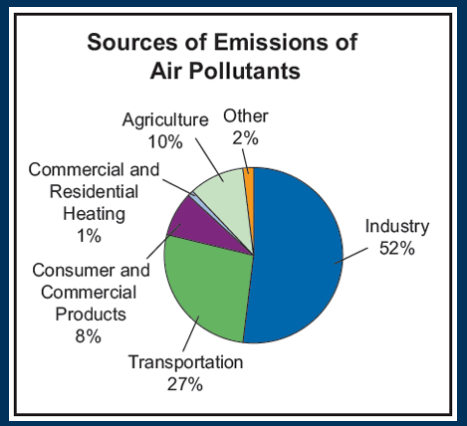
# GGS 319
# Part 1: Air Pollution Fundamentals

- ✓ The atmosphere and its components
- ✓ ***How air pollutants are categorized***
- ✓ ***The source/cycle of air pollutants***
- ✓ How pollution affects health and welfare
- ✓ Clean air acts
- ✓ Air quality management & standards








# History of Air Pollution in the U.S.

- Late 1800's: Industrial revolution (began after civil war, 1860-1890) in the U.S. caused a major increase in air pollution emissions
- 1943: First recognized episodes of smog occurred in Los Angeles
- 1948: The first known air pollution disaster in the U.S. occurred in Donora, PA

# History of Smog

1943: First recognized episodes of smog occurred in Los Angeles.

Visibility was only three blocks and people suffered from itchy eyes, respiratory discomfort, nausea, and vomiting.

The phenomenon was termed a "gas attack“ and blamed on a nearby butadiene plant.







Protests at Pasadena City Hall on November 9, 1954, following fifteen days of smog in October.

# Donora, Pennsylvania, 1948

- Donora, Pennsylvania, air pollution episode killed 20 people, and half the town's 12,000 residents became ill due to uncontrolled emissions from industrial facilities and stagnant weather.
- An air inversion in the narrow river valley of Donora, PA and surrounding areas trapped air pollutant emissions from the local zinc works as well as other local sources of sulfur, carbon, and heavy metals.






1948: Donora, PA at noon.

# Importance of learning about ozone pollution

- **Economic:**

  - $1-2 billion lost annually in the U.S. from ozone damage to agriculture and commercial forestry alone.

  - Several billion more from health related issues

- **Health Issues:** Respiratory Problems
  - Coughing
  - Congestion
  - Chest Pain
  - Throat Irritation
  - Worsens respiratory diseases such as asthma, bronchitis and emphysema

# Ground Level Ozone

- Primary Pollutants
  - Dangerous substance when emitted into the atmosphere
  - Directly cause lung damage and respiratory distress
    - NOx
    - VOCs
    - $PM_{2.5}$
    - $PM_{10}$

# Ground Level Ozone

- Secondary Pollutants
  - Chemical that is not emitted per se, but forms from chemical interactions between or among primary pollutants in the atmosphere
    - $PM_{2.5}$
    - Photochemical Smog
    - Ozone

# Ground Level Ozone

- The dominant pollutant in most of the big cities of the world
- Main component is ozone ($O_3$), which in high concentrations can cause breathing problems and burning eyes
- Primary Pollutants involved in ozone formation are:
  - NOx
  - VOCs

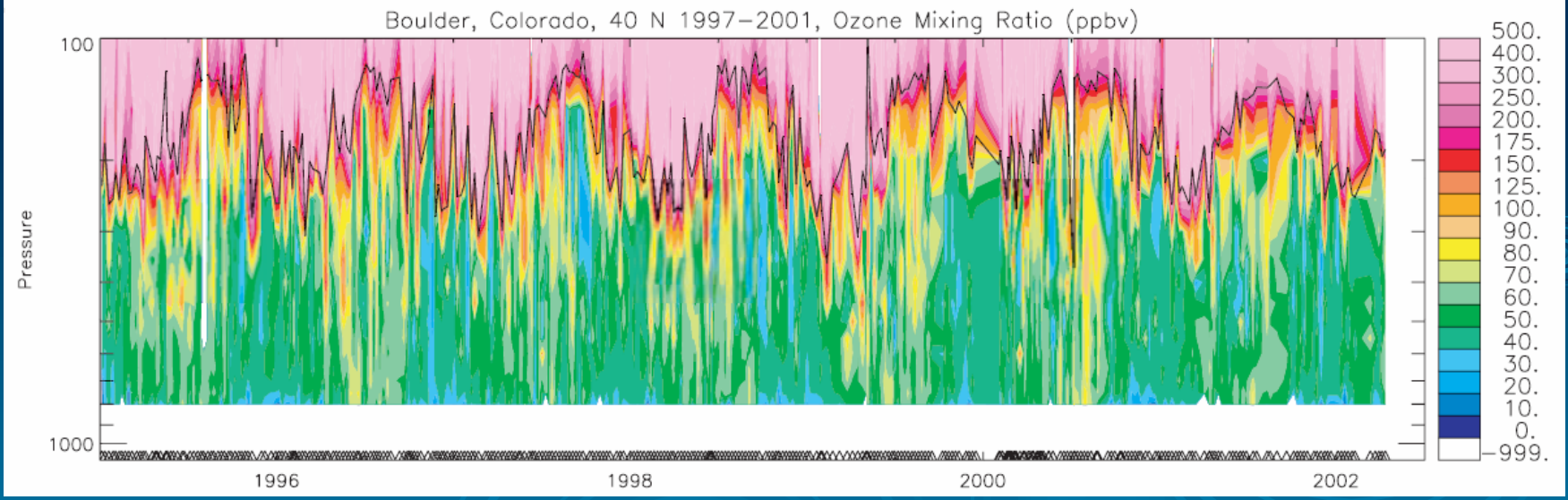
# Ozone Formation Summary

VOC + NOx + Heat + Sunlight = Ozone

- Motor vehicle exhaust and industrial emissions, gasoline vapors, and chemical solvents are some of the major sources of NOx and VOC that help to form ozone.

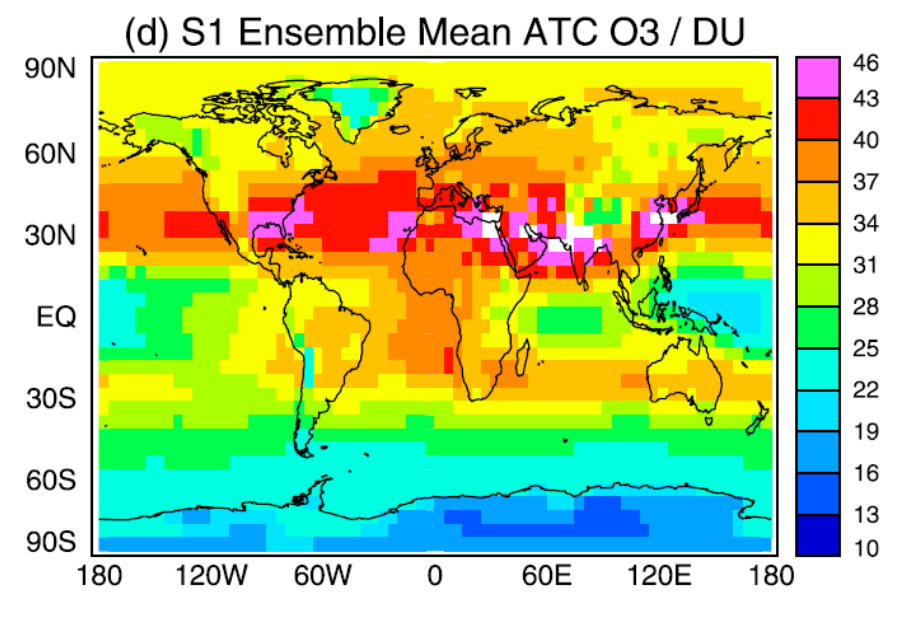
# Variability of Ozone

- 8 years of weekly ozonsondes from Boulder Colorado



# Variability of Ozone

- Tropospheric Ozone Sources
  - Transport from stratosphere:
    552 Tg (+/- 168 Tg)
  - Chemical productions from NOx & VOCs:
    5110 Tg (+/- 606 Tg)
- Tropospheric Ozone Sinks
  - Surface deposition:
    1003 Tg (+/-200 Tg)
  - Chemical loss:
    4668 Tg (+/- 727 Tg)
- Tropospheric Ozone Burden
  - 344 Tg about 11% (+/- 39 Tg)
- Tropospheric Ozone Lifetime
  - ~22 days (+/- 2 days)

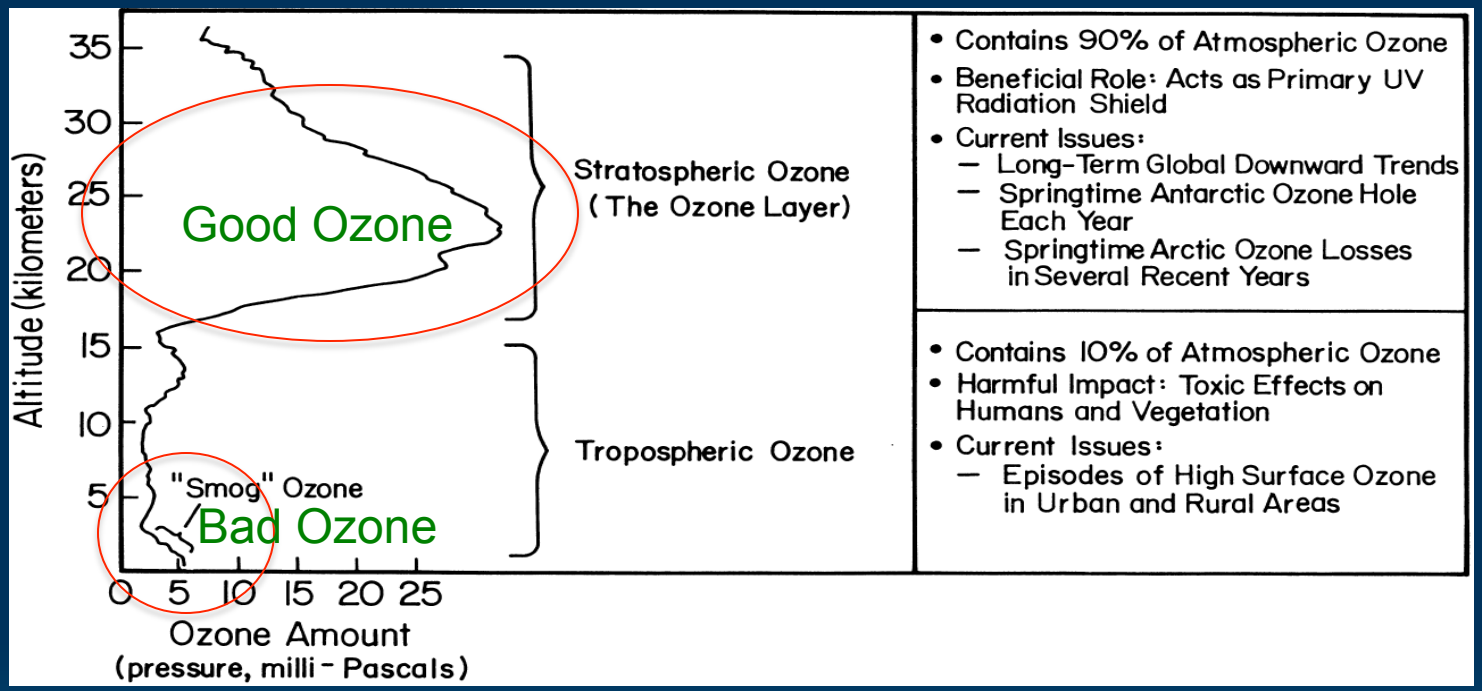



Tropospheric column ozone (Dobson units) for the year 2000.

# Good and Bad Ozone

- Ozone has the same chemical structure whether it occurs miles above the earth or at ground level
- "Good" ozone occurs naturally in the stratosphere approximately 10 to 30 miles above the earth's surface and forms a layer that protects life on earth from the sun's harmful rays.
- In the earth's lower atmosphere, ground-level ozone is considered "bad."

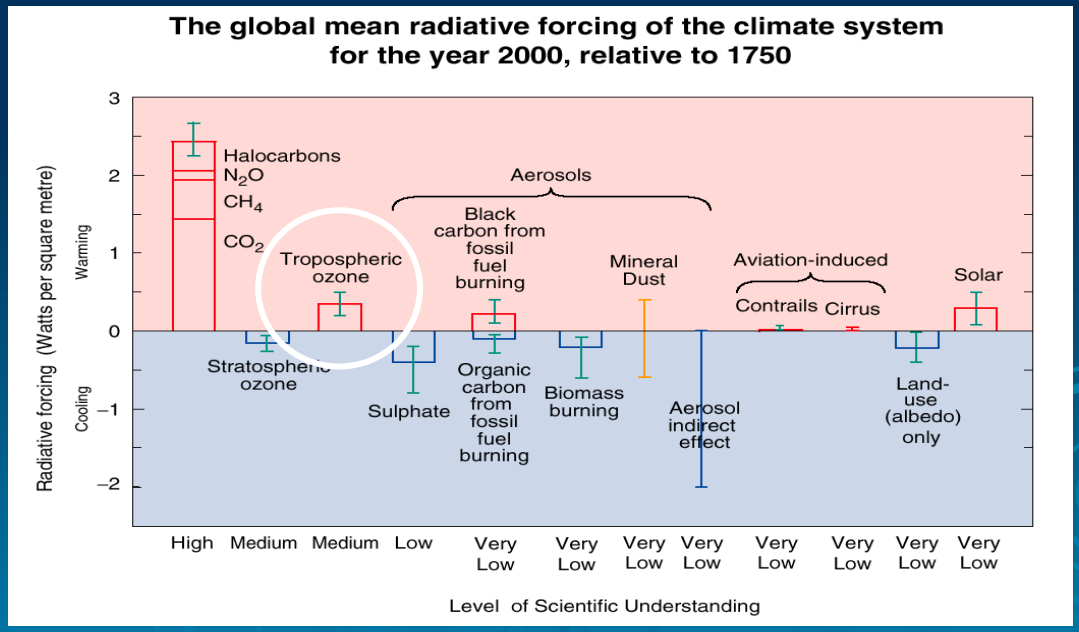
# Tropospheric Ozone




- Tropospheric ozone concentrations due to industrial air pollution ("smog")
- Stratospheric ozone concentrations comprise the "ozone layer"
- We are concerned with "smog" ozone in this lecture

# Tropospheric Ozone Budget and Long-range transport of pollution

- So far we have emphasized the beneficial nature of stratospheric ozone
- In surface air, however, ozone is toxic to humans and vegetation because it oxidizes biological tissue.




from IPCC 2001

# Ground Level Ozone

- Ground level ozone is also called "photochemical smog"
- Chemical Reactions
  - Given chemical species A, B, C & D

$$A + B \rightarrow C + D$$

  - A reacts with B to produce C and D
    - A & B are "reactants"
    - C & D are "products"
- Photochemical Reactions

$$A + UV \rightarrow B + C$$

  - "A" absorbs sunlight and chemically broken down to produce "B" & "C"

# Why are we Interested in Tropospheric Ozone?

**Pollution:**
$O_3$ is an important component of photochemical smog

**Tropospheric oxidation:**
$O_3$ regulates oxidation through control of OH and controls removal of $CH_4$, VOCs, etc.

**Climate:**
Direct: $O_3$ is a greenhouse gas
Indirect: $O_3$ governs lifetime of other GHGs via OH

**Anthropogenic Influence:**
Surface and Tropospheric $O_3$ is increasing due to human activity

- Environmental impacts on local, regional and global scales
- Secondary pollutant: sensitive to many variables
  - Chemical production can be fast in polluted conditions
  - Lifetime is sufficiently long for global-scale transport

# Chemical Formation…..

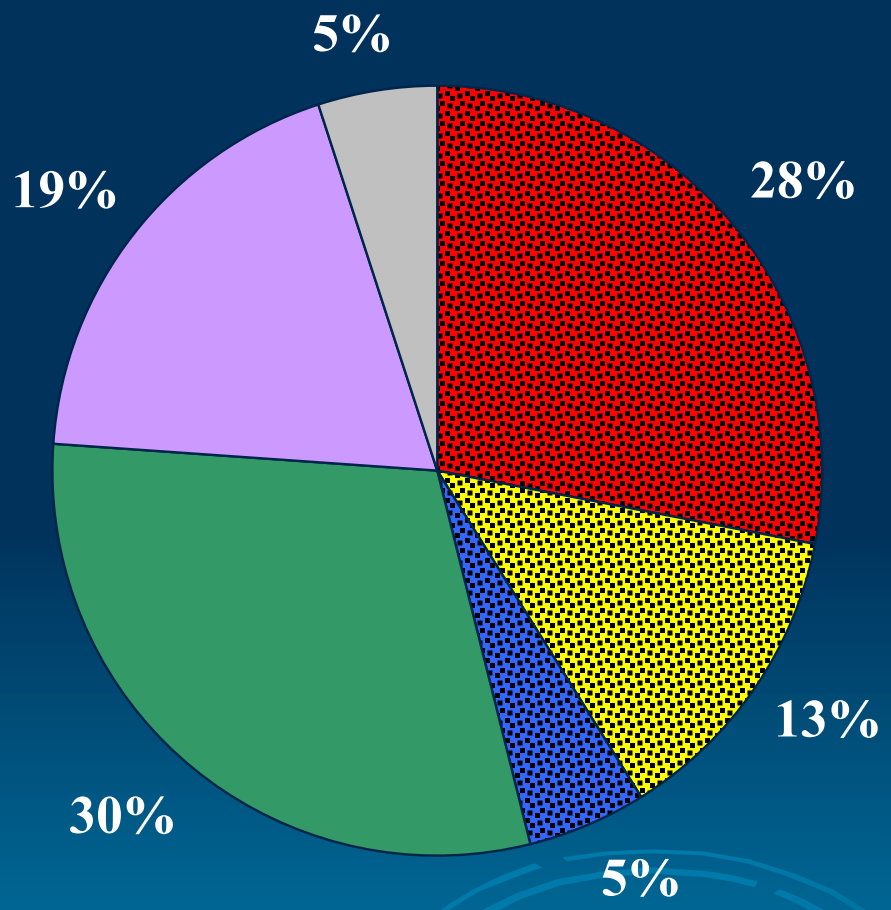
- Specific Hydrocarbons "precursors" proving additional pathways to produce $NO_2$
  - Alkanes (methane, ethane, propane, butane, etc..)
  - Aromatics (toluene, xylene, benzene, etc..)
  - Terpenes (biogenic emissions)
  - Alcohol (ethanol, methanol, etc..)
  - Aldehydes (formaldehyde, etc..)

$$NO + VOCs \rightarrow NO_2 + VOC^{*}s$$

$$NO + VOC^{*}s \rightarrow NO_2 + VOC^{**}s$$

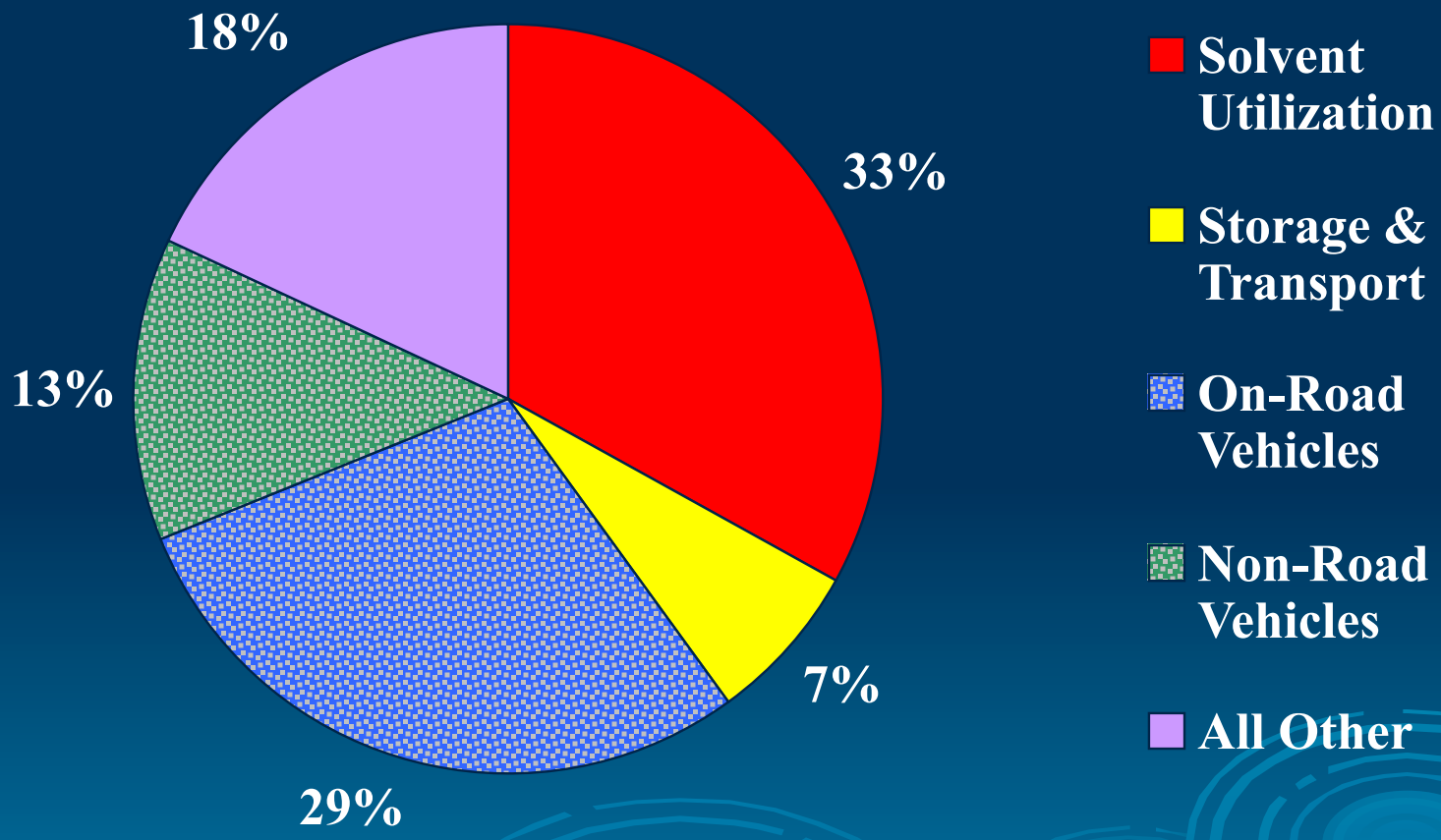
$$NO + VOC^{**}s \rightarrow NO_2 + VOC^{***}s$$

# $NO_x$ emission inventory



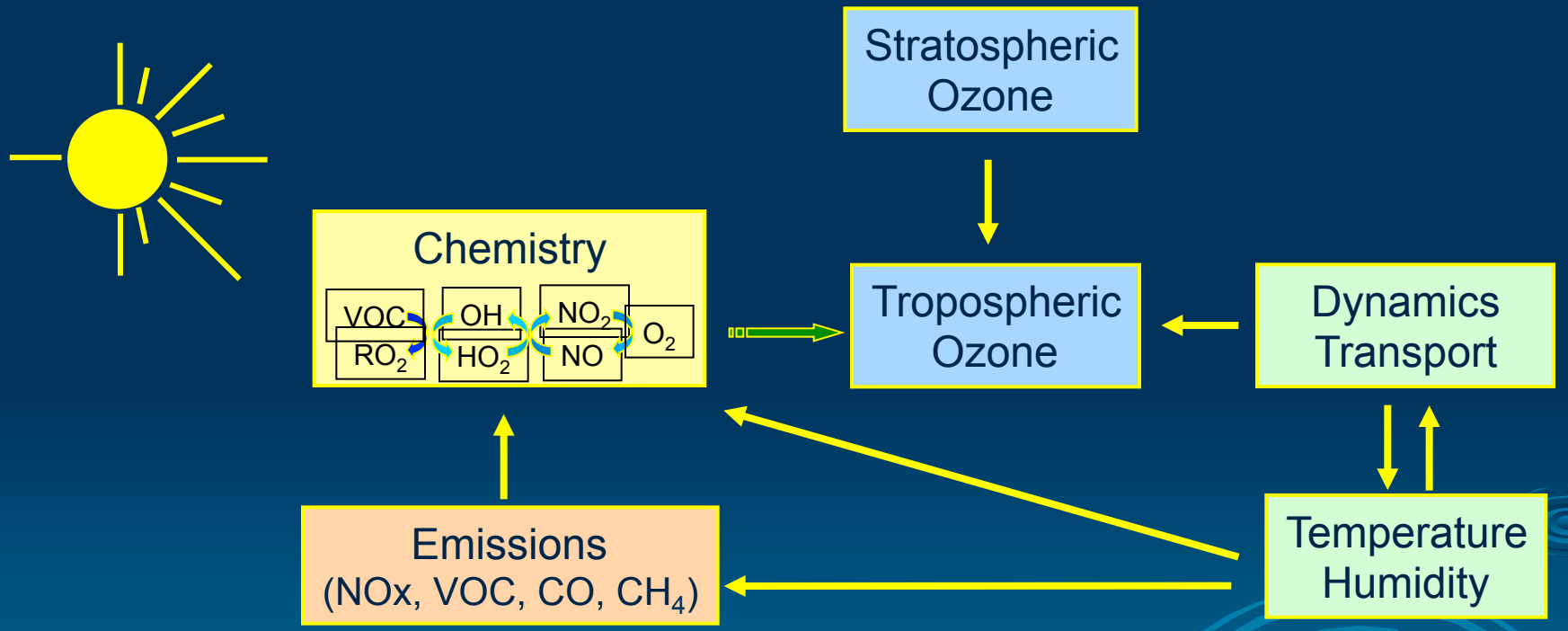

- Fuel Combustion - Electric Utility
- Fuel Combustion - Industrial
- Fuel Combustion - Other
- On-Road Vehicles
- Non-Road Vehicles
- All Other

# VOC Emissions



# Factors controlling the tropospheric ozone budget

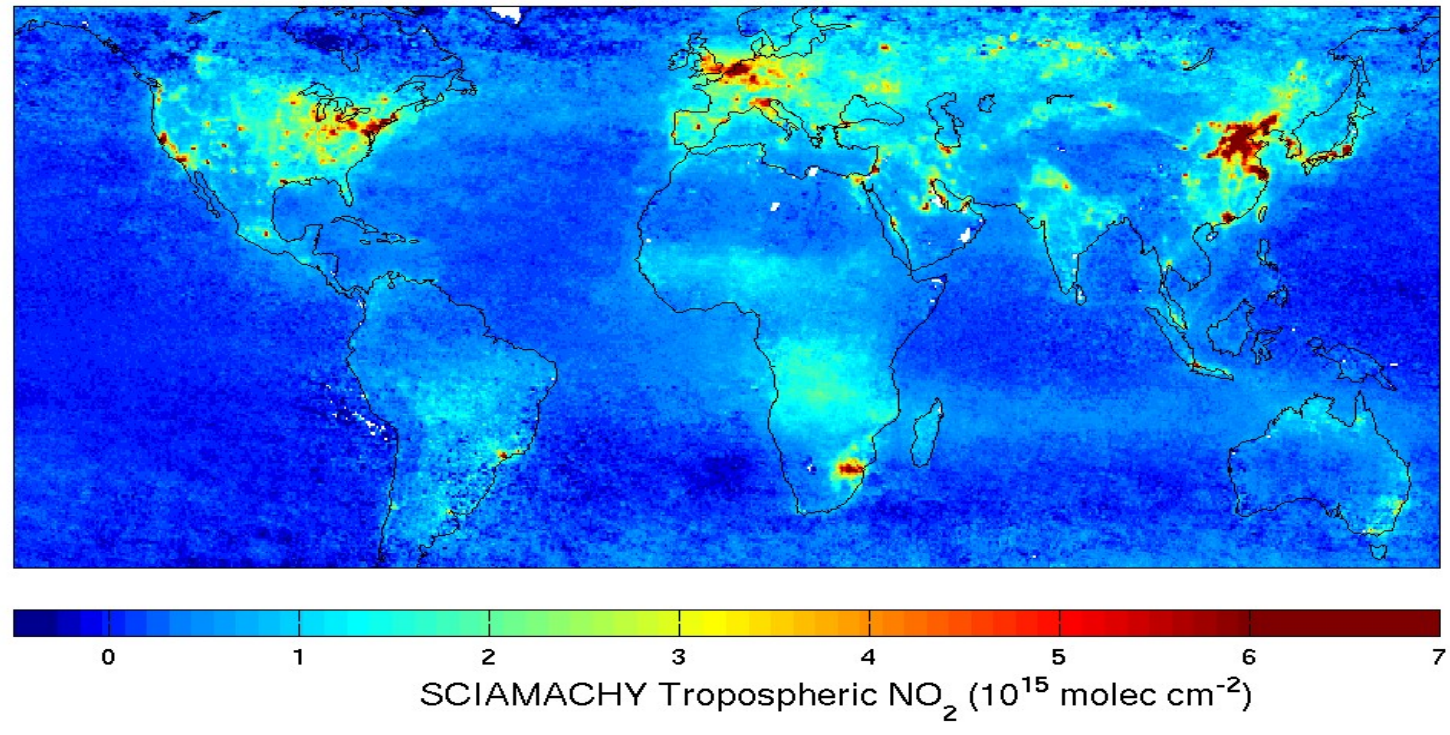
- "Background" tropospheric ozone concentration ~ 10-40 ppb




- Maintained in the troposphere by
  - Mixing of stratospheric ozone into tropsophere
  - Chemical/photochemical reactions involving NO & $NO_2$

# Global $NO_2$ Observations

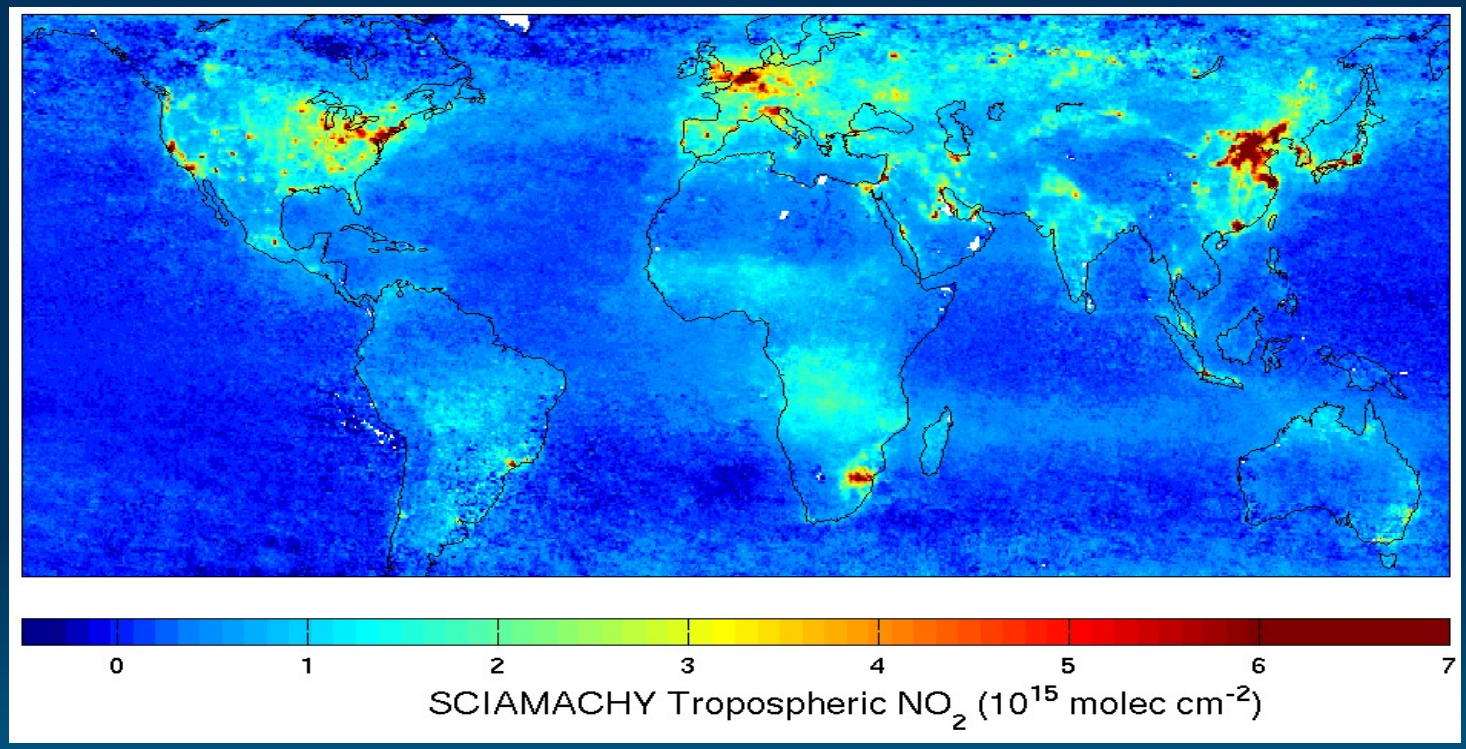
## $NO_2$ Columns Observed from the SCIAMACHY Satellite Instrument




- In densely populated regions with high emissions of NOx and hydrocarbons, rapid ozone production can take place and result in a surface air pollution problem.
- Industrial emission regions located at similar latitudes
  - Transport times about 1 week; chemical lifetime 3-4 weeks

# Global $NO_2$ Observations

$NO_2$ Columns Observed from the SCIAMACHY Satellite Instrument



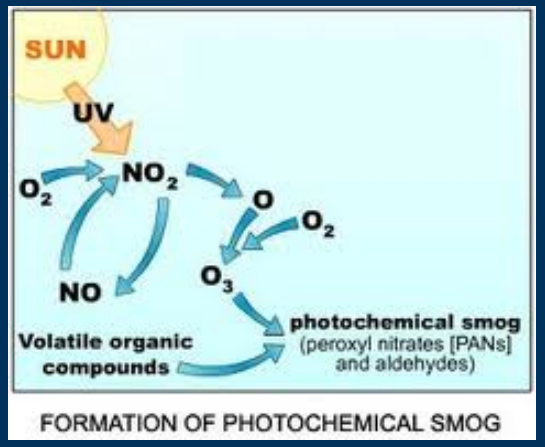

- How much do major emission regions affect each other?
  - How much do they contribute to background $O_3$?
  - Could this affect attainment of air quality standards

# Chemical Formation…..

- Source

$$NO_2 + UV \rightarrow NO + O \qquad (\lambda < 420\,nm)$$

$$O_2 + O \rightarrow O_3$$

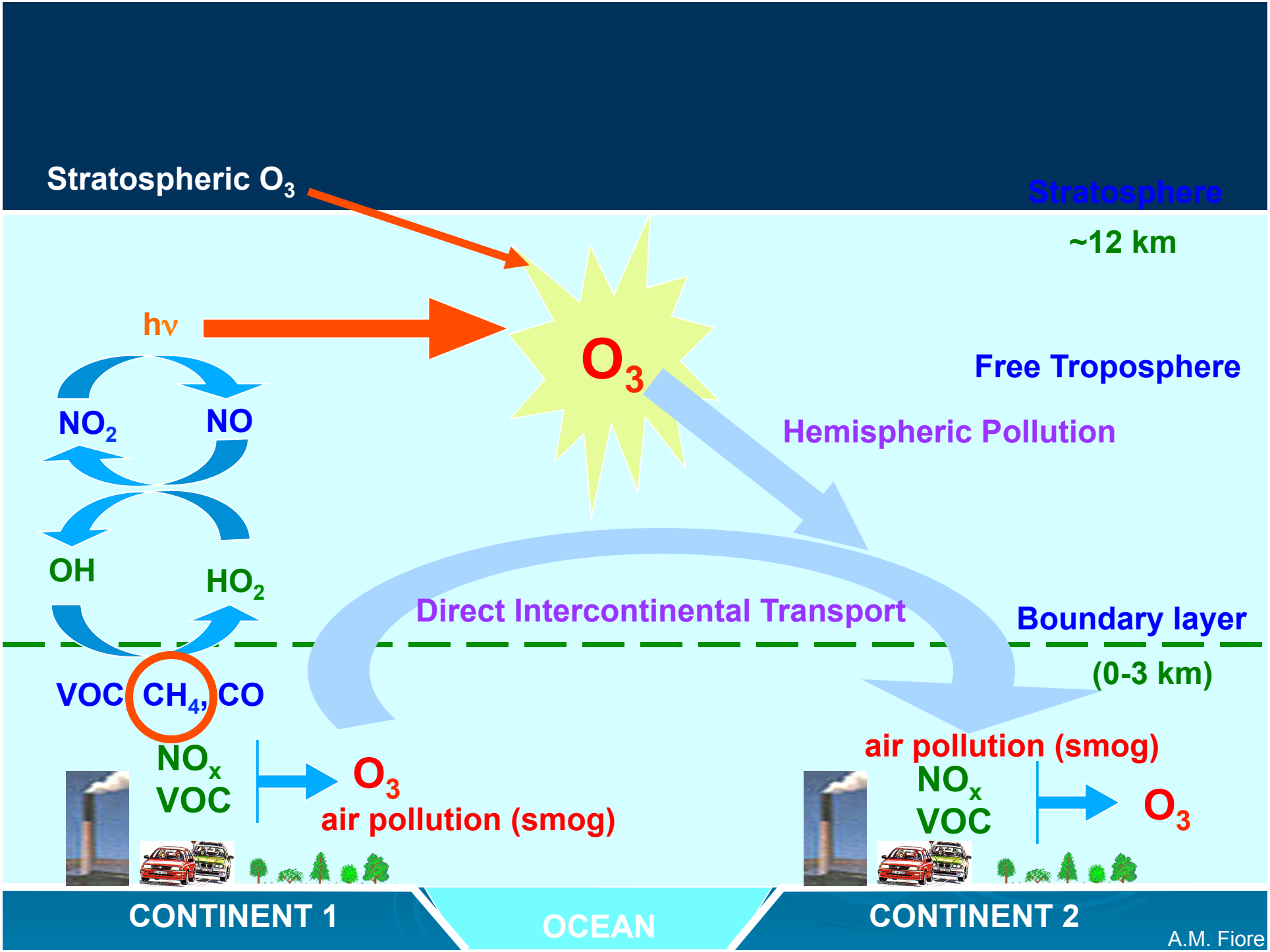


FORMATION OF PHOTOCHEMICAL SMOG

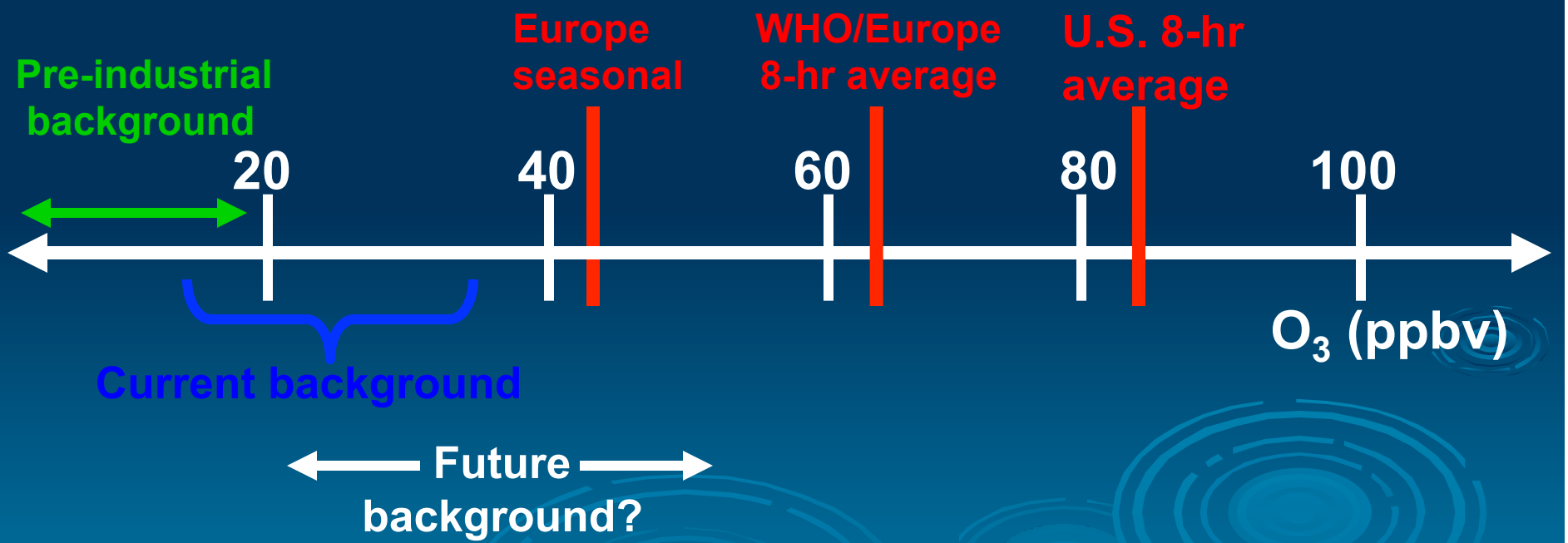
- Sink

$$NO + O_3 \rightarrow NO_2 + O_2$$

- Forming ozone at about the rate that it is being destroyed.
- Sources balance sinks
- Therefore, more or less a constant amount of ozone in the free troposphere at concentration of 10-40 ppb.
- Sunlight is required to break down $NO_2$
- Chemical reaction rates increase with temperature
- Therefore, higher O3 concentrations during hot days (typically)


Stratospheric $O_3$
Stratosphere
~12 km
hν
$O_3$
Free Troposphere
$NO_2$
NO
Hemispheric Pollution
OH
$HO_2$
Direct Intercontinental Transport
Boundary layer
(0-3 km)
VOC $CH_4$, CO
$NO_x$
VOC
$O_3$
air pollution (smog)
air pollution (smog)
$NO_x$
VOC
$O_3$
CONTINENT 1
OCEAN
CONTINENT 2
A.M. Fiore

Recent observational analyses suggest that surface $O_3$ background is rising
[e.g. *Lin et al.*, 2000; *Jaffe et al.*, 2003, 2005; *Vingarzan*, 2004; *EMEP/CCC-Report 1/2005* ]



# Chemical Formation…..

"LA Smog":
Brown-air smog in Los Angeles

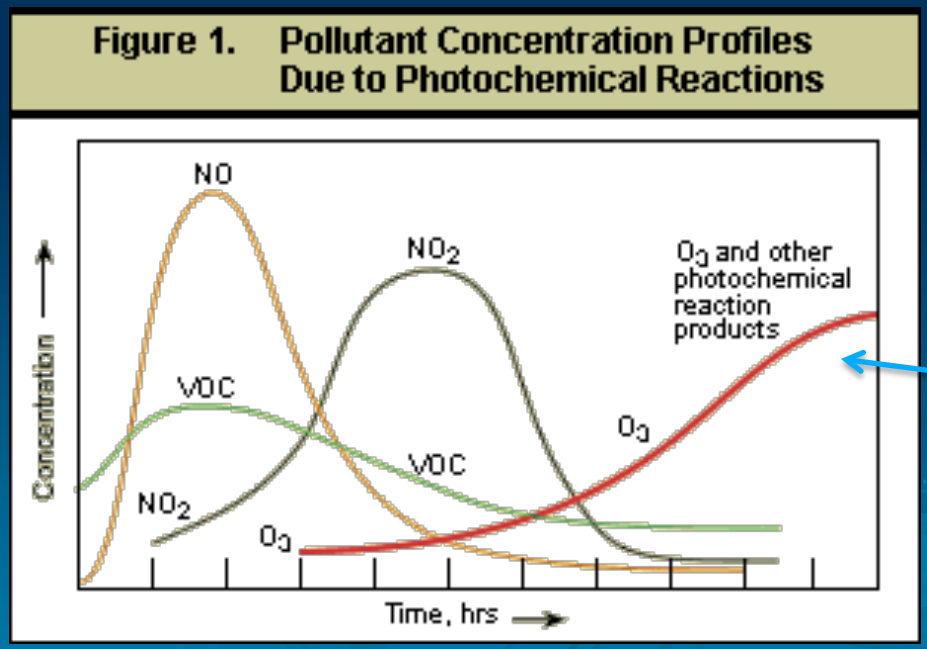


- $NO_2$ absorbs blue & green visible wavelengths
- Lets yellow, orange & red wavelengths pass through
- Visible to eye as "brown"

# Diurnal Cycle of Ozone Concentration…..

- Diurnal variation of emissions of NOx & VOCs
- The reactions begin quickly following the injection of nitrogen oxides, organic compounds, and carbon monoxide.
- Nitric oxide (NO) emitted from fossil-fuel-fired boilers, automobiles, trucks, and other fuel burning emission sources is rapidly converted to nitrogen dioxide ($NO_2$) due to photochemically initiated reactions.

**Figure 1. Pollutant Concentration Profiles Due to Photochemical Reactions**

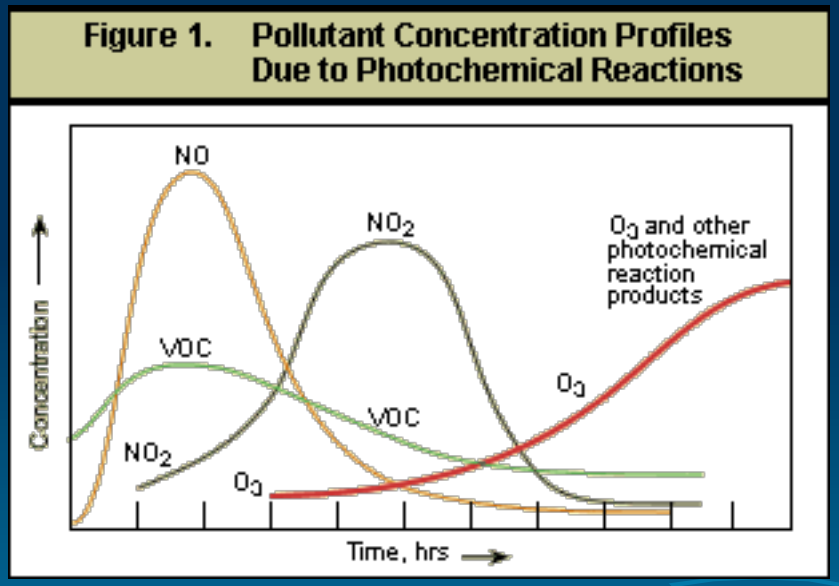



Peak ozone in late afternoon

Low ozone at night

# Diurnal Cycle of Ozone Concentration…..

- The formation of nitrogen dioxide further stimulates the photochemical smog-forming reactions because nitrogen dioxide is very efficient at absorbing sunlight in the ultraviolet portion of its spectrum.




$$NO + VOCs \rightarrow NO_2 + VOC^* s$$

$$NO + O \rightarrow NO_2 + O_2$$

$$NO_2 + UV \rightarrow NO + O \qquad (\lambda < 420\,nm)$$

$$O_2 + O \rightarrow O_3$$

# Observations over LA Basin

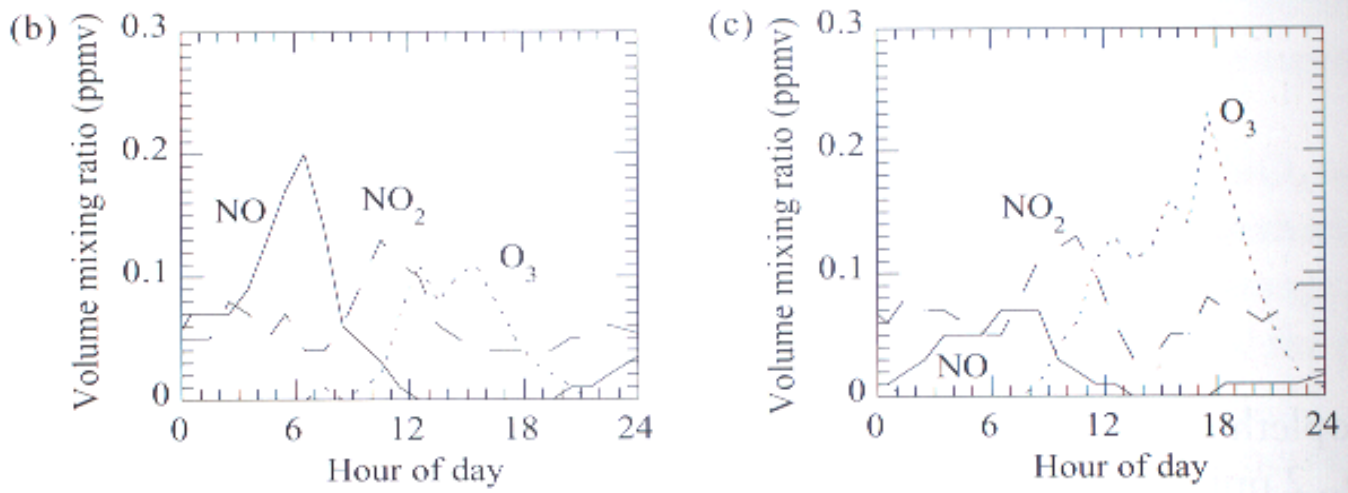
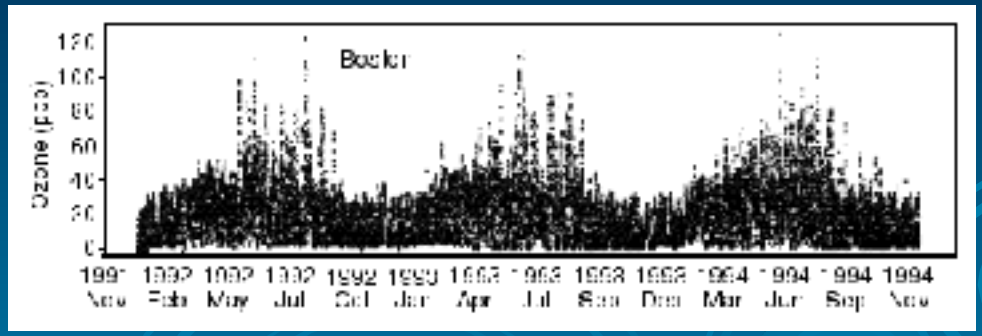


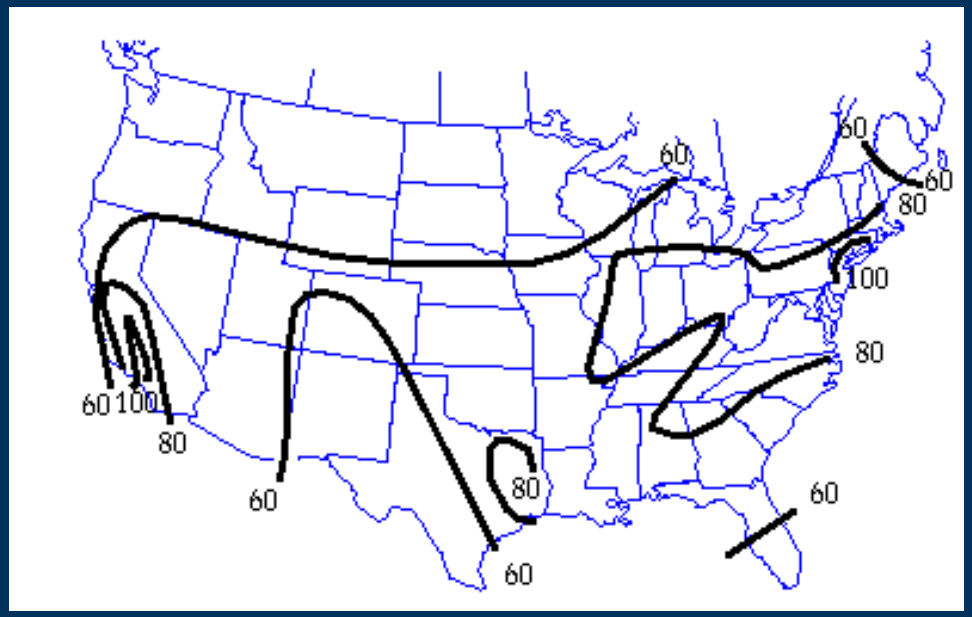

**Figure 11.2** (a) Wind speeds at Hawthorne from August 26 to 28, 1987. The other panels show the evolution of the NO, $NO_2$, and $O_3$ mixing ratios at (b) central Los Angeles and (c) San Bernardino on August 28. Central Los Angeles is closer to the coast than is San Bernardino. As the sea breeze picks up during the day, primary pollutants, such as NO, are transported from the western side of the Los Angeles basin (e.g., central Los Angeles) toward the eastern side (e.g., San Bernardino). As the pollution travels, organic peroxy radicals convert NO to $NO_2$, which forms ozone, a secondary pollutant.

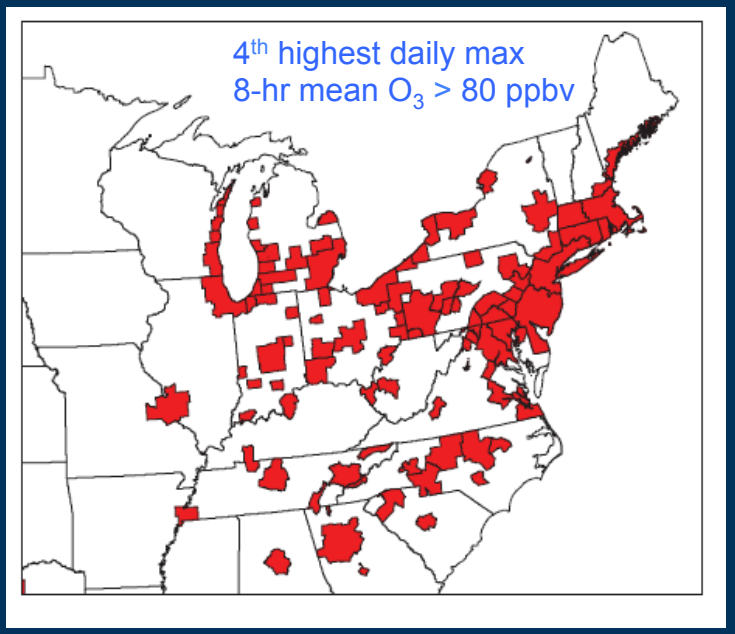
# Chemical Formation…..

- Concentrations of ozone in clean surface air are in the range of 5-30 ppbv
- The air quality standards for ozone in the US is a maximum 8-hour average ozone concentration of 84 ppbv not to be exceeded more than 3-times per year.



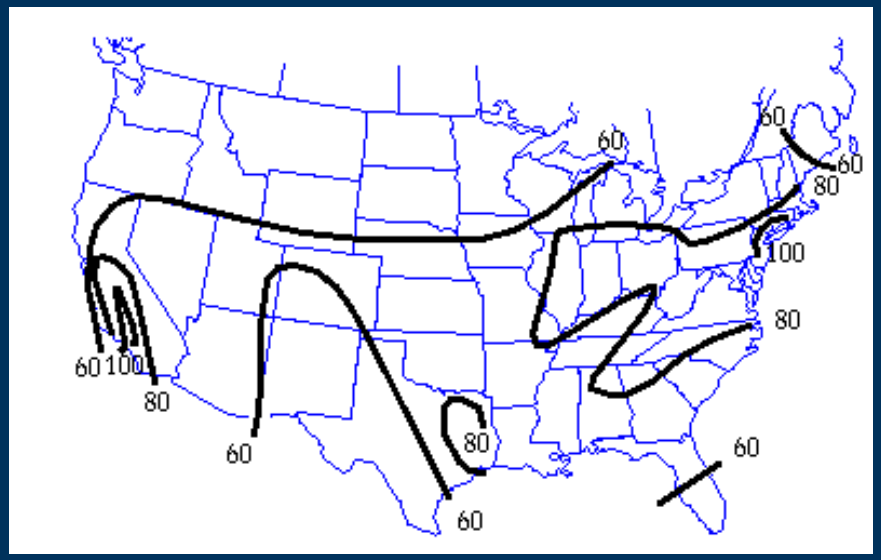
# U.S. Ozone Concentration

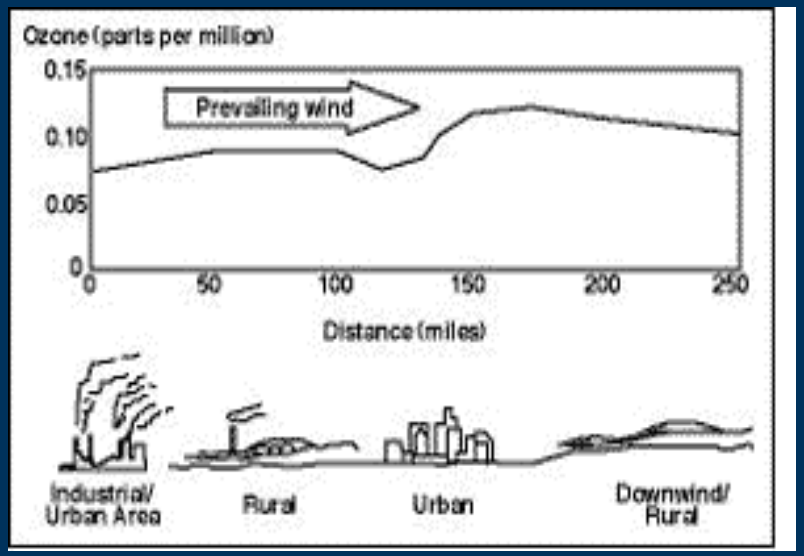



- 90th percentile (means that concentrations are higher 10% of the time) concentrations of summer over the U.S.
- Values in exceed of 80 ppbv are found over large areas of the country reflecting roughly the distribution of population
- The U.S. ozone smog problem is spatially widespread, affecting >100 million people

# U.S. Ozone Concentration



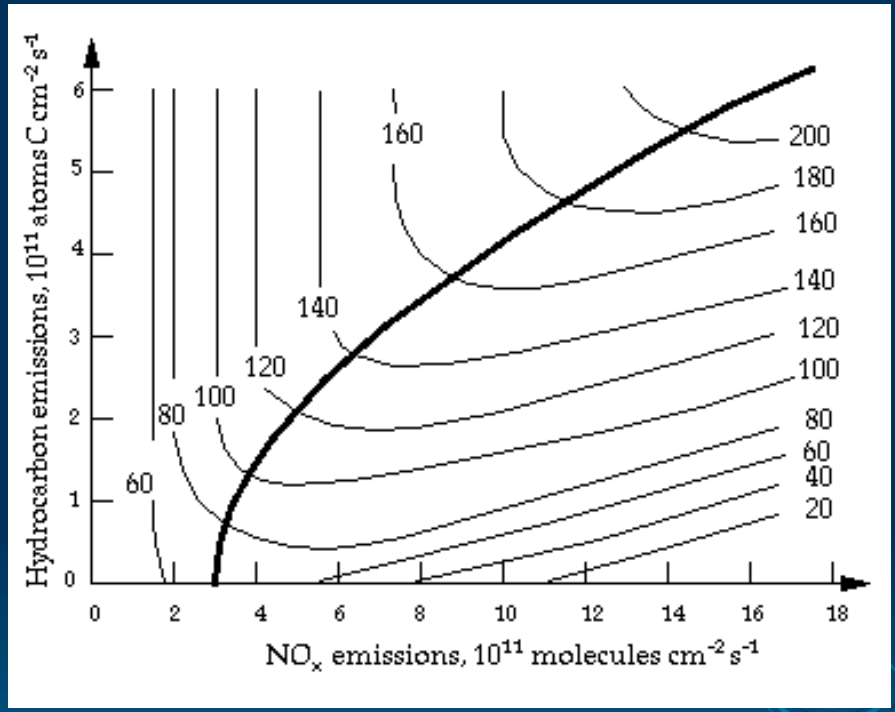

- Ozone air pollution is a regional rather than urban pollution problem
- Ozone and the pollutants that form it can cause air quality problems hundreds of miles away

# U.S. Ozone Concentration

- The presence of high concentrations of O3 in smog was first discovered in Los Angeles in the 1950s.
- Laboratory chamber experiments conducted at the time showed that O3 was generated by photochemical reactions in the atmosphere involving hydrocarbons and NOx emitted from automobiles.
- This atmospheric mechanism for O3 production helped to explain why O3 concentrations are often higher downwind of urban areas than in the urban areas themselves.
- The details of the chemical mechanism were poorly understood until the 1970s, however, because the essential role of OH as a hydrocarbon oxidant was not

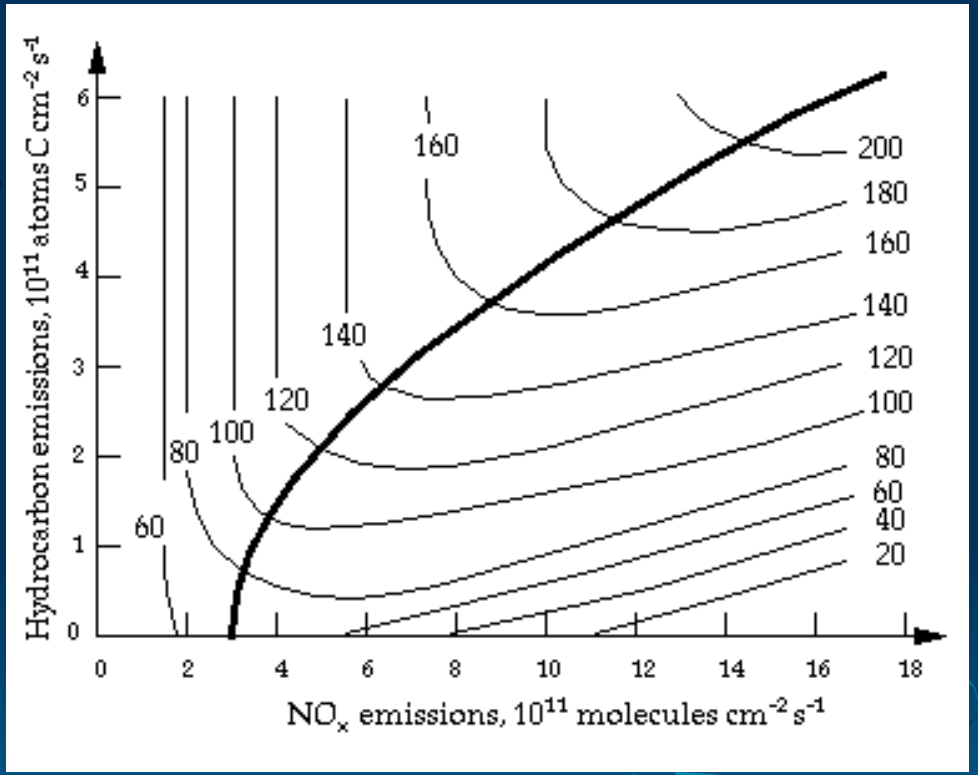
# U.S. Ozone Control Strategies

- O3 concentrations simulated over the eastern United States are plotted as a function of NOx and hydrocarbon emissions.
- The thick line on the Figure separates the NOx- and hydrocarbon-limited regimes.
- To the left of the line is the NOx-limited regime: O3 concentrations increase with increasing NOx and are insensitive to hydrocarbons.
- To the right of the line is the hydrocarbon-limited regime: O3 concentrations increase with increasing hydrocarbons and decrease with increasing NOx.



# U.S. Ozone Control Strategies

- The non-linear dependence of O3 on precursor emissions is readily apparent. In the NOx-limited regime, hydrocarbon emission controls are of no benefit for decreasing O3.
- In the hydrocarbon-limited regime, NOx emission controls cause an increase in O3.

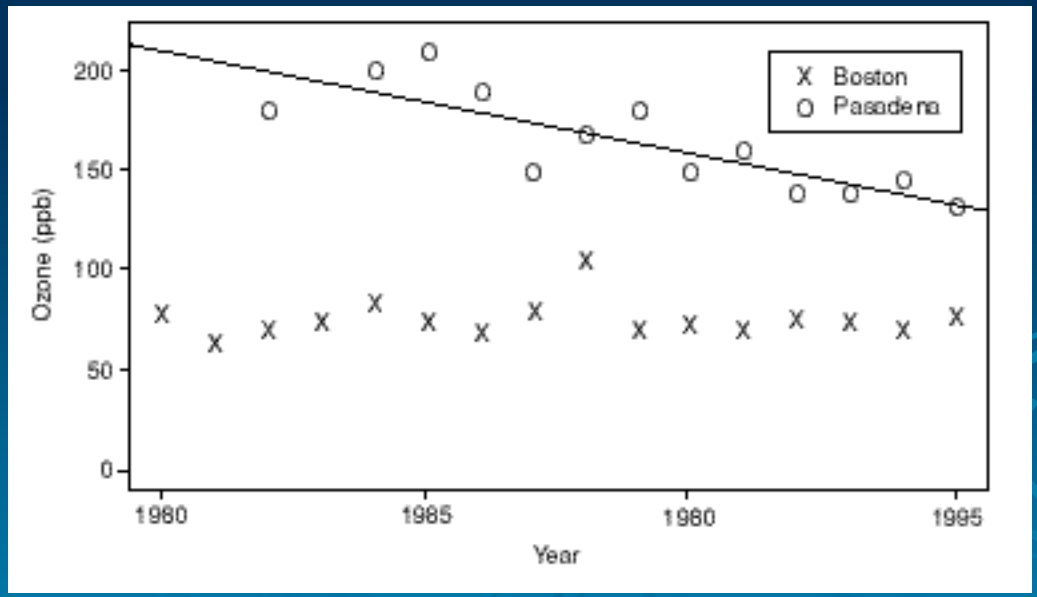


# U.S. Ozone Control Strategies

- In 1970s, strong regulatory effort to control hydrocarbon emissions from automobiles and industry is implemented.
- Emissions of NOx were also controlled, due at least initially to concern over the health effects of NO2 (a hazardous pollutant in its own right), but the effort was less than for hydrocarbon emissions.
- Controlling emissions has been an uphill battle because of the continuously rising population and fuel combustion per capita.
- Between 1980 and 1995, anthropogenic emissions of hydrocarbons in the United States decreased by 12% and NOx emissions remained constant, a significant achievement considering that population grew by 20% and automobile usage rose by 60%.

# U.S. Ozone Control Strategies

- Have these control strategies been successful?
- Analyses of long-term trends in O3 concentrations for the past two decades indicate significant decreases in the Los Angeles Basin and in the New York City metropolitan area, but no significant improvement over the rest of the country.
- This mixed success has caused air pollution control agencies to rethink their emission control strategies.



# U.S. Ozone Control Strategies

- An important discovery in the past decade is that the focus on hydrocarbon emission controls to combat O3 pollution may have been partly misdirected.
- Measurements and model calculations now show that O3 production over most of the United States is primarily NOx-limited, not hydrocarbon-limited.
- The early models were in error in part because they underestimated emissions of hydrocarbons from automobiles, and in part because they did not account for natural emission of biogenic hydrocarbons from trees and crops.
- It appears on the basis of present knowledge that future improvements in O3 air quality over the United States will require a vigorous program of NOx emisssion controls.

# Ozone Production Efficiency

- We saw that O3 production in the NOx-limited regime depends linearly on the NOx concentration.
- One might hope under these conditions that a reduction in NOx emissions would lead to a proportional decrease of O3 production
- This is however not the case
- An important concept introduced in late 1980s is the O3 production efficiency (e) defined as the number of O3 molecules produced per molecule of NOx consumed

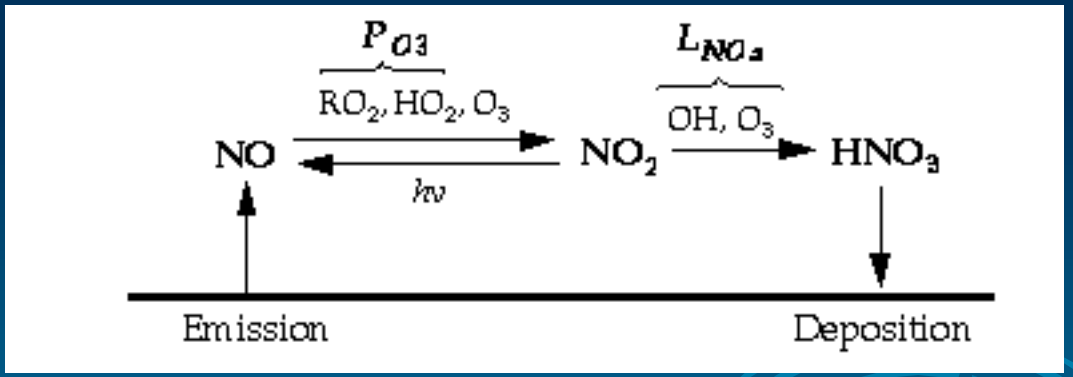
$$e = \frac{P_{O_3}}{L_{NOx}}$$

- where LNOx is the loss rate of NOx.

# Ozone Production Efficiency

- We see that the O3 production efficiency increases with increasing hydrocarbon concentrations and decreases with increasing NOx concentration.

$$e = \frac{P_{O_3}}{L_{NOx}}$$



# Ozone Concentrations Depend On…

- Concentration and ratio of NOx and VOCs
- Wind speed and direction
- Terrain
- Temperature
- Stagnant conditions (depends on wind and temperature)
- Time of year (“ozone season”)



# Effects of Temperature

Temperature inversions represent a situation in which the atmosphere is very stable and the mixing depth is significantly restricted.

When an inversion exists and winds are light, diffusion is inhibited and high pollution concentrations are to be expected in areas where pollution sources exist.

Surface-temperature inversions form because the ground is a more effective radiator than the air above.

Inversions aloft are associated with sinking air that characterizes centers of high air pressure.

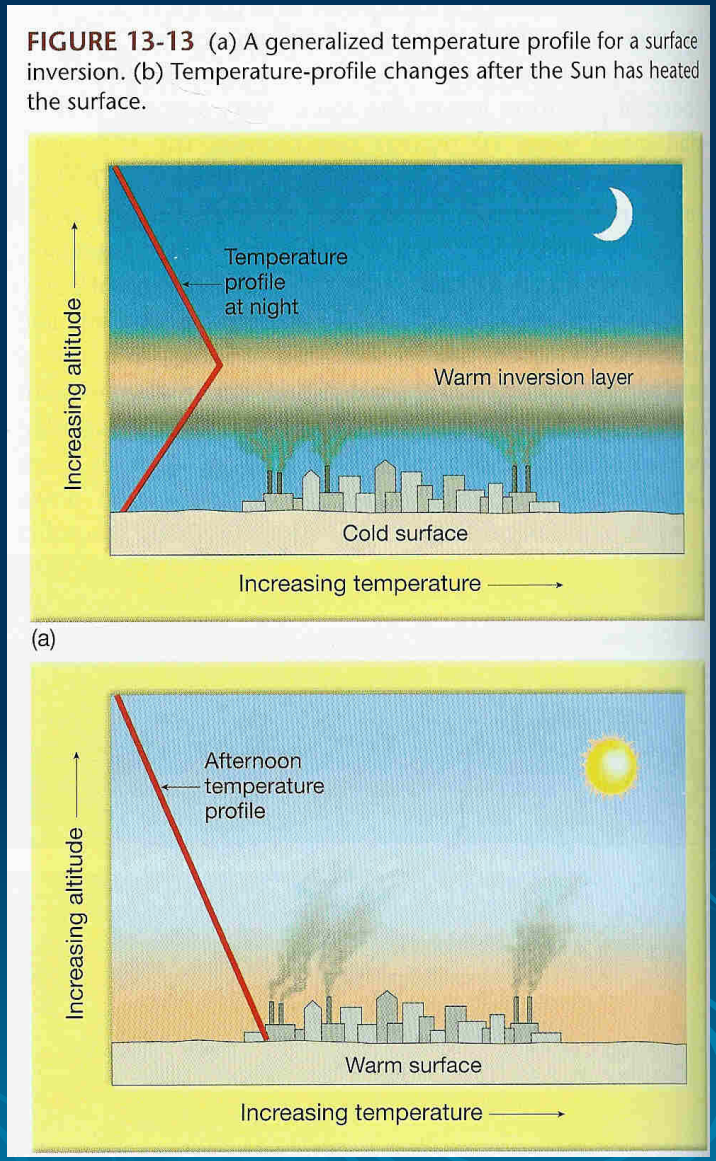
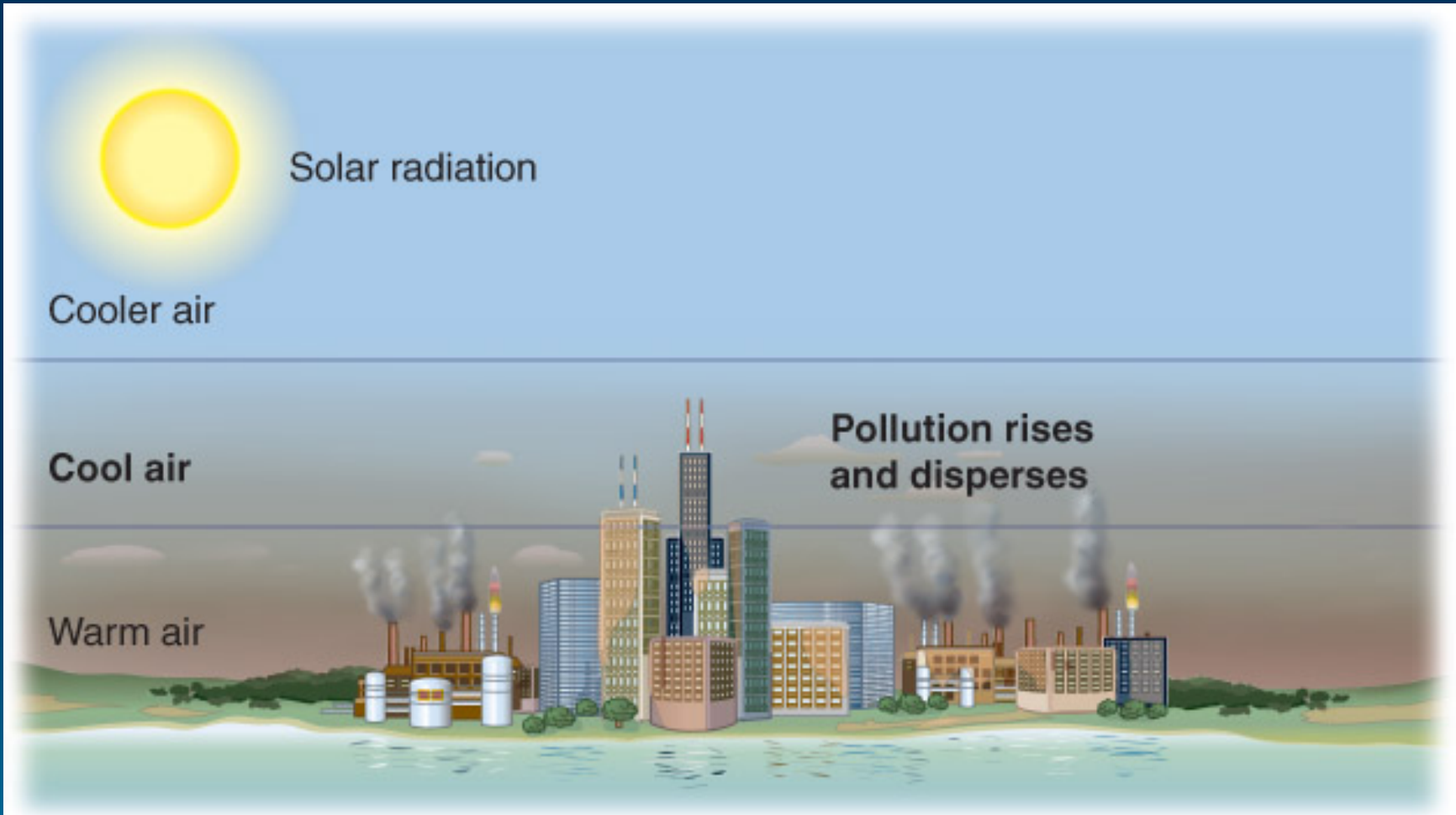


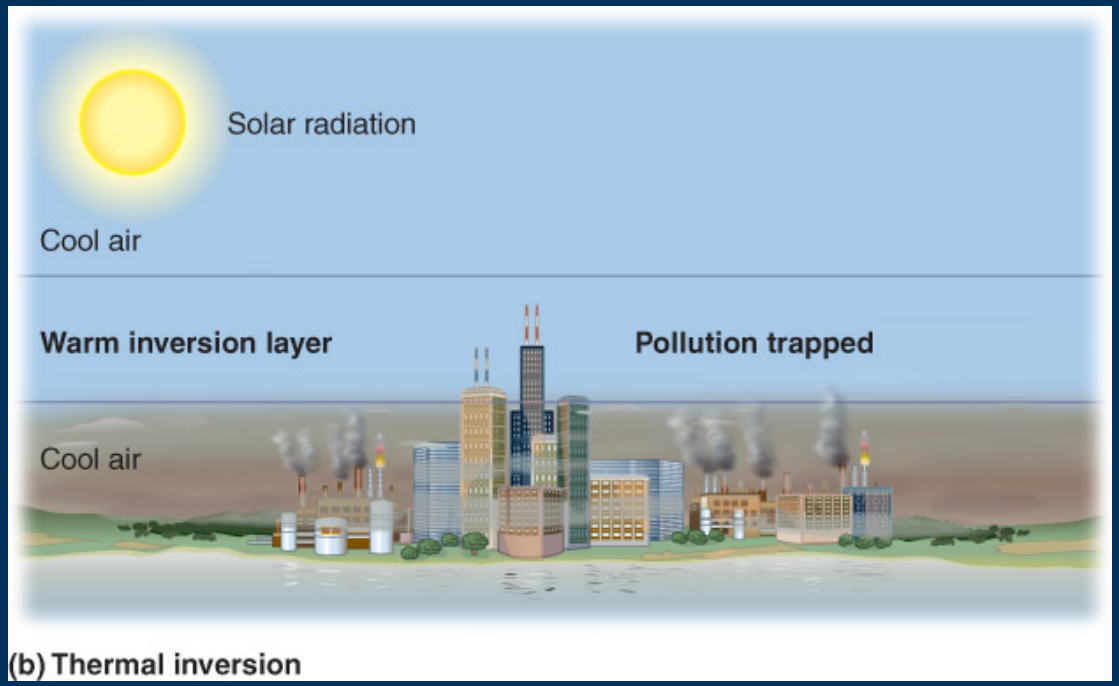
FIGURE 13-13 (a) A generalized temperature profile for a surface inversion. (b) Temperature-profile changes after the Sun has heated the surface.

# Effects of Temperature

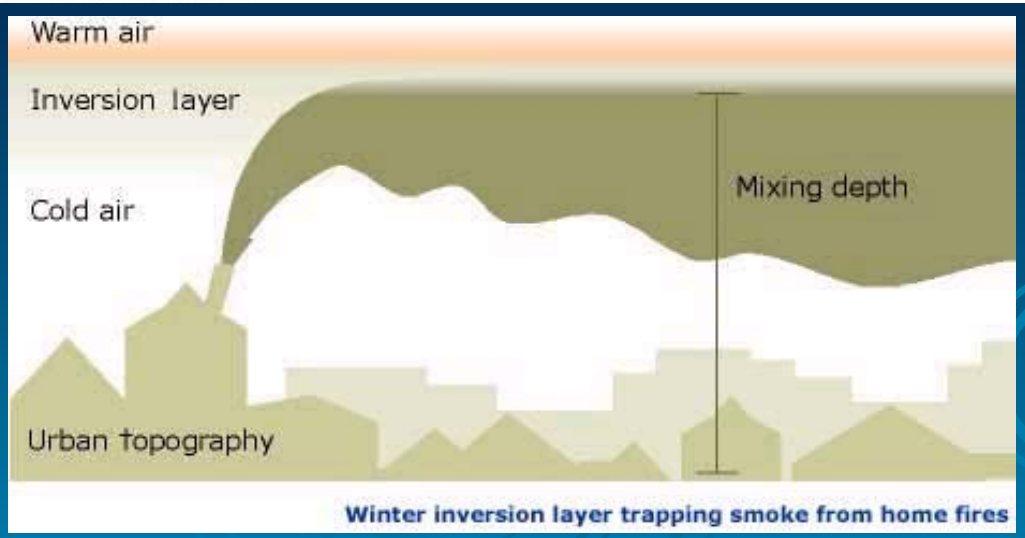



(a) Normal pattern

# Effects of Temperature




(b) Thermal inversion




Winter inversion layer trapping smoke from home fires

# Effects of Wind




**FIGURE 13-11** Effect of wind speed on the dilution of pollutants. The concentration of pollutants increases as wind speed decreases.

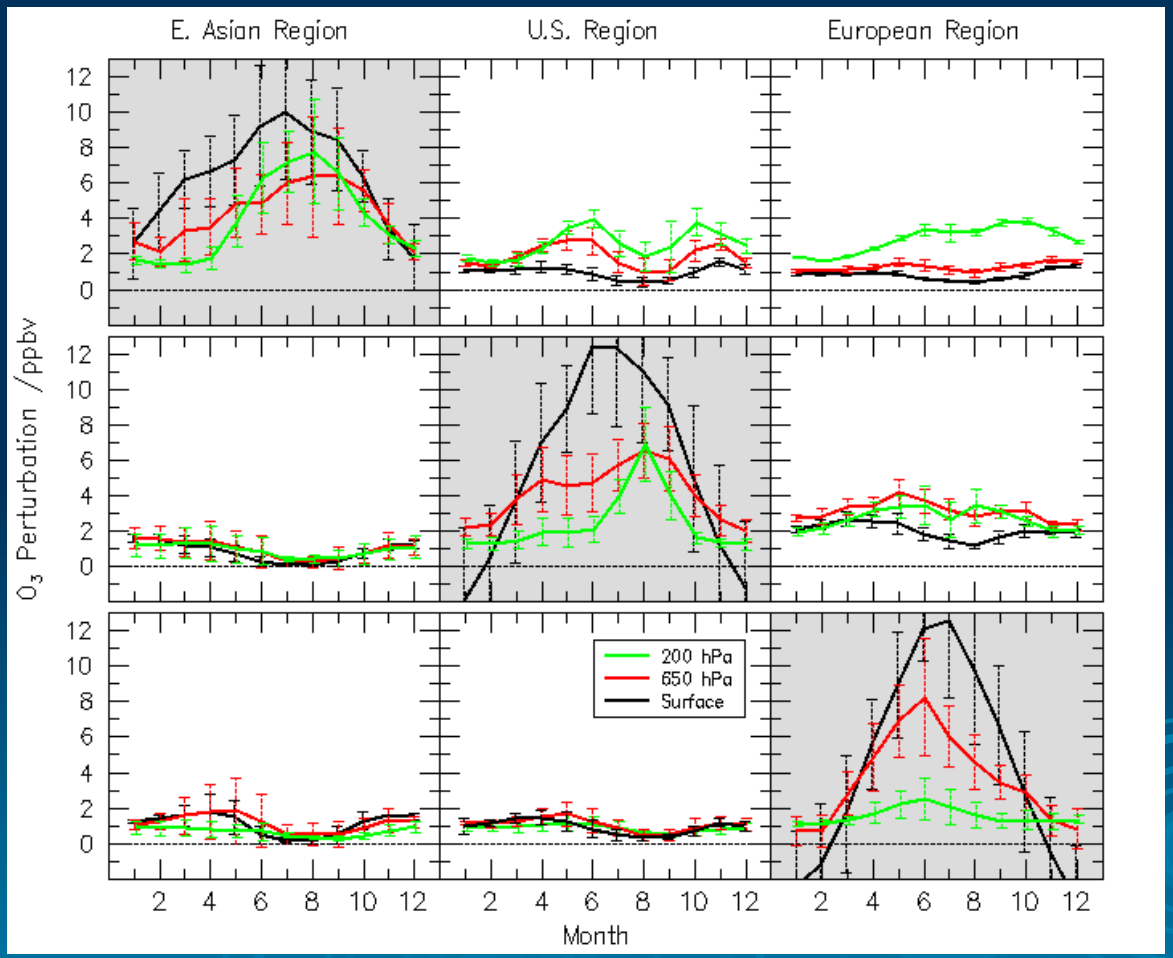
The direct effect of wind speed is to influence the concentration of pollutants.

# Effects of Wind & Time of Year

East Asian Emissions

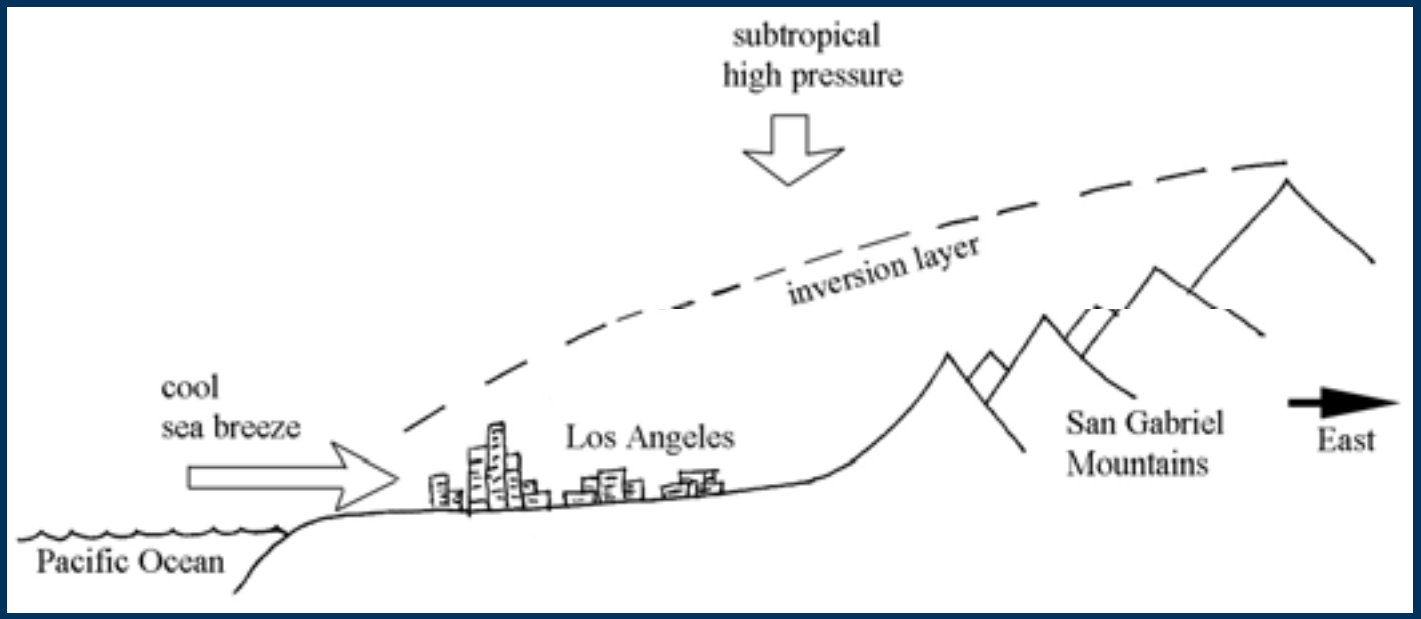
US Emissions

European Emissions



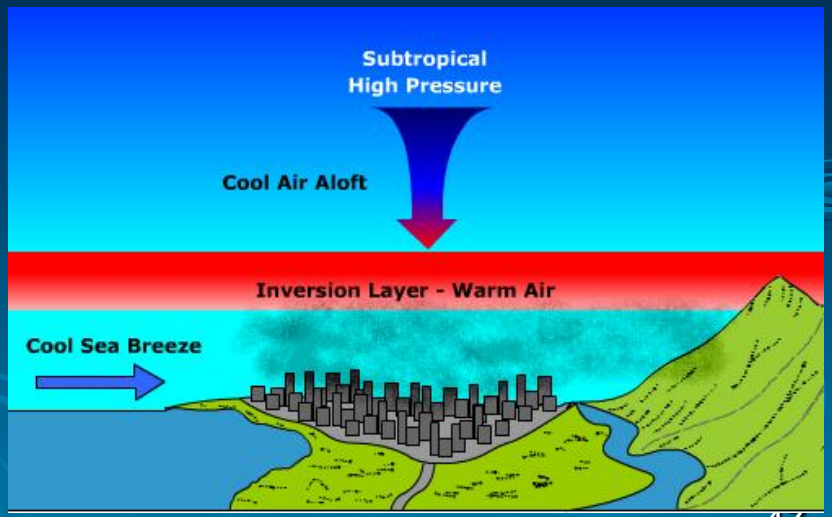

Source-Receptor Matrix

# Effects of Topography

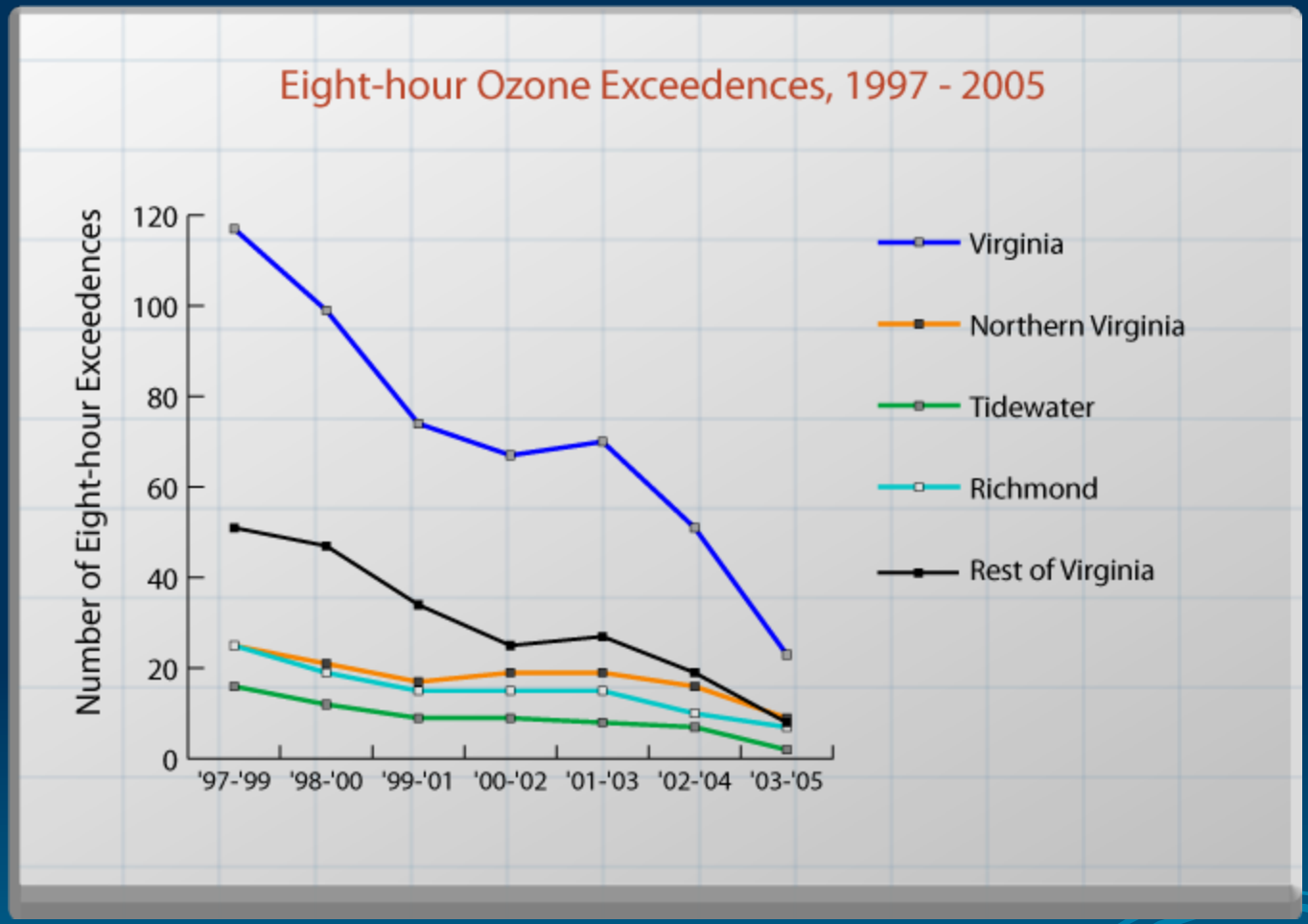








# Atmospheric Ozone




http://www.vaperforms.virginia.gov/images/graphs/AirQuality-Ozone-large.png

# Summary

- Air is said to be “Polluted” when it is **no longer tasteless**, **odorless**, **colorless**
- Two types of ozone, Stratospheric (good) and Tropospheric (bad)
- Ozone pollution has major effects on economics, human health, and environmental health.
- Ozone is a secondary pollutant and its precursors are NOx and VOCs.
- Precursors of ozone reach to a region by long distance transport
- Environmental health is most effected in rural areas.