Urban Air Pollution

- Public Health and Environmental Concerns
  - Elevated levels of toxic compounds
    - Primary (directly emitted) and Secondary (formed *in situ)* Pollutants
- Regional and Global Impacts
  - Atmospheric Chemistry and Composition
  - Climate

The Urban Smog Problem

Smog – "Smoke" + "Fog"
•Coined due to reduced visibility associated with pollution episodes

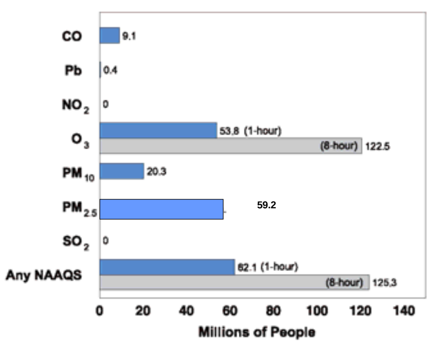
Major components:
•"invisible": O_3, CO, SO_2
•"visible": PM (aerosols) + some gases (NO_2)

Ingredients
•Sun (photochemistry)
•Stagnation
•Emissions of NO_x, SO_2, PM and VOC

← Houston, TX
Aug. 2000

Air Quality—Societal Problem

Number of people in U.S. living in non-attainment areas



Violating O_3 NAAQS

US EPA National Ambient Air Quality Standards for O_3
- **1hr avg<120 ppb**
- **8hr avg < 75 ppb***

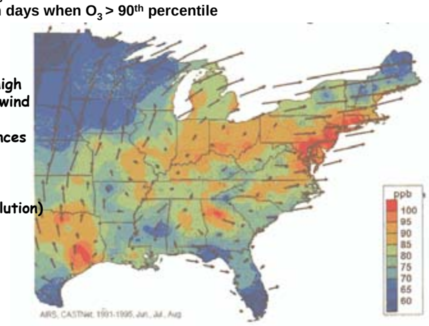
*To attain this standard, the 3-year average of the fourth-highest daily maximum 8-hour average ozone concentrations measured at each monitor within an area over each year must not exceed 0.075 ppm.

Figure 4. Counties Where Fourth Highest Daily Maximum 8-Hour Ozone Concentration Is Above the Level of the 8-Hour Standard in 2003.

Surface O_3 and Transport

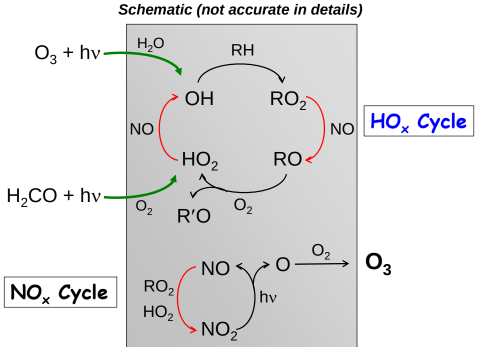
90th percentile O_3 concentrations for summers 1991-1995 and mean 850hPa winds on days when O_3 > 90th percentile

- Large regions with high O_3 tend to have low wind speed
  - stagnation enhances impact of local chemistry
- Elevated O_3 (Air Pollution) is not just an urban problem



Photochemical O_3 Production

Schematic (not accurate in details)



$$P_{O3} = k_{RO2+NO}[RO_2][NO] + k_{HO2+NO}[HO_2][NO]$$

Chain Termination and HO_x Steady State

Generally: $P_{HOx} = L_{HOx}$

LOW NO_x: $L_{HOx} \sim 2k[HO_2]^2$ ⟶ $P_{HOx} \approx 2k[HO_2]^2$

**$HO_2 + HO_2 + M \rightarrow H_2O_2 + O_2 + M$

$RO_2 + HO_2 \rightarrow ROOH$

$OH + HO_2 \rightarrow H_2O + O_2$

High NO_x: $L_{HOx} \sim k[OH][NO_2]$ ⟶ $P_{HOx} \approx k[OH][NO_2]$

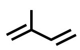
**$OH + NO_2 + M \rightarrow HNO_3 + M$

$RO_2 + NO + M \rightarrow RONO_2 + M$

**Typically most important reactions in each regime

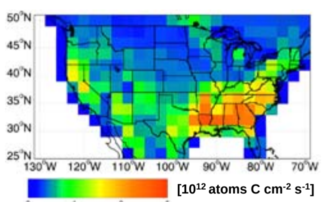
Biogenic VOCs

Isoprene

 $+ OH \xrightarrow{O_2} RO_2$ Important source of peroxy radicals: enhance O_3 production

Many other reactive biogenic VOC: influence P_{O3} and aerosol mass

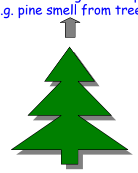
US isoprene emissions > than the sum of US anthropogenic hydrocarbon emissions

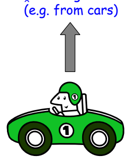


GEIA Isoprene Emissions In July, *Guenther, et al*

Chemical ingredients for photochemical smog

VOC = volatile organic compound (e.g. pine smell from trees) + NO_x = nitrogen oxides (e.g. from cars) → O_3 = photochemical smog

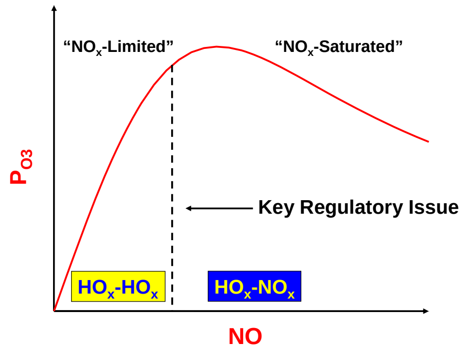




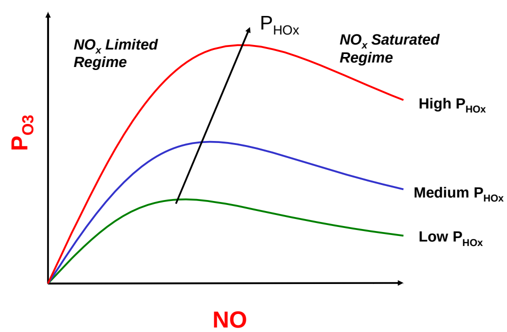
"Trees cause more pollution than automobiles do." Ronald Reagan 1981

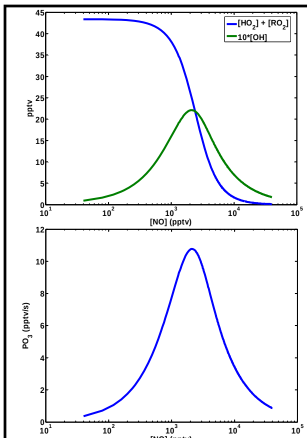
Also requires emissions from cars/industry!

P_{O3} Dependence on NO



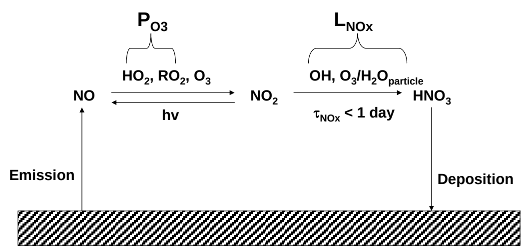
P_{O3} Dependence on P_{HOx} and NO





Explain these features of HO_x, NO_x, and PO_3

Ozone Production Efficiency = P_{O3}/L_{NOx}



Questions

1. A NO_x-emitting power plant wants to reduce its contribution to O_3 pollution in its immediate region. It asks you, an environmental consultant, if it should spend $10 million dollars to cut its NO_x emissions by 20%. You find, by modeling O_3 production, that the immediate region is NO_x-saturated. How do you answer?

2. Even though some of the single largest NO_x emitters are located in the Tennessee Valley, O_3 production in this region is generally NO_x-limited. Why?

3. What time of year would you expect the fastest and slowest P_{HOx}? Where would you expect the fastest P_{HOx}: Arizona or South Carolina?

4. Is there a time of year NO_x-saturated O_3 production would be more likely, if so, when?