Lecture 10, March 2016 - Urban Pollution Control Strategies

If you have access to Holloway and Wayne, Atmospheric Chemistry

- Basics - pages 31-55
- Health effects of particulate matter – 5.4.3, p162-166
- Health effects of HCs – 5.4.4, p166-167
- Health effects of NOx – 5.4.5, p167-168
- Health effects of ozone – 5.4.6, p169-170
- Federal Monitoring Requirements – 7.1.3, p229-230
- Air Quality Monitoring Networks – 7.1.3.1, p230-231
- Air Quality Index – 7.1.3.5, p239-240
- Regulation and Public Policy – 8.1, p257-259
- Regulatory Strategies and Tactics – 8.2, p259-265
- Federal Legislative History – 8.3, p265-267
- Air Pollution Control 1970-1990 – 8.4, p268-287

In the case of ozone depletion in the stratosphere, the world decided to simply ban all production and sales of chlorofluorocarbons and any other compounds with similar properties that would live long enough in the troposphere to reach the stratosphere, releasing atoms that could initiate catalytic cycles that destroy ozone.

As noted in class last time, this was a rare example of the world's sovereign nations coming together to avoid a threat before any evidence existed to prove that the threat was real. As it turned out, the ozone hole was a warning – in fact, these chemicals could deplete ozone, and it was a good thing countries agreed to ban CFCs and other ODS (ozone depleting substances).

See my 2012 lecture at the U.S. Department of State for more on this issue.

In the case of smog formation in the troposphere, the problem is far more complex, and every city/region has its own unique mix of chemicals (from various sources of emissions) and meteorology (winds and transport) that makes regulating the problem very difficult. A different set of regulations is probably needed for each unique environment. Therefore, a framework was established in the 1980s and 1990s to address these differences, and rather than simply "ban" emissions of compounds such as volatile organic compounds (VOCs), nitrogen oxides (NOx), carbon monoxide (CO), and particulate matter (PM), a partnership-like approach was adopted, where scientists worked together with local industries and civic leaders to establish a rational set of rules to reduce the most important pollutants, called "criteria pollutants." Specialized, but highly constrained models are used to assess the impacts of all the individual pollutants, and rules address those that have the greatest impact on reducing smog.

Urban Pollution Control Strategies

What we know so far:

- Different regions have different issues, but two types of ‘smog’ stand out
  - London-type (cold, damp, smoke, fog, sulfur)
  - Los Angeles-type (photochemical) (sunny, warm, NOx, HCs, ozone, CO)

- Pollution is made worse by meteorological conditions called “inversions”

- In all cases, it’s important to *reduce emissions*, but in the case of the photochemical pollution, there are primary and secondary pollutants to be concerned with – e.g. ozone. One doesn’t ‘reduce emissions’ of these secondary pollutants. Rather, one identifies the mechanism of formation and goes after the primary pollutants that are responsible for the formation of the secondary pollutants.

Urban Pollution Control Strategies

What we know so far:

- Generic scheme for photochemical smog:

$$RH + OH \rightarrow R + H_2O$$
$$R + O_2 + M \rightarrow RO_2 + M$$
$$RO_2 + NO \rightarrow RO + NO_2$$
$$RO + O_2 \rightarrow R'CHO + HO_2$$
$$HO_2 + NO \rightarrow OH + NO_2$$
$$2\{NO_2 + h\nu \rightarrow NO + O\}$$
$$2\{O + O_2 + M \rightarrow O_3 + M\}$$

net: $RH + 4O_2 + h\nu \rightarrow R'CHO + 2O_3 + H_2O$

Urban Pollution Control Strategies

What we know so far:

Primary pollutants: NO, hydrocarbons (RH), CO
Secondary pollutants: NO_2, R'CHO (HCs), O_3

HC = hydrocarbon
VOC = volatile organic compound

We typically call species that appear on both sides of a series of reactions "intermediates", although we call those intermediates that speed up the overall reaction scheme "catalysts".

We know that the catalyst OH is formed by the reaction of H_2O with $O(^1D)$ (which comes from ozone photolysis)

Let’s examine the evolution of photochemical smog on a typical day in Los Angeles

Early morning (6 – 9 am): Automobile traffic and industrial emissions begin. Largest concentrated emissions of CO, RH, and NO. Winds generally slack and air is relatively stagnant, with a low inversion layer.

Midday (9 am – 2 pm): Primary emissions continue. Photochemical transformations take place. Sea breeze picks up and transports pollutants inland. Maximum sun intensity around noon.

Late afternoon (3 – 5 pm): Ozone concentrations peak. Inversion usually broken, so vertical transport moves pollutants upward and sometimes out of region.

Evening (5 – 7 pm): More primary emissions from traffic. Low sun angles, so difficult to make secondary pollutants. Primary pollutants can accumulate. Ozone concentrations begin to fall.

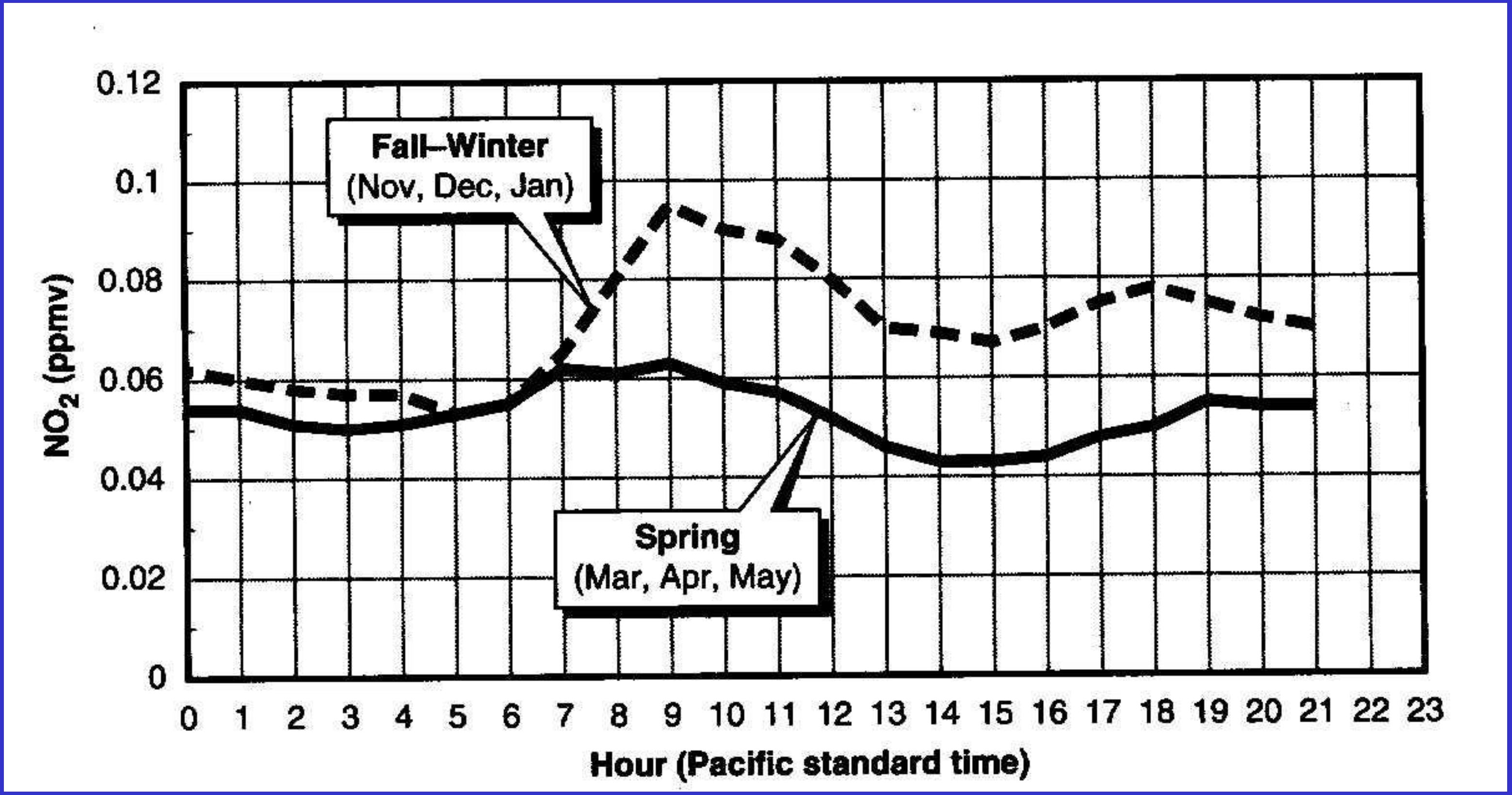
Late evening (7 – 9 pm): Sea breeze dies. Temperature inversion re-forms, usually leaving day's pollution above (accounts for layered structure of multiple day's smog).

Overnight (9 pm – 6 am): Pollutants are converted to reservoir species, such as HNO_3 and peroxy acetyl nitrate (PAN = $CH_3C(O)O_2NO_2$).

Species like PAN can be very toxic, so regulations are often established to reduce their buildup in urban regions

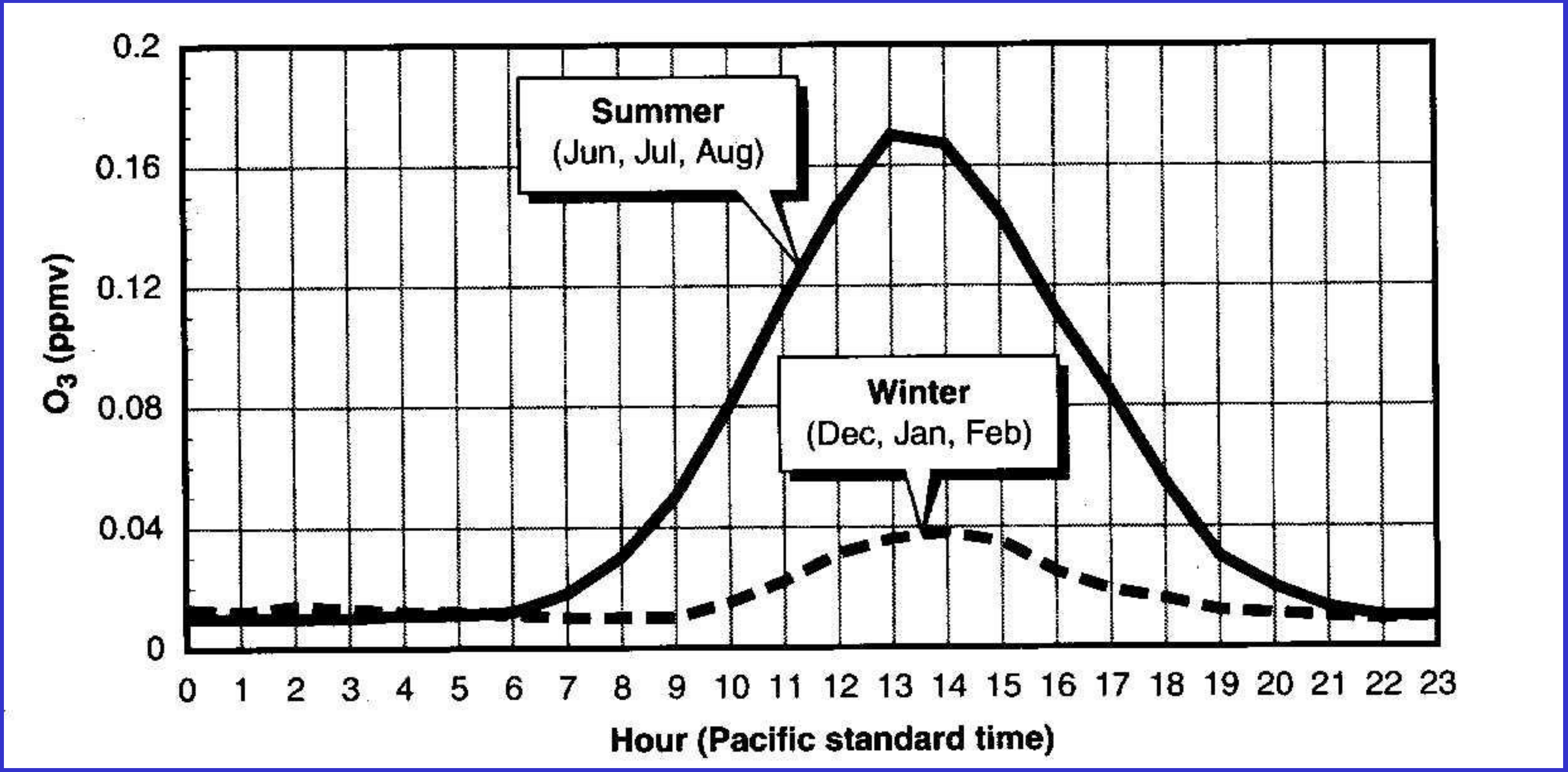
Diurnal Behavior of Various Species

Nitrogen dioxide (NO_2)



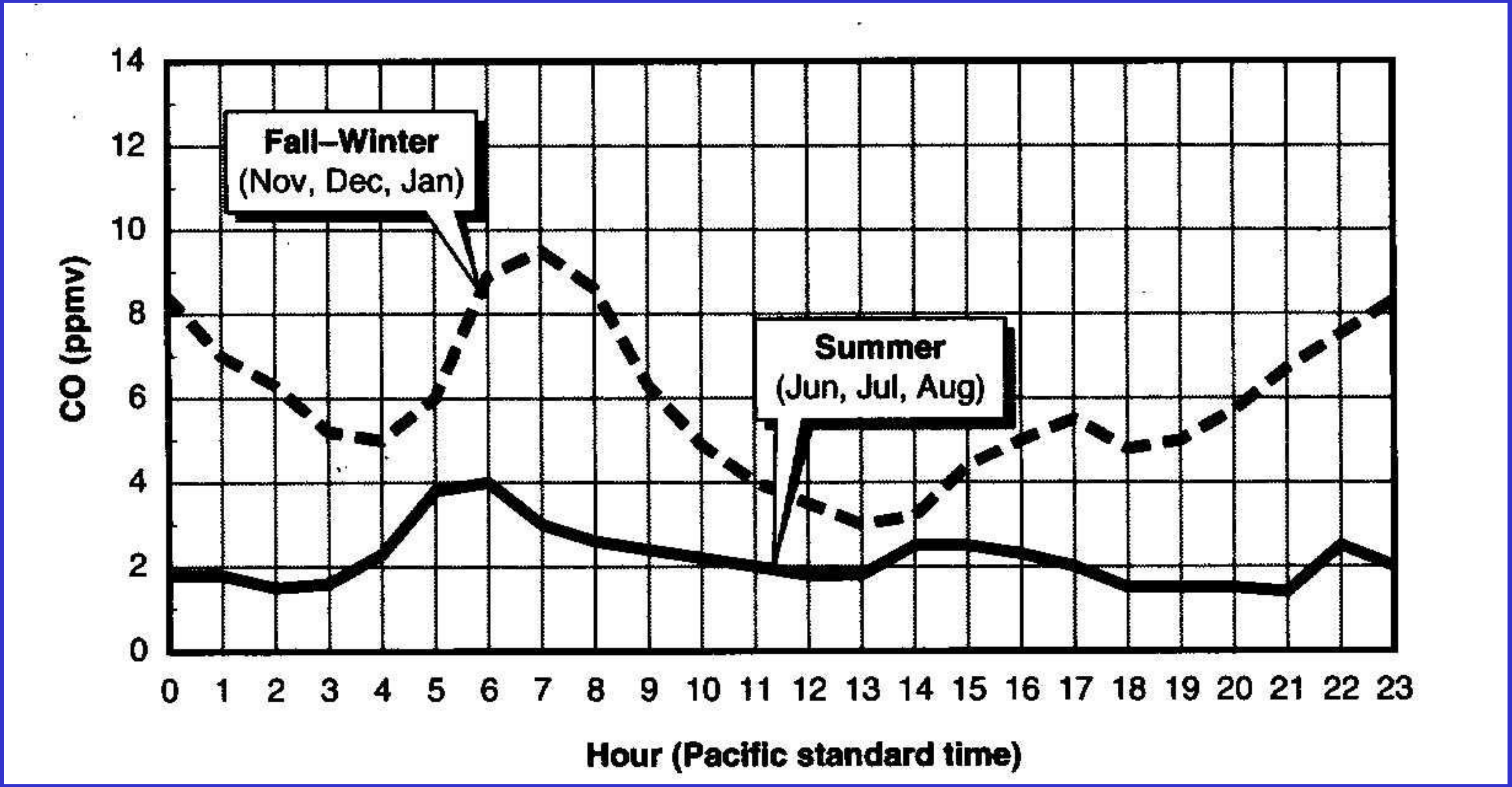
Diurnal Behavior of Various Species

Ozone (O_3)



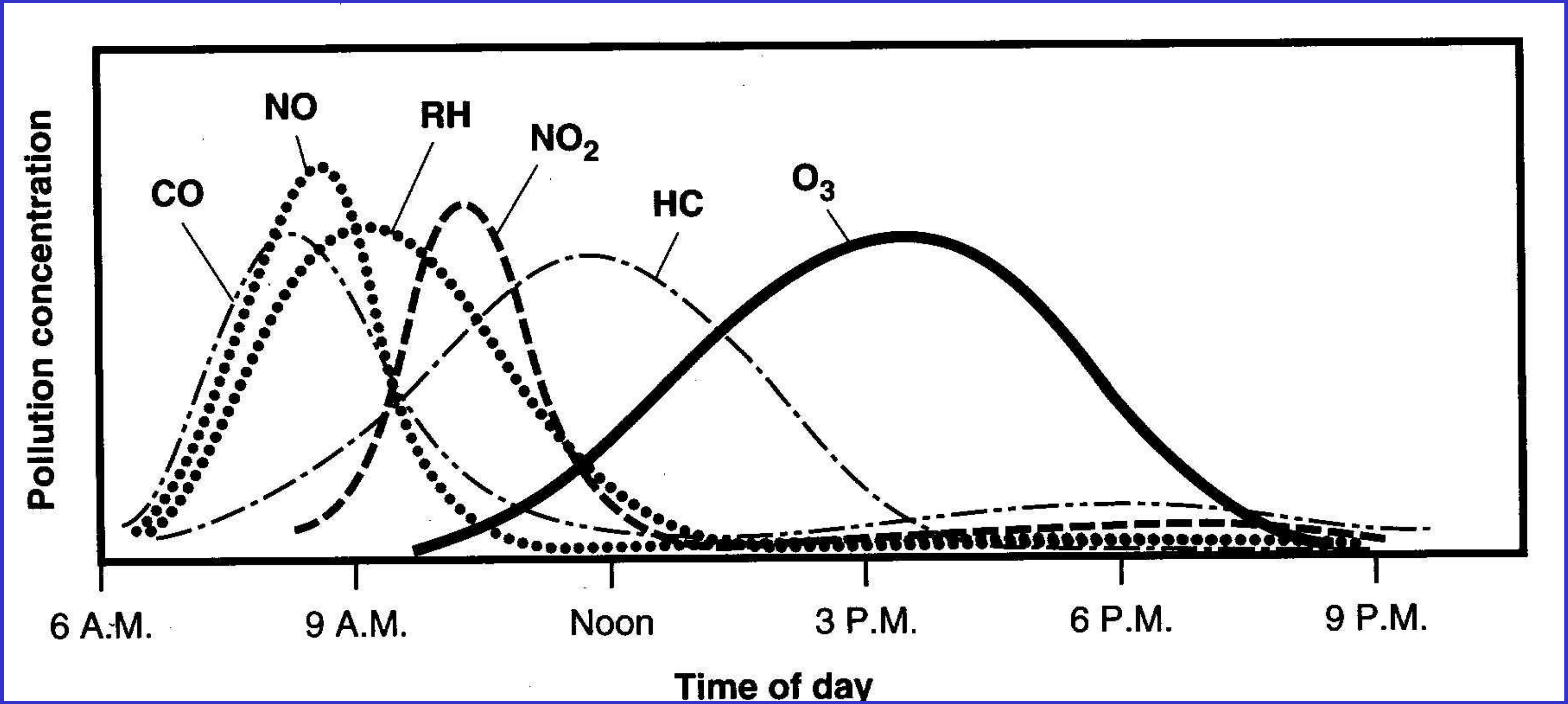
Diurnal Behavior of Various Species

Carbon Monoxide (CO)



Diurnal Behavior of Various Species

Putting it all together:

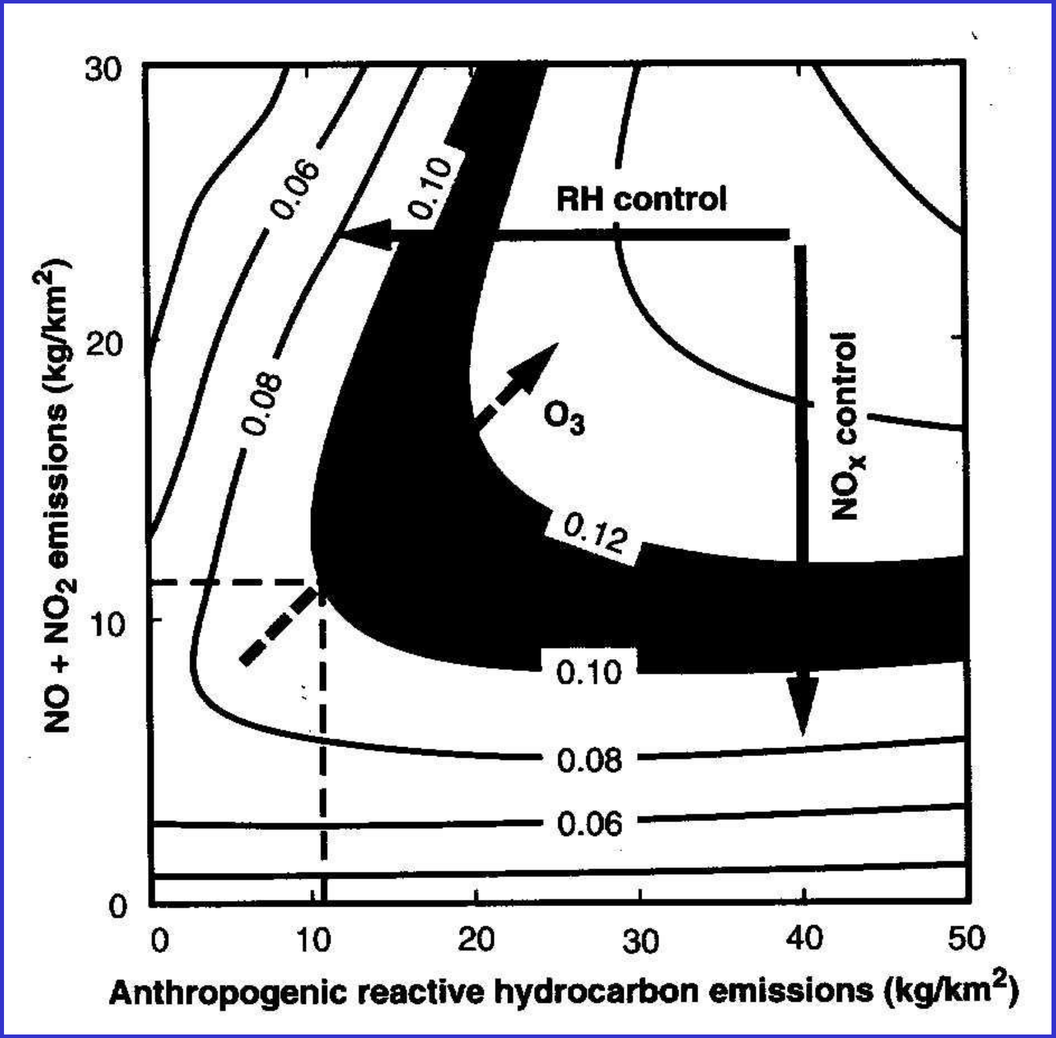


Controlling Smog

Requires a combination of RH and NO_x controls

In regions with relatively high VOCs (e.g. near forests), reductions in NOx are effective in reducing O_3.

In regions of low VOCs, reducing NOx can actually increase ozone (although this isn't necessarily a bad thing because it could reduce products like PAN!).



Unlike acid rain, can't really fix or forestall damage once pollutants are emitted. Instead, need to control emissions (sources)

Culprit #1: Old cars ("heaps" or "junks")

- emit much more than newer cars
- 10%/90% issue
- identifying worst polluters?

Culprit #2: Industry

- concept of waivers or allowances
- advantage of always reducing pollution
- does it send a bad message?

Culprit #3: Energy usage

- alternative fuels
- population; lifestyles