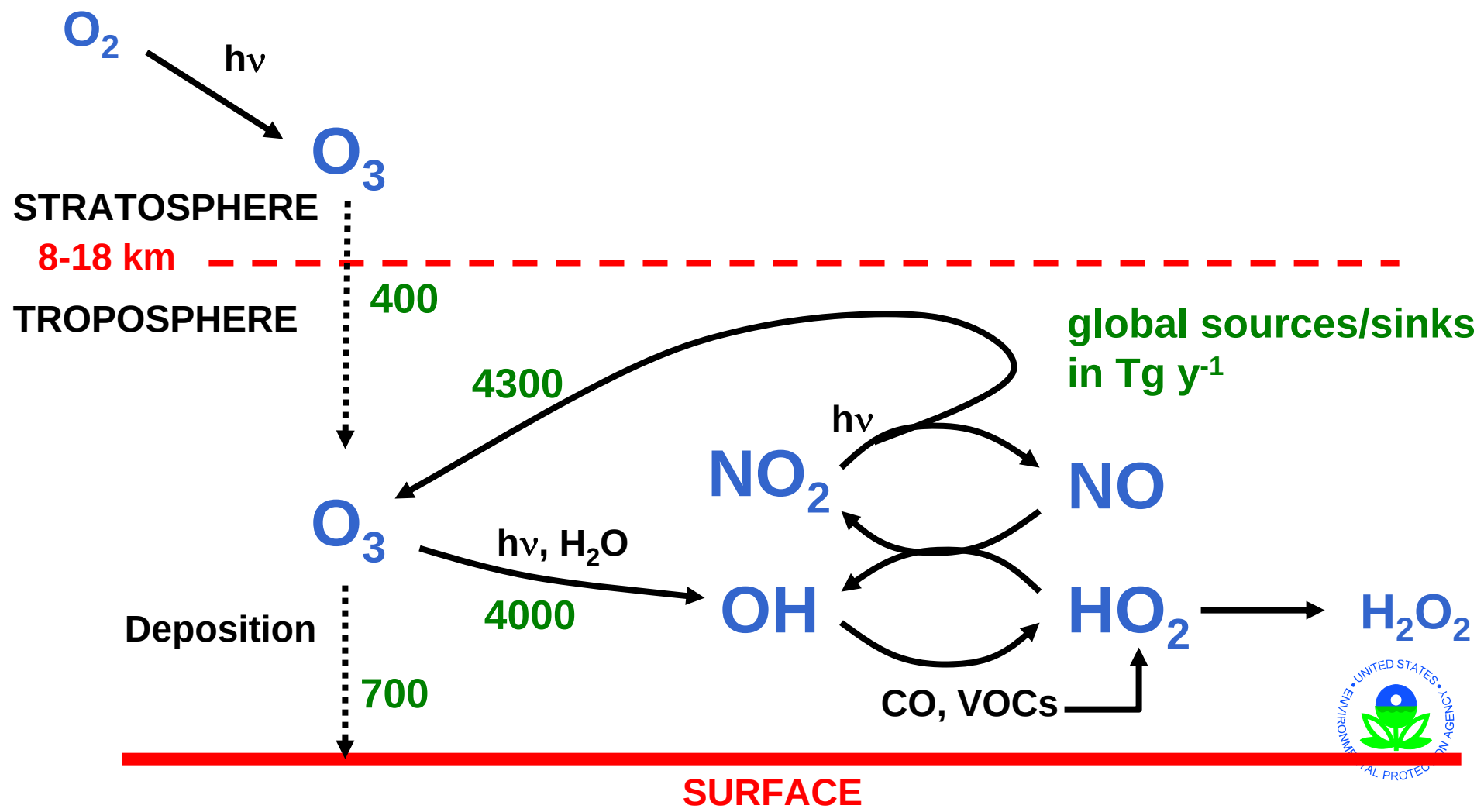


Tropospheric ozone precursors

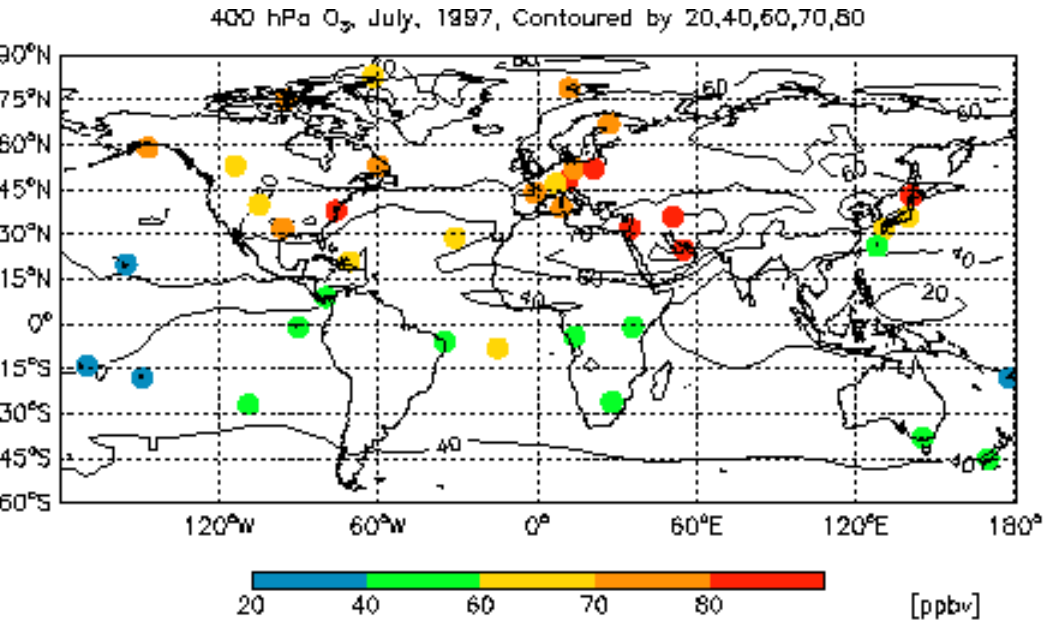
- **Nitrogen oxide radicals; NO_x = NO + NO_2**
  - ***Sources: combustion, soils, lightning***
- **Volatile organic compounds (VOCs)**
  - **Methane**
    - ***Sources: wetlands, livestock, natural gas…***
  - **Non-methane VOCs (NMVOCs)**
    - ***Sources: vegetation, combustion***
- **Carbon monoxide (CO)**
  - ***Sources: combustion, VOC oxidation***

Radical Cycle Controlling Tropospheric OH and O_3 Concentrations

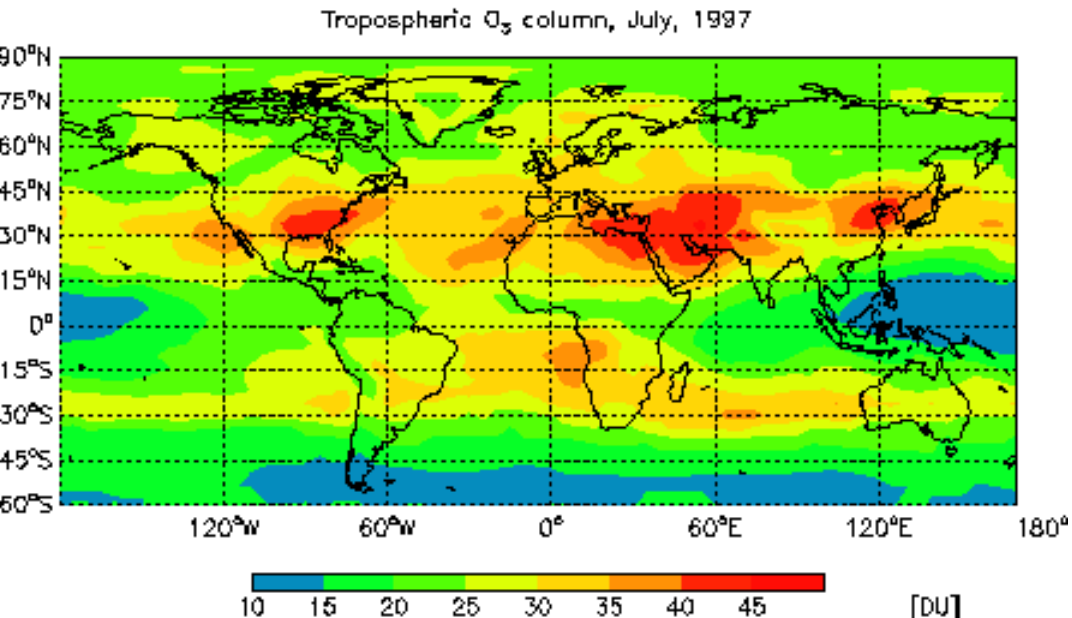
GEOS-Chem simulation for tropospheric ozone includes 120 coupled species to describe HO_x-NO_x-VOC-aerosol chemistry



Global Distribution of Tropospheric O_3



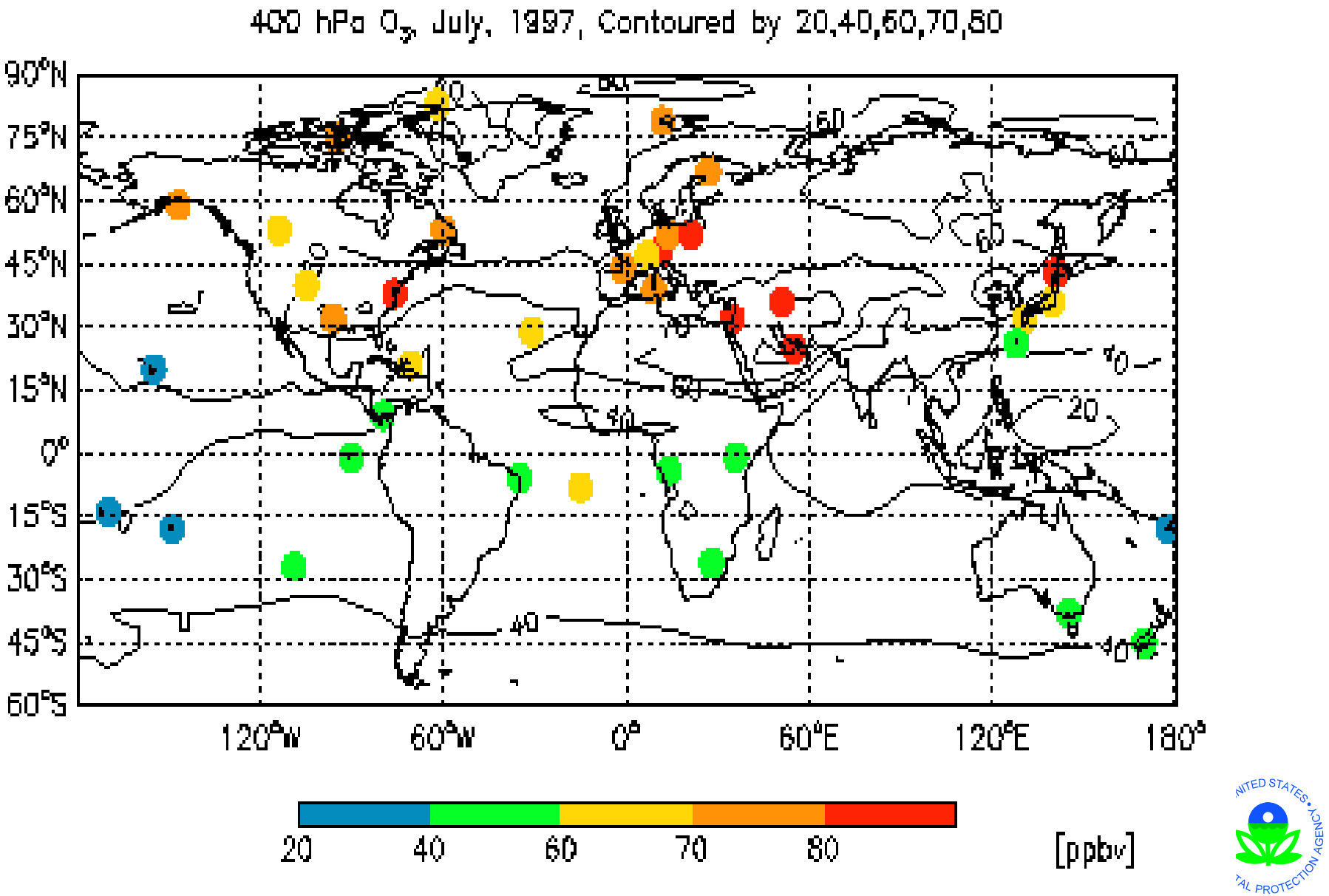
Climatology of observed ozone at 400 hPa in July from ozonesondes and MOZAIC aircraft (circles) and corresponding GEOS-Chem model results for 1997 (contours).

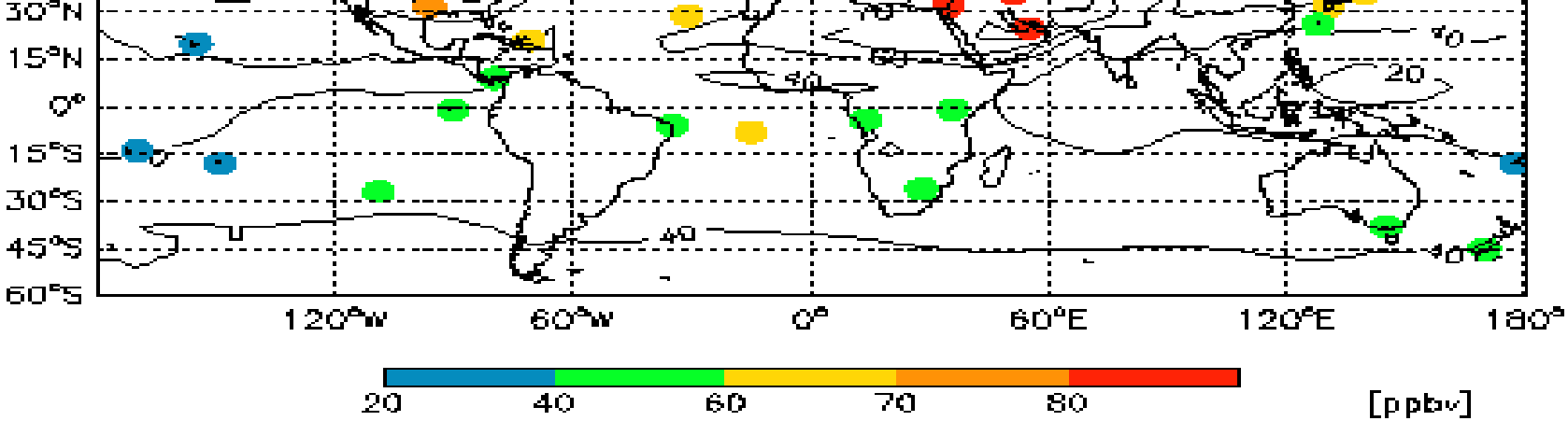


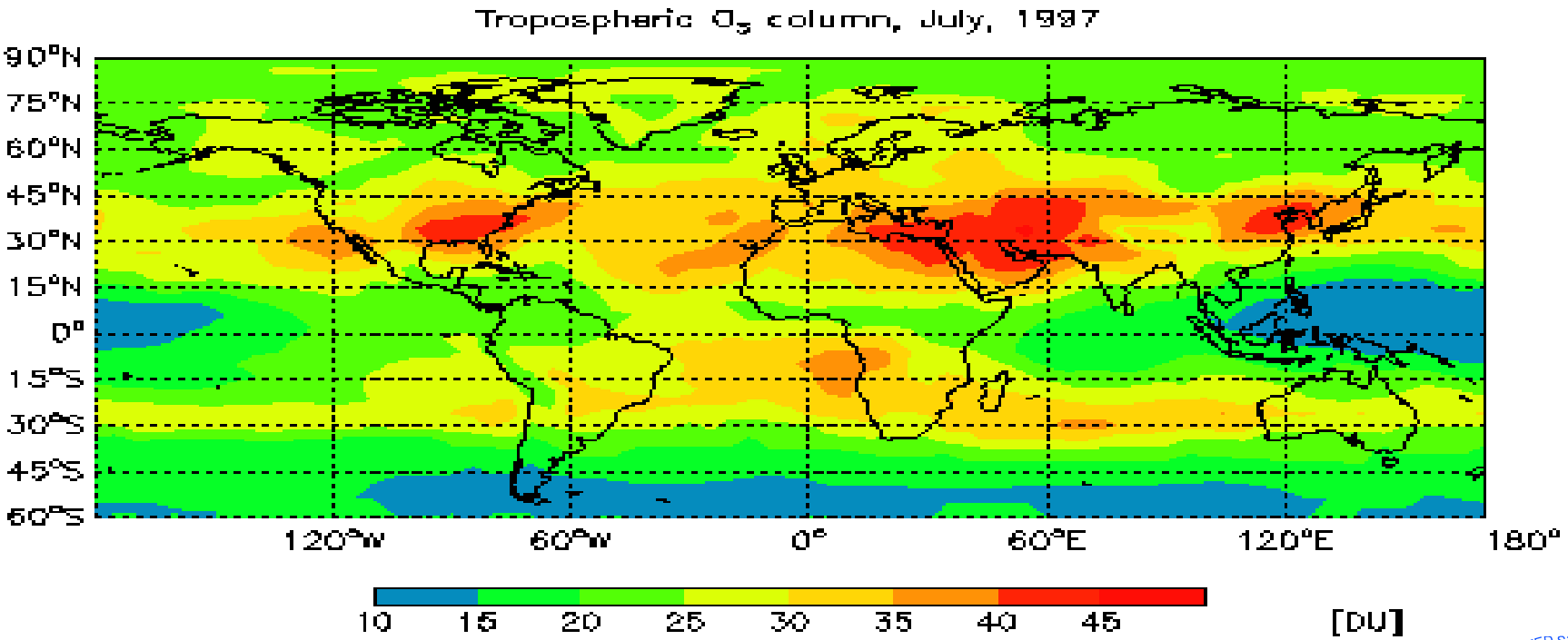
GEOS-Chem tropospheric ozone columns for July 1997.

Li et al., JGR [2001]

Global Distribution of Tropospheric O_3

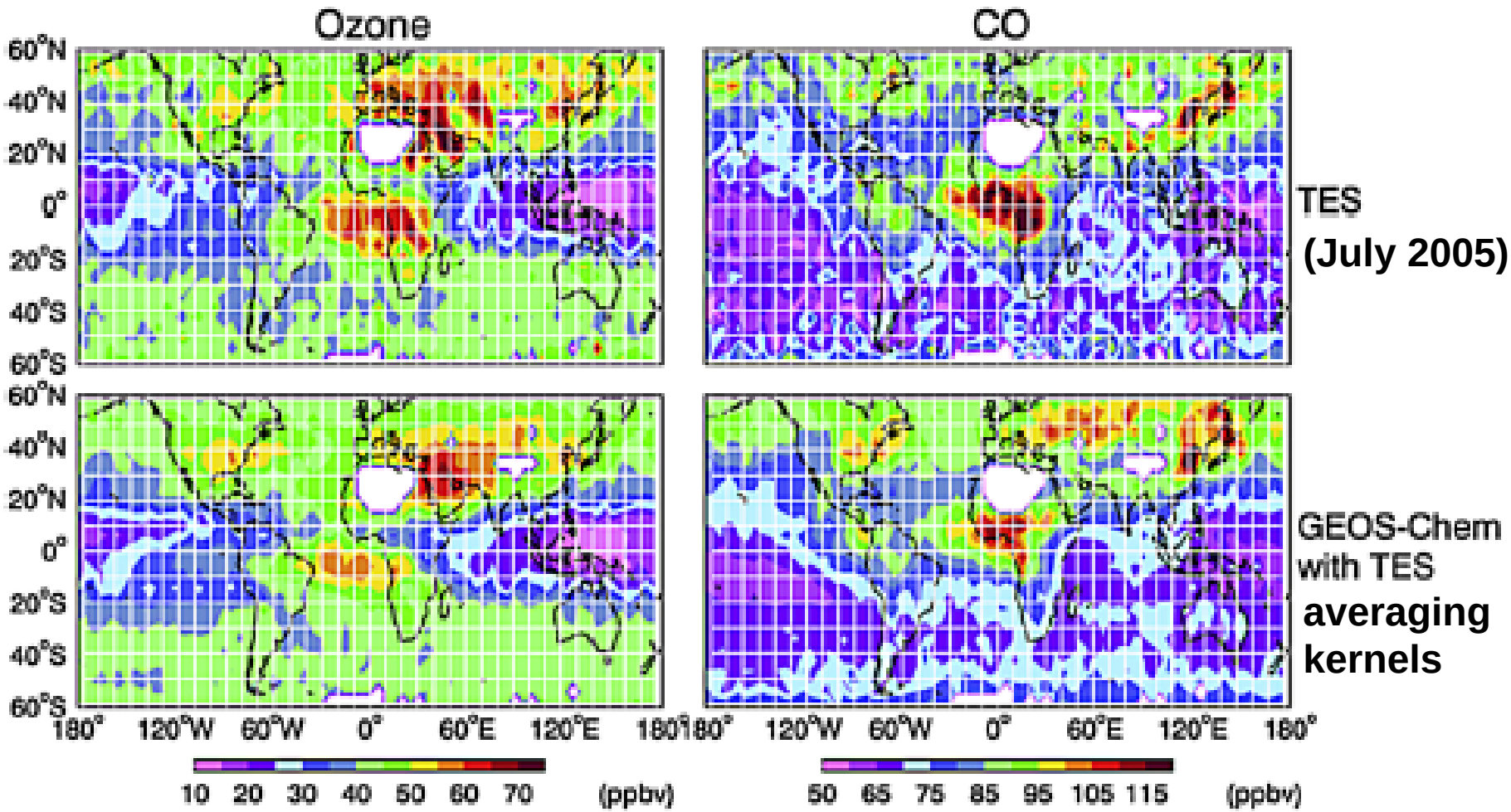






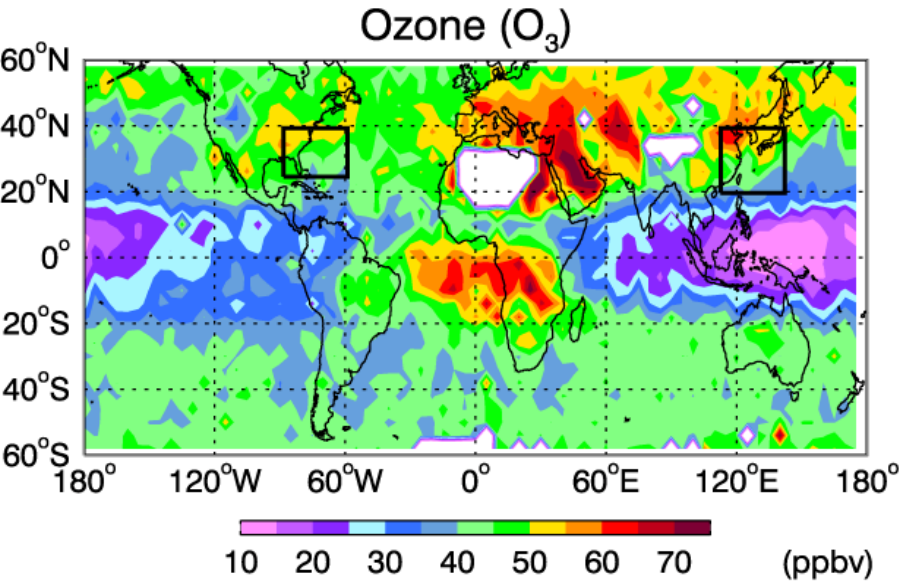
GEOS-Chem tropospheric O_3 columns for July 1997.

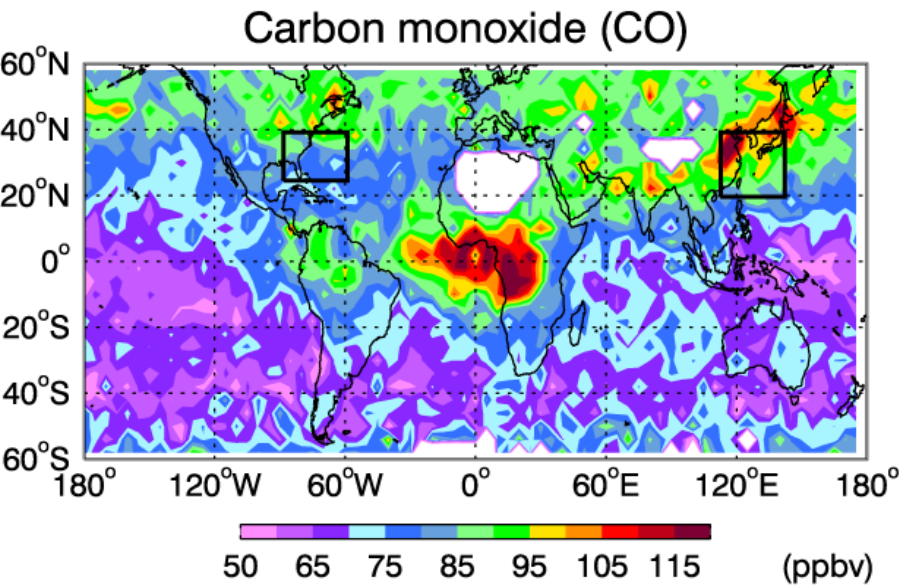
COMPARISON TO TES SATELLITE OBSERVATIONS IN MIDDLE TROPOSPHERE

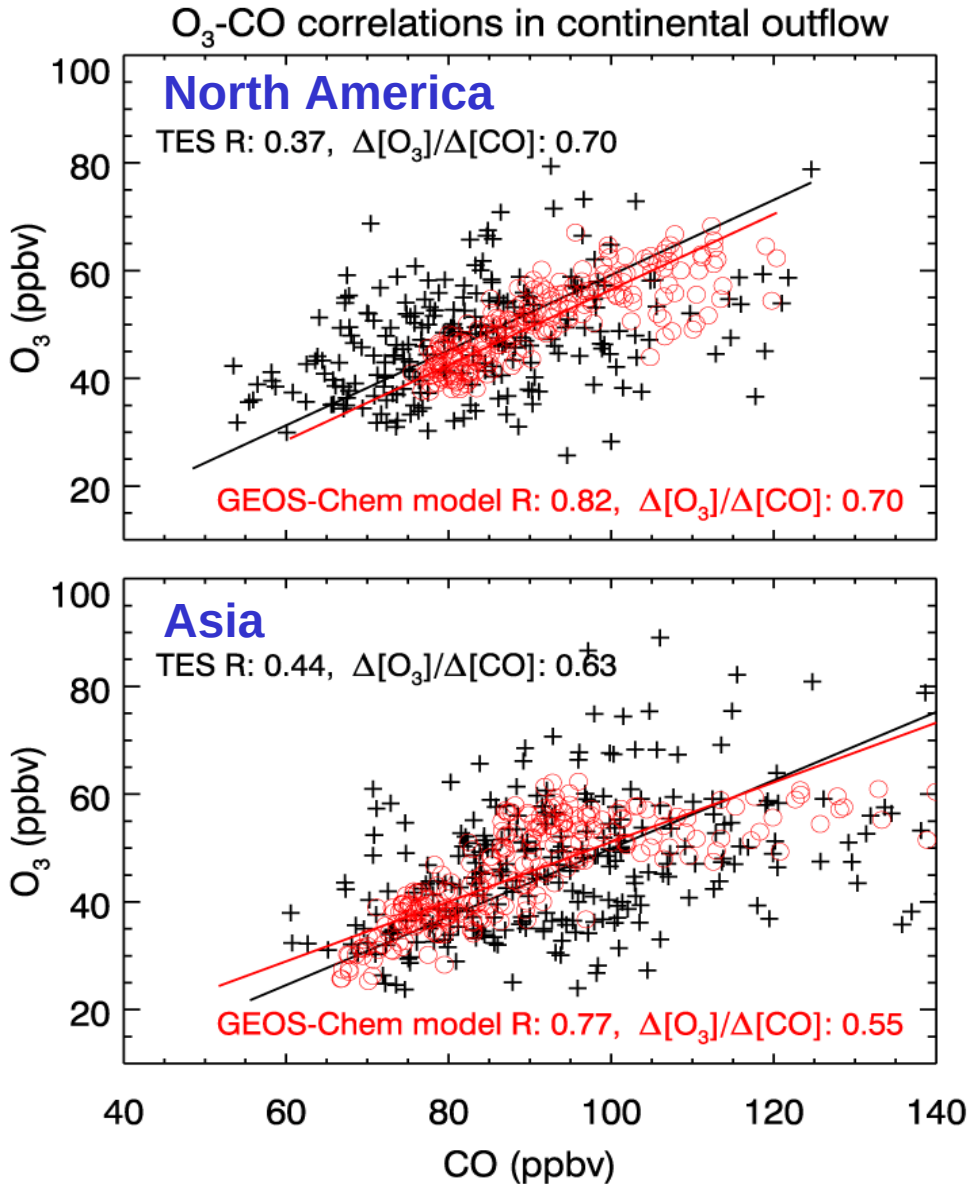


Zhang et al. [2006]

TES ozone and CO observations in July 2005 at 618 hPa



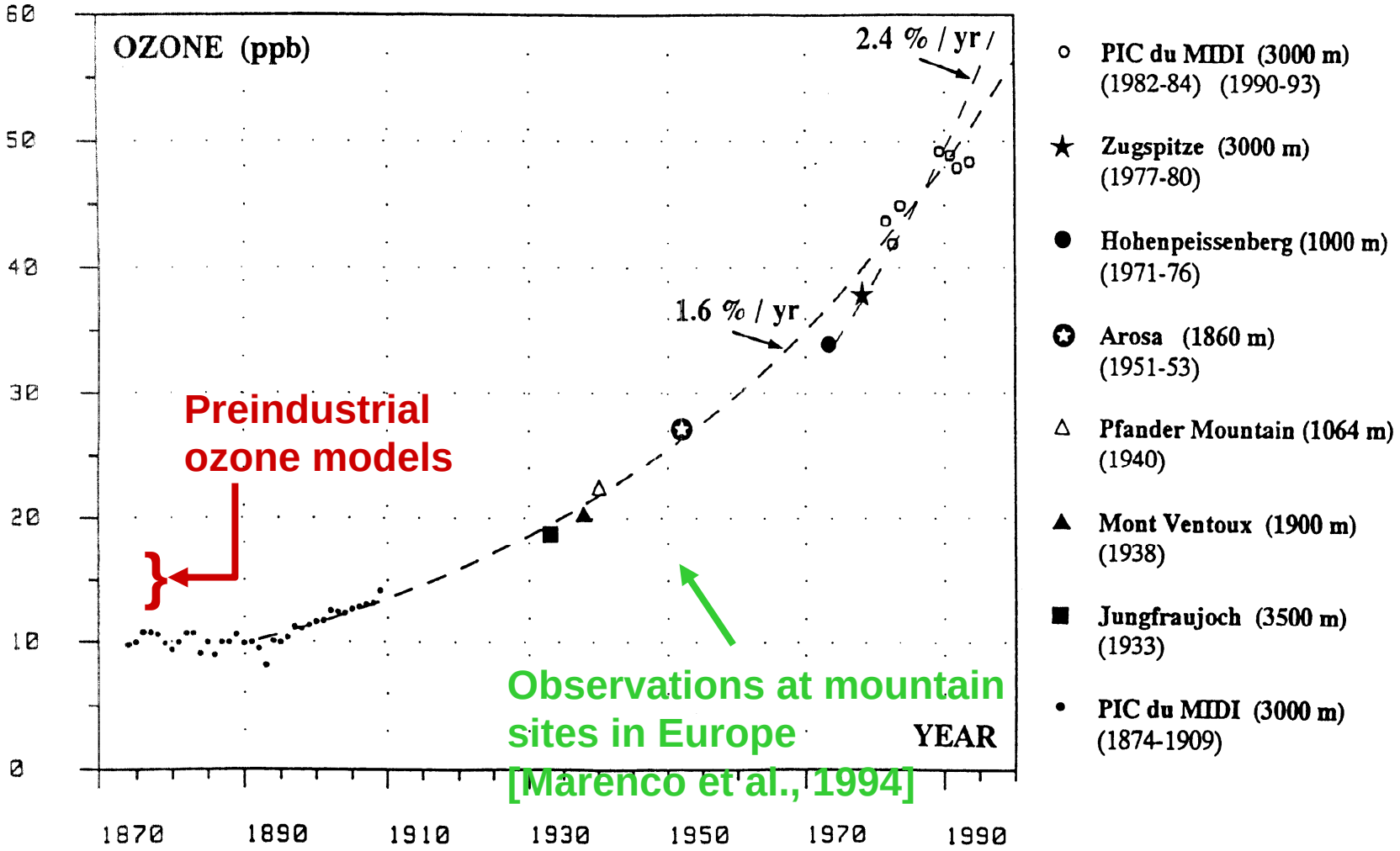




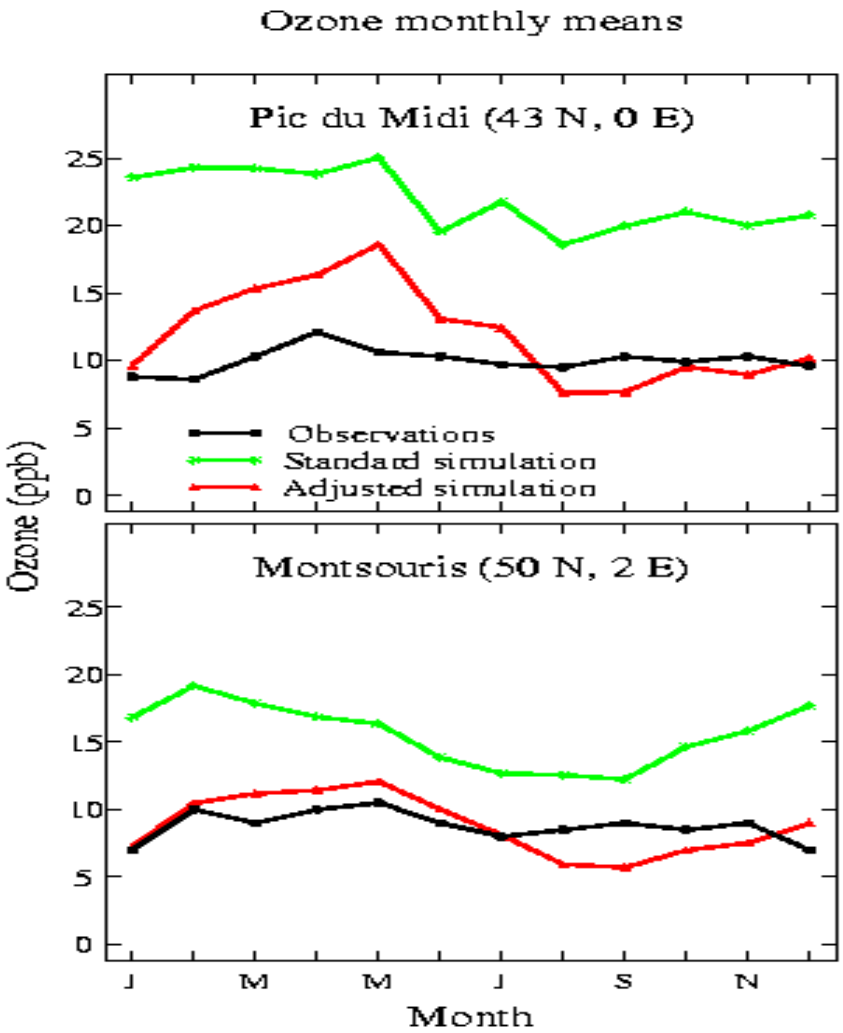
TES observations of ozone-CO correlations test GEOS-Chem simulation of ozone continental outflow

Zhang et al., 2006

IPCC Radiative Forcing Estimate For Tropospheric Ozone (0.35 W m^{-2}) Relies on Global Models



Radiative Forcing By Tropospheric Ozone Could Thus Be Much Larger *Than IPCC Value*



Global simulation of late 19th century ozone observations [Mickley et al., 2001]

Standard model:

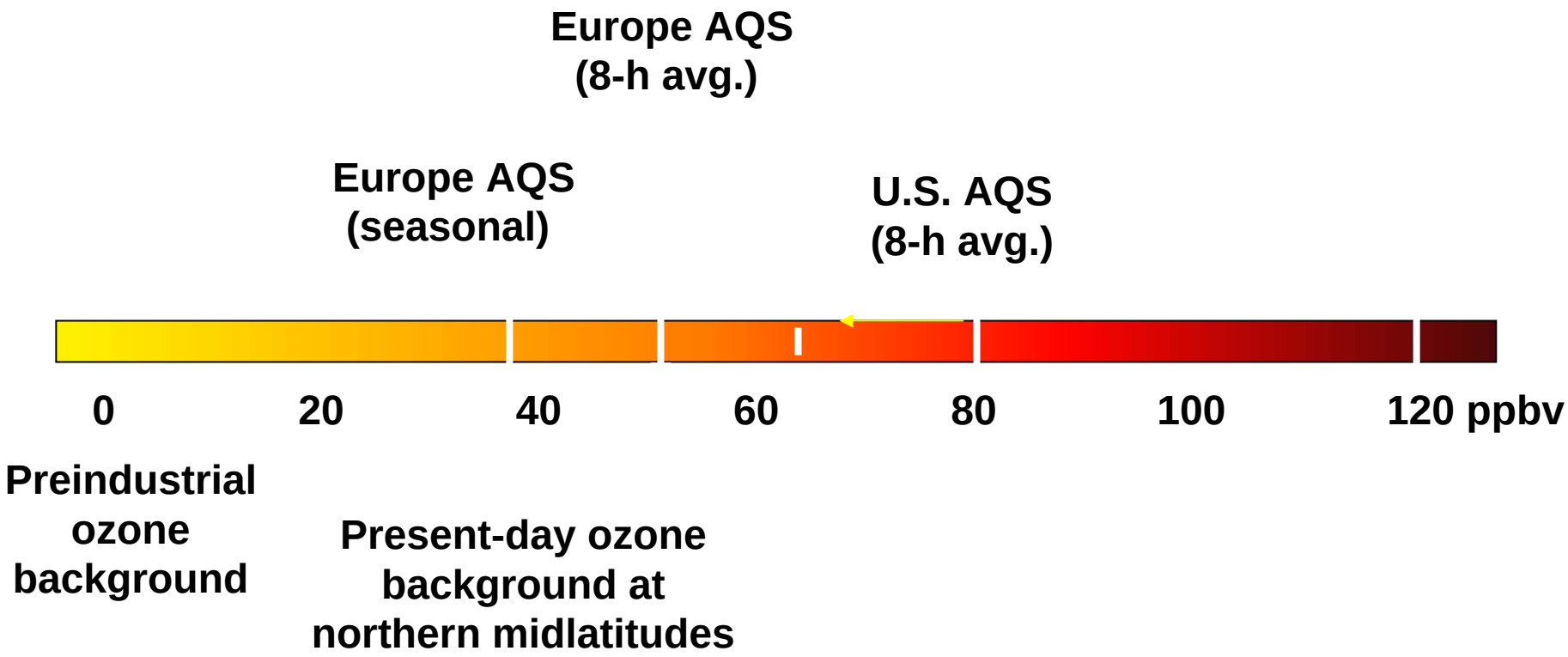
$\Delta F = 0.44$ W m^{-2}

"Adjusted" model

(lightning and soil NOx decreased, biogenic hydrocarbons increased):

$\Delta F = 0.80$ W m^{-2}

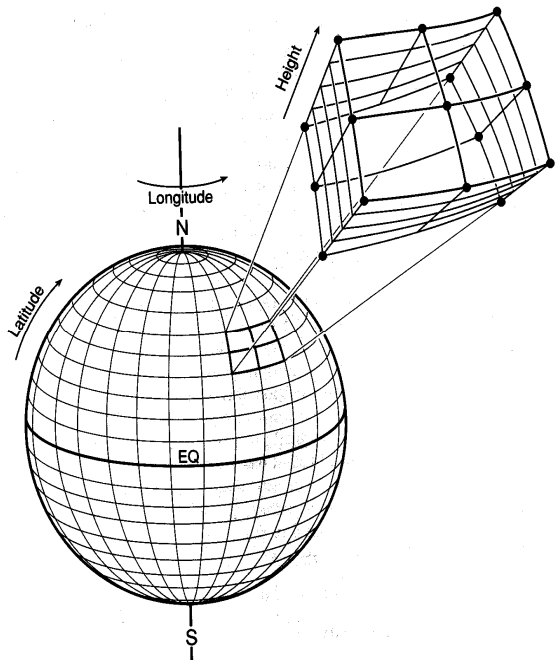
Implication of Increasing O_3 Background For Meeting Air Quality Standards



Shutting down North American anthropogenic emissions in GEOS-Chem reduces frequency of European exceedances of 55 ppbv standard by 20%

U.S. EPA defines a "policy-relevant background" (PRB) as the O_3 concentration that would be present in U.S. surface air in the absence of North American anthropogenic emissions

- This O_3 background cannot be directly observed, must be estimated from models
- Because chemistry is strongly nonlinear, sensitivity simulations are necessary



(1) Standard simulation; include all sources

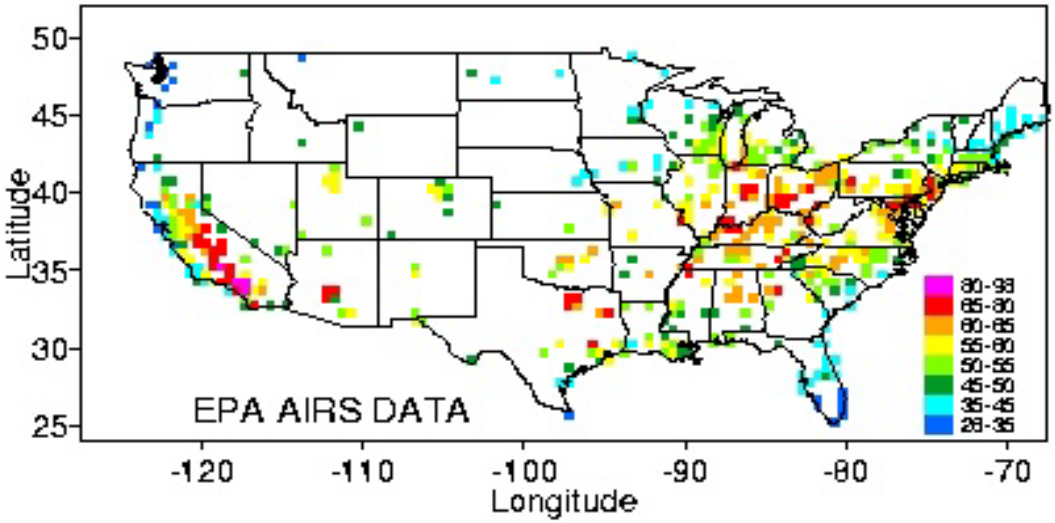
(2) Set U.S. or N. American anthropogenic emissions to zero ⇨ infer policy-relevant background

(3) Set global anthropogenic emissions to zero ⇨ estimate natural background

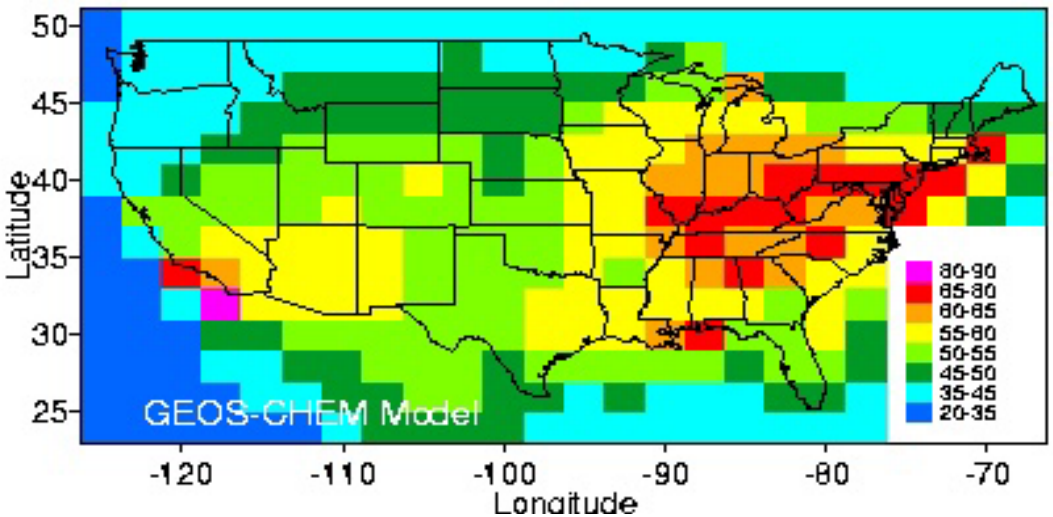
Difference between (1) and (2) ⇨ regional pollution

Difference between (2) and (3) ⇨ background enhancement from hemispheric pollution

Summer 1995 afternoon (1-5 p.m.) ozone in surface air over the U.S.



Observations



GEOS-CHEM standard simulation

Fiore et al. [2002]

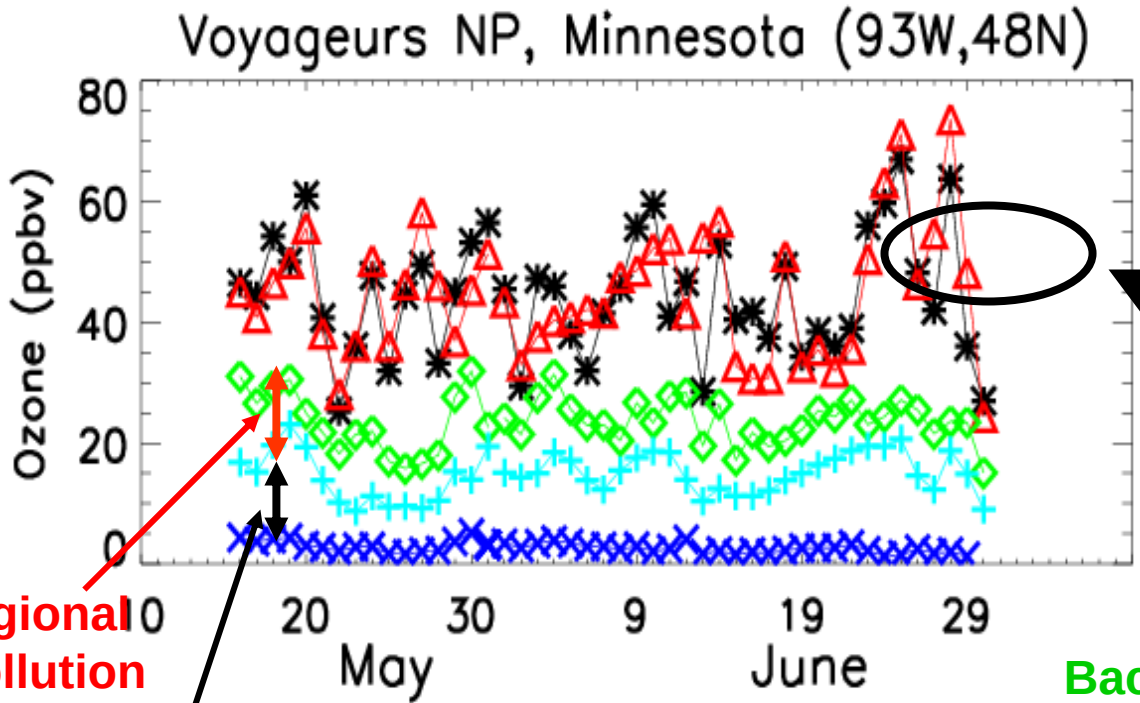
r = 0.66, bias=5 ppbv

Examine a clean site:
Voyageurs National Park, Minnesota
(May-June 2001)

* CASTNet observations
▲ Model
◆ Background
\+ Natural O_3 level
X Stratospheric

Δ = } Regional pollution

} Δ = Hemispheric pollution



regional pollution

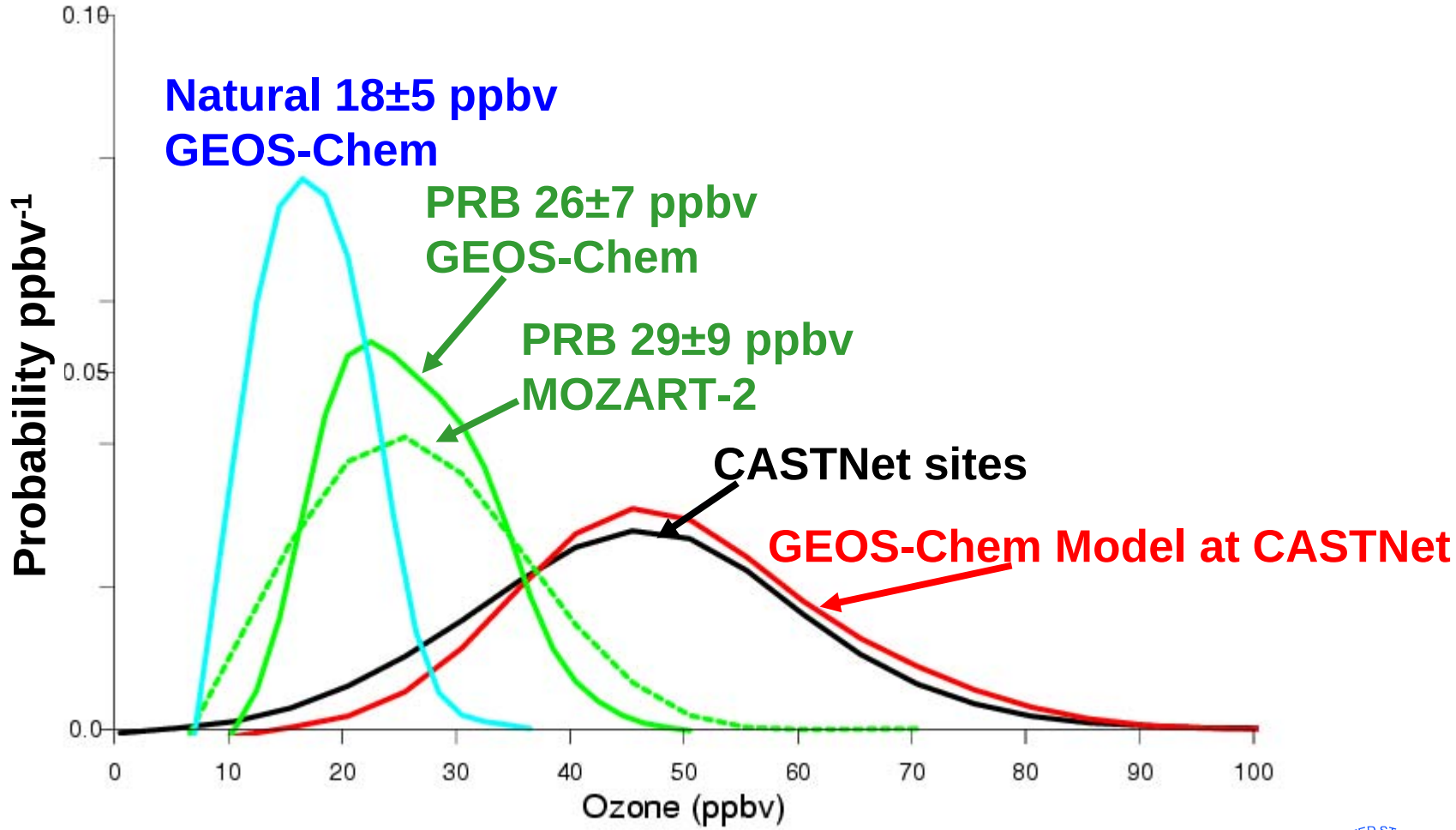
hemispheric pollution

High-O_3 events: dominated by regional pollution; minor stratospheric influence (~2 ppbv)

Background: 15-36 ppbv
Natural level: 9-23 ppbv
Stratosphere: < 7 ppbv

Fiore et al. [2003]

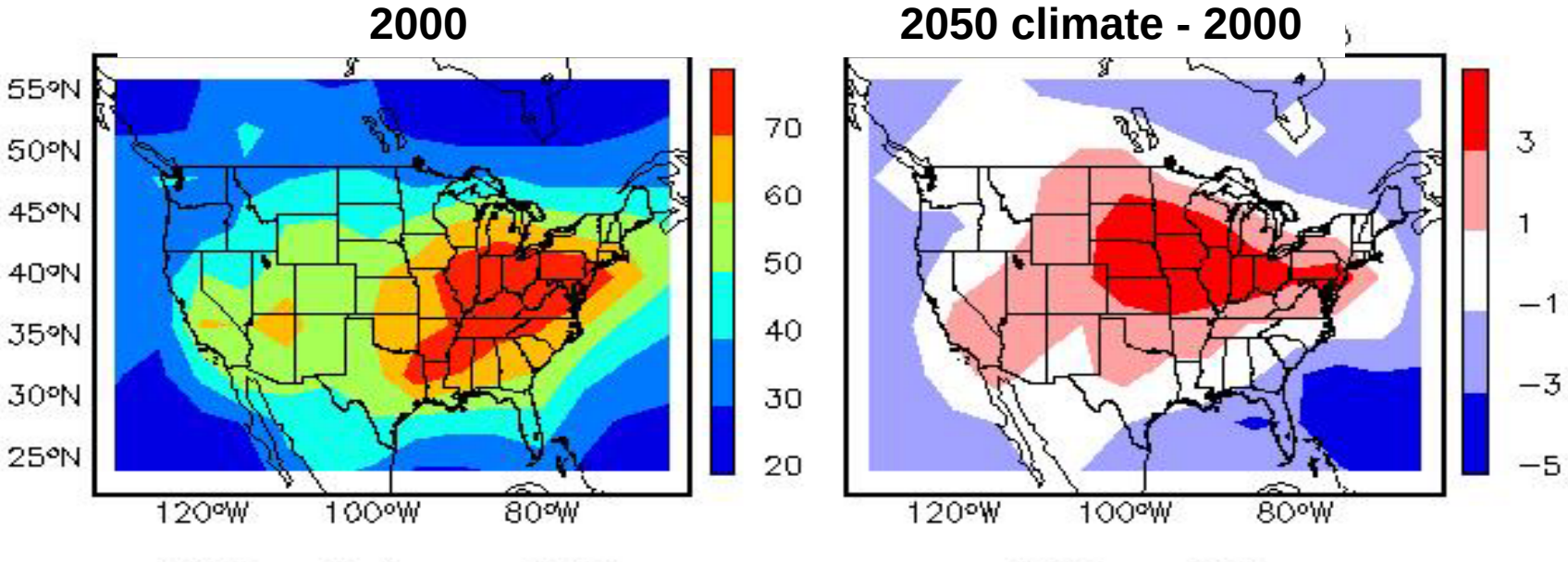
Compiling daily afternoon (1-5 p.m. mean) surface O3 from all CASTNet rural sites for March-October 2001: Policy-relevant background ozone is typically 20 - 35 ppbv



Fiore et al., JGR 2003

EFFECT OF 2000-2050 Climate Change on U.S. Ozone Pollution

Run GEOS-Chem driven by GISS GCM for present vs. 2050 climate

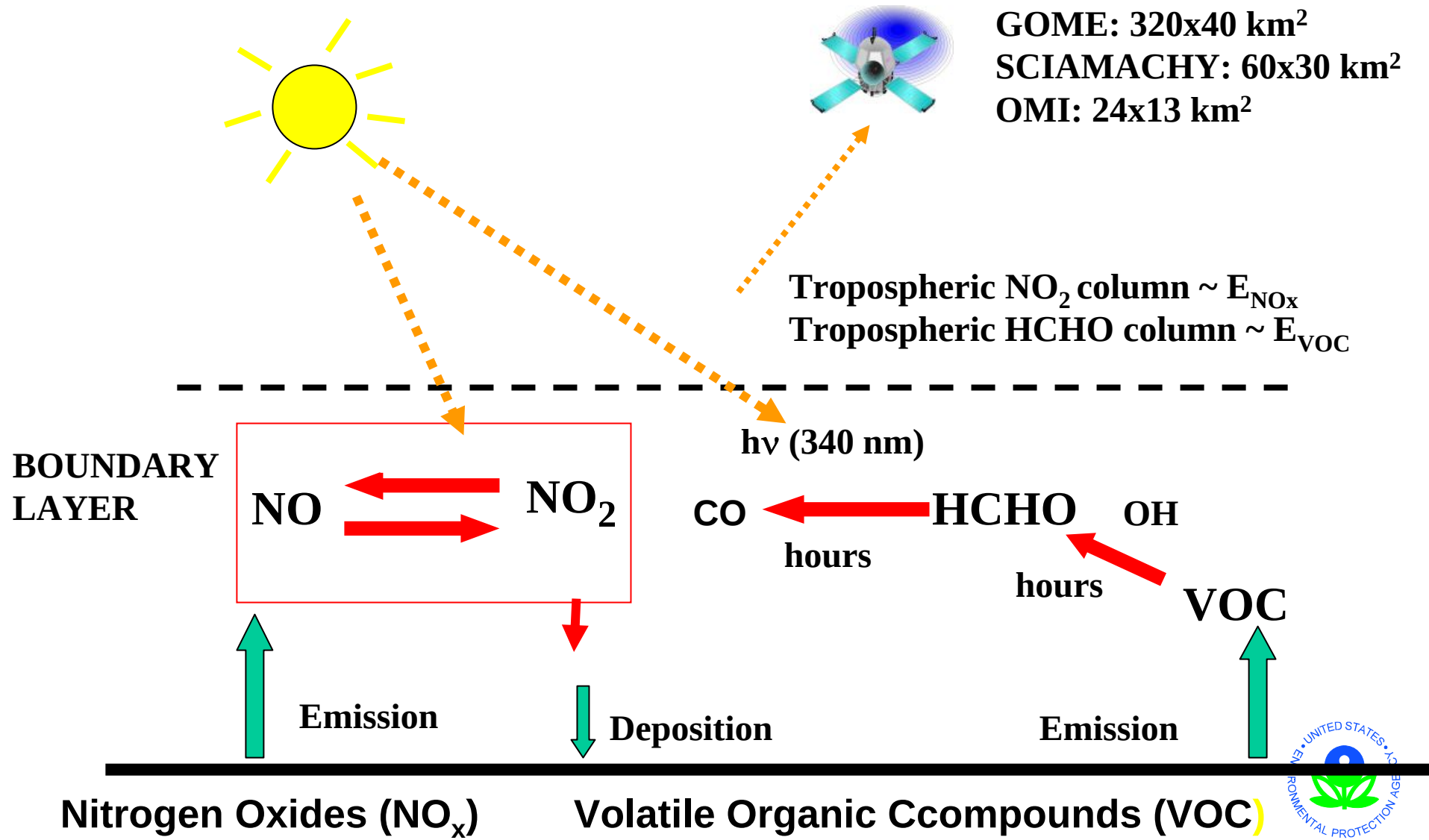


Climate change decreases the background ozone because higher water vapor increases ozone loss;

but water vapor aggravates ozone pollution episodes due to less ventilation (fewer mid-latitudes cyclones), faster chemistry, higher biogenic VOC emissions

Wu et al. [2007]

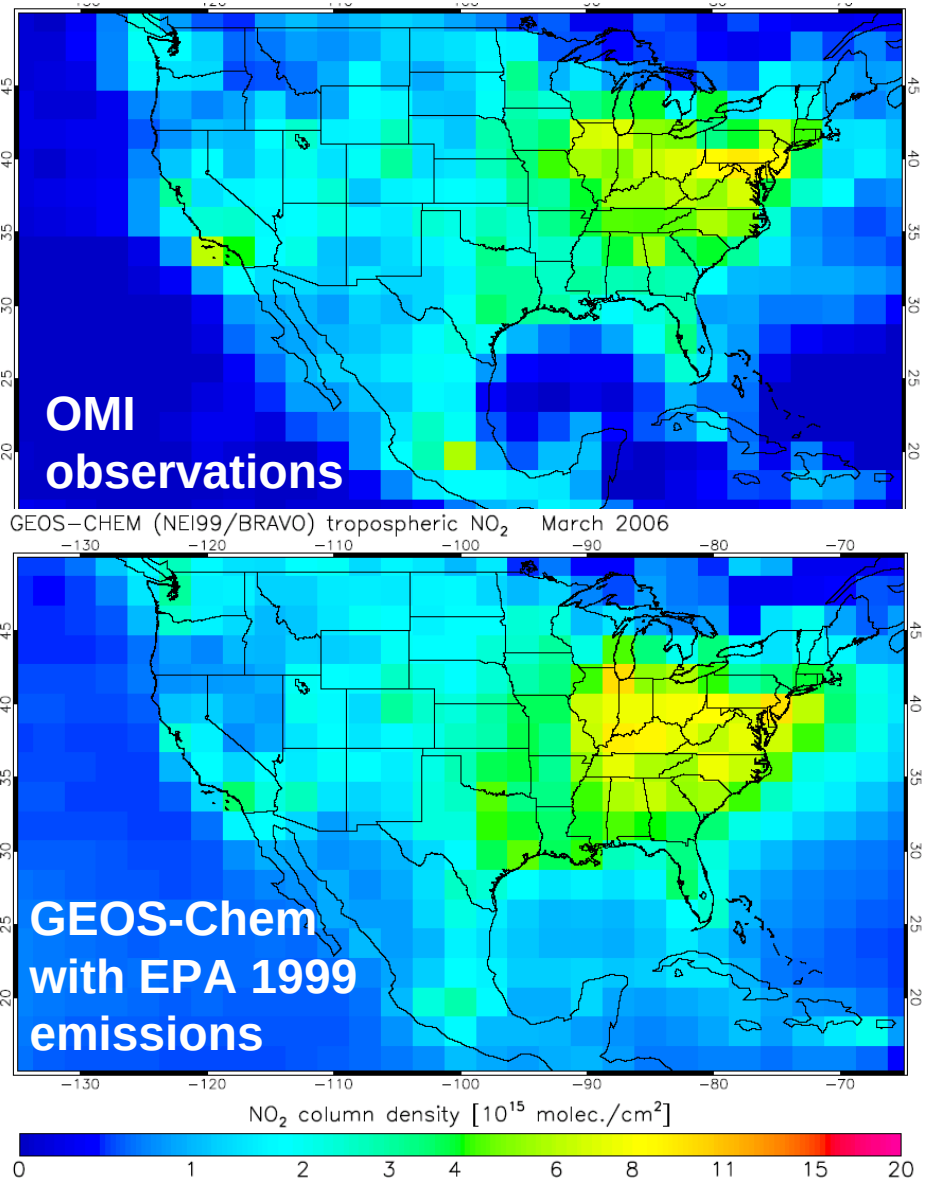
Constraining NO_x and Reactive VOC Emissions With NO_2 and Formaldehyde (HCHO) Measurements From Space



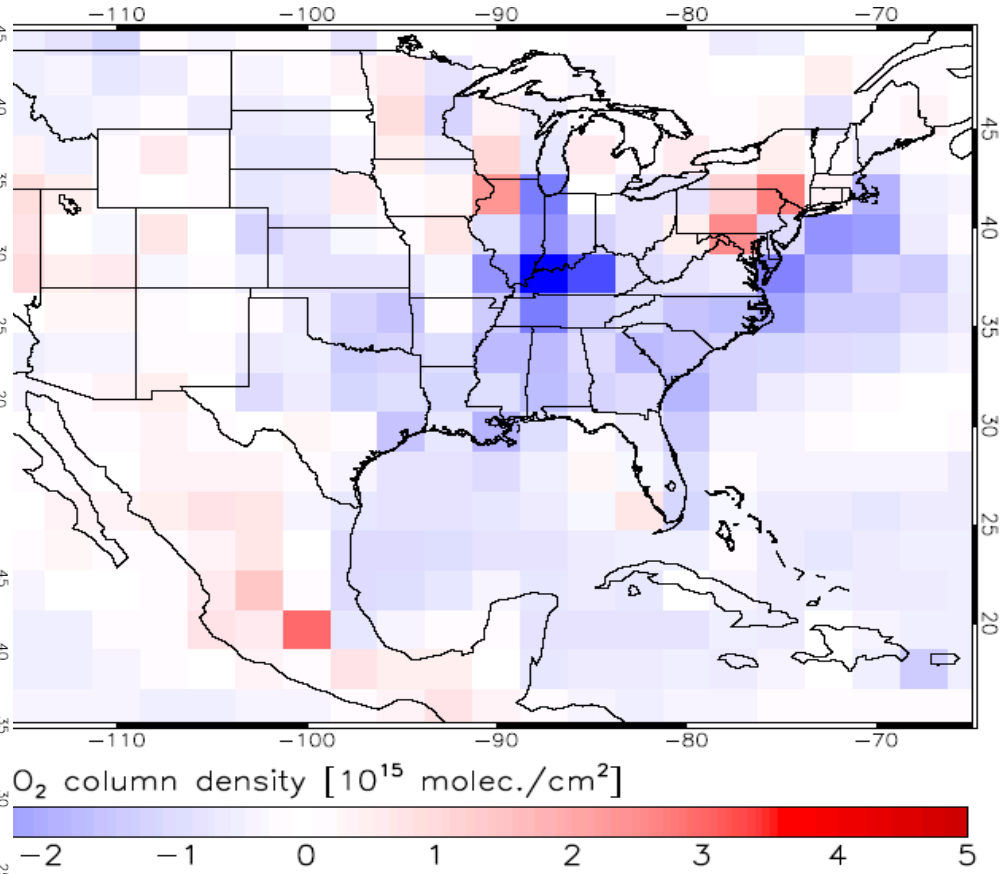
TOP-DOWN CONSTRAINTS ON NO_x EMISSION INVENTORIES FROM OMI NO_2 DATA INTERPRETED WITH GEOS-Chem

Boersma et al. [2007]

Tropospheric NO_2 (March 2006)



OMI – GEOS-Chem difference



Fitting OMI NO_2 with GEOS-Chem requires

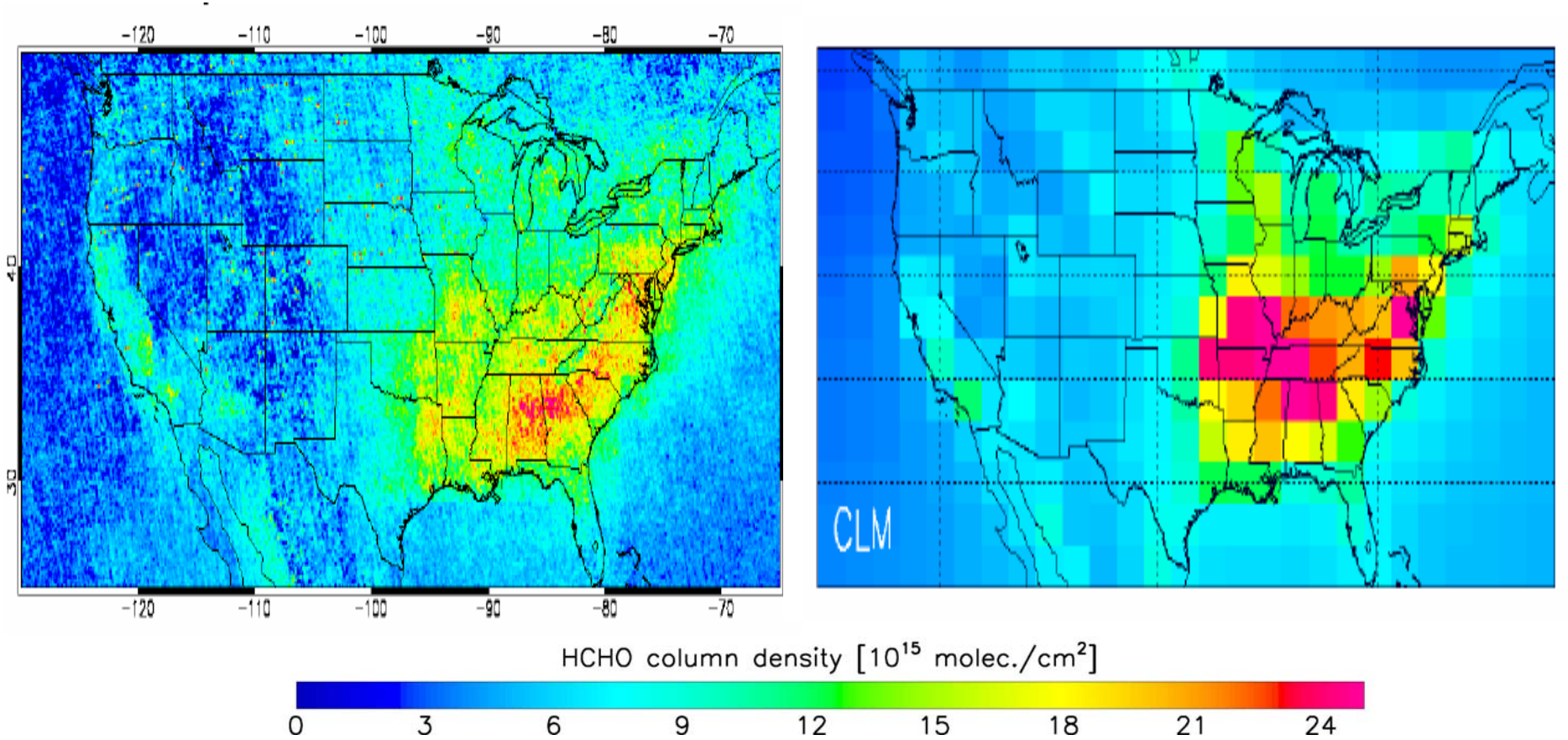
- **25% decrease in power plant emissions**
- **30% increase in vehicle emissions**

relative to EPA 1999 official inventory

Formaldehyde Columns From OMI (Jun-Aug 2006): high values are due to biogenic isoprene (main reactive VOC)

OMI

GEOS-Chem model w/best prior (MEGAN) biogenic VOC emissions



Millet et al. [2007]