

Urban Air Pollution

READING: Chapter 12 of text

- 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)

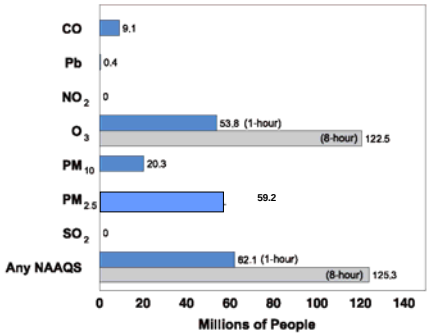
Ingredients

- 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



Pollutant	1-hour Standard (Millions)	8-hour Standard (Millions)
CO	9.1	-
Pb	0.4	-
NO ₂	0	-
O ₃	53.8	122.5
PM ₁₀	20.3	-
PM _{2.5}	59.2	-
SO ₂	0	-
Any NAAQS	82.1	125.3

Violating O₃ NAAQS

US EPA National Ambient Air Quality Standards for O₃

- 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.



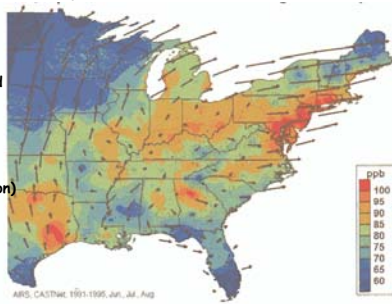
Figure 4. Counties where fourth highest daily maximum 8-hour ozone concentration is above the level of the 8-hour standard in 2003.

Surface O₃ and Transport

90th percentile O₃ concentrations for summers 1991-1995 and mean 850hPa winds on days when O₃ > 90th percentile

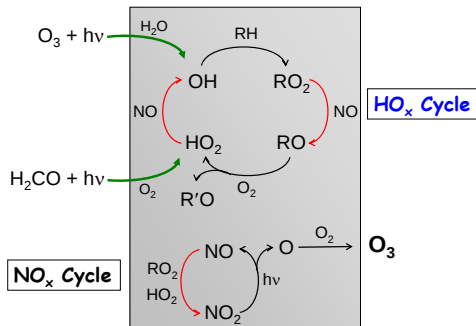
- Large regions with high O₃ tend to have low wind speed
- stagnation enhances impact of local chemistry

•Elevated O₃ (Air Pollution) is not just an urban problem



Photochemical O₃ Production

Schematic (not accurate in details)



Chain Termination and HO_x Steady State

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

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

**HO₂ + HO₂ + M → H₂O₂ + O₂ + M

RO₂ + HO₂ → ROOH

OH + HO₂ → H₂O + O₂

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

**OH + NO₂ + M → HNO₃ + M

RO₂ + NO + M → RONO₂ + M

**Typically most important reactions in each regime

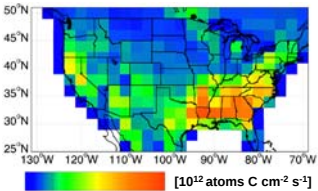
Biogenic VOCs

Isoprene

CC(=C)C + OH $\xrightarrow{O_3}$ RO₂ Important source of peroxy radicals: enhance O₃ production

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

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

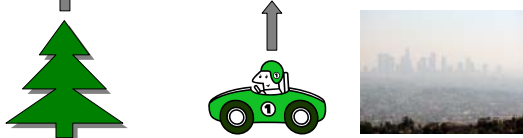


GEIA Isoprene Emissions in July, Guenther, et al

[10¹² atoms C cm⁻² s⁻¹]

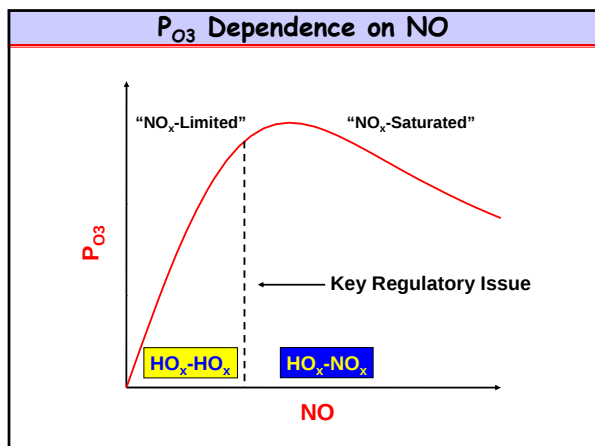
Chemical ingredients for photochemical smog

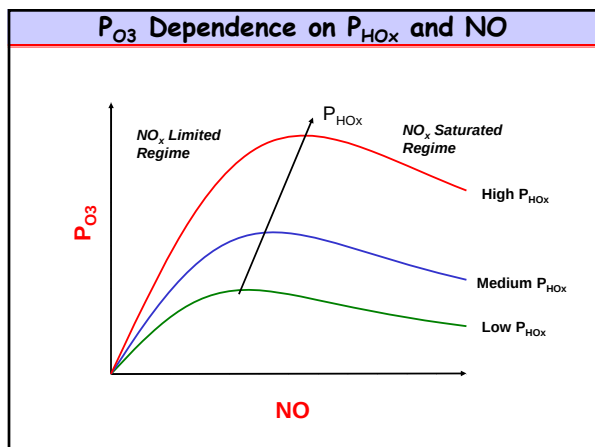
VOC = volatile organic compound (e.g. pine smell from trees) + NO_x = nitrogen oxides (e.g. from cars) → O₃ = photochemical smog

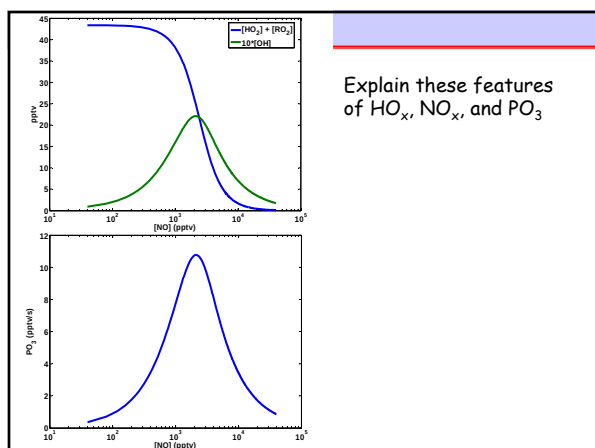



*Trees cause more pollution than automobiles do." Ronald Reagan 1981

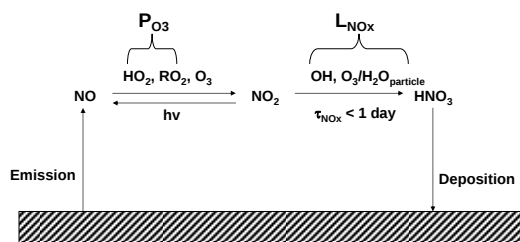
Also requires emissions from cars/industry!







Ozone Production Efficiency = P_{O_3}/L_{NO_x}



Questions

1. A NO_x-emitting power plant wants to reduce its contribution to O₃ 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 O₃ 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, O₃ production in this region is generally NO_x-limited. Why?
3. What time of year would you expect the fastest and slowest P_{HO_x} ? Where would you expect the fastest P_{HO_x} : Arizona or South Carolina?
4. Is there a time of year NO_x-saturated O₃ production would be more likely, if so, when?
