ATOC 3500
Urban Pollution Control Strategies

Reading: pages 422-437

Details to come

Ozone pollution basics:

✓ Formed by the reaction of pollutants in heat and sunlight

OZONE

NOx + VOC + Heat & Sunlight = Ozone

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 about the general chemical scheme for formation of photochemical smog:

$$R\text{-}CH_3 + OH \rightarrow R\text{-}CH_2 + H_2O$$
$$R\text{-}CH_2 + O_2 + M \rightarrow R\text{-}CH_2OO + M$$
$$R\text{-}CH_2OO + NO \rightarrow R\text{-}CH_2O + NO_2$$
$$R\text{-}CH_2O + O_2 \rightarrow R\text{-}CHO + HO_2$$
$$HO_2 + NO \rightarrow OH + NO_2$$
$$2\{NO_2 + h\nu \rightarrow NO + O\}$$
$$2\{O + O_2 + M \rightarrow O_3 + M\}$$

$$\text{net: } R\text{-}CH_3 + 4O_2 + h\nu \rightarrow R\text{-}CHO + 2O_3 + H_2O$$

Urban Pollution Control Strategies

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 = $CH_3C(O)O_2NO_2$).

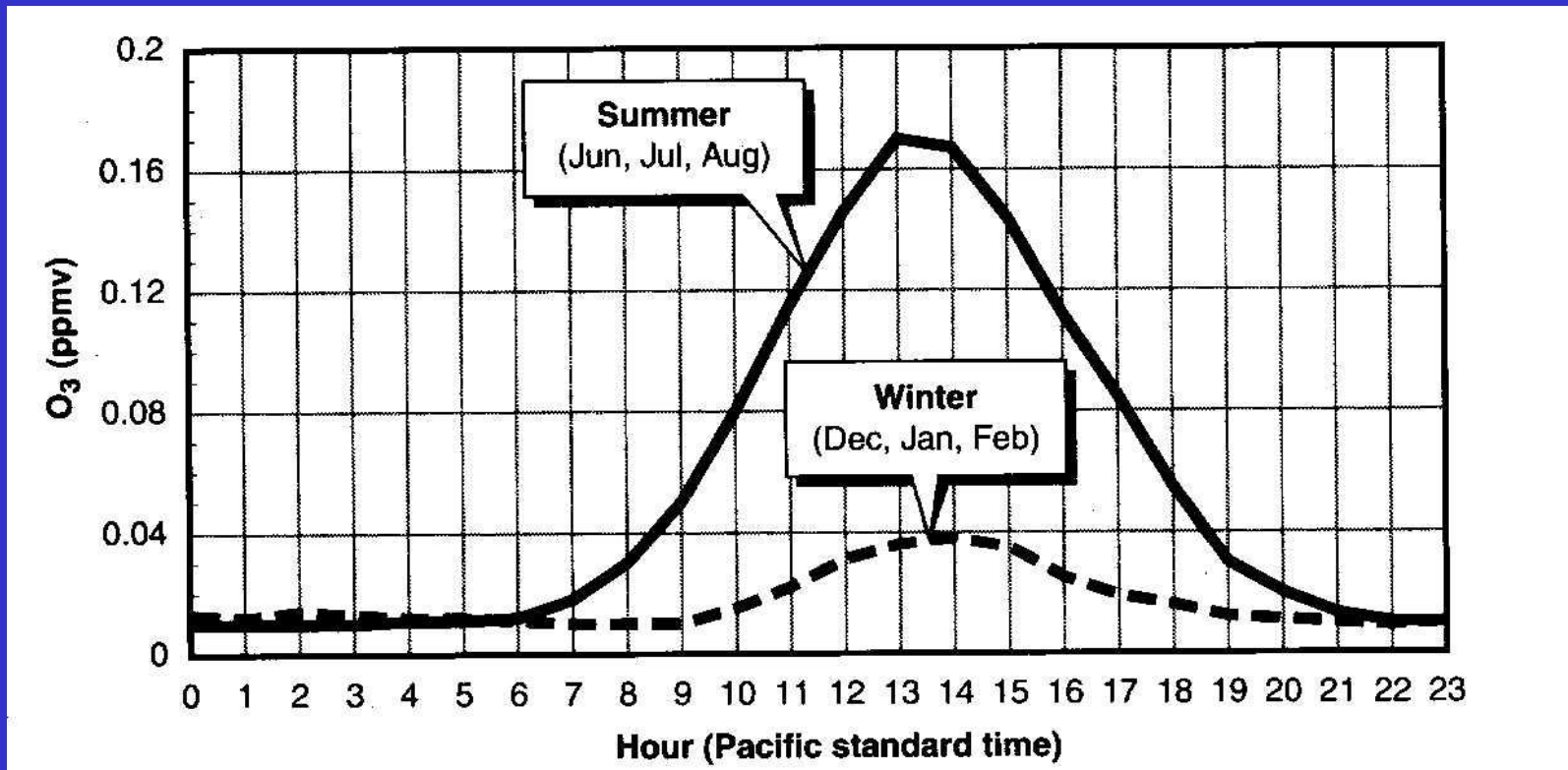Species like PAN can be very toxic, so regulations are often established to reduce their buildup in urban regions

Diurnal Behavior of Various Species

Nitrogen dioxide (NO$_2$)
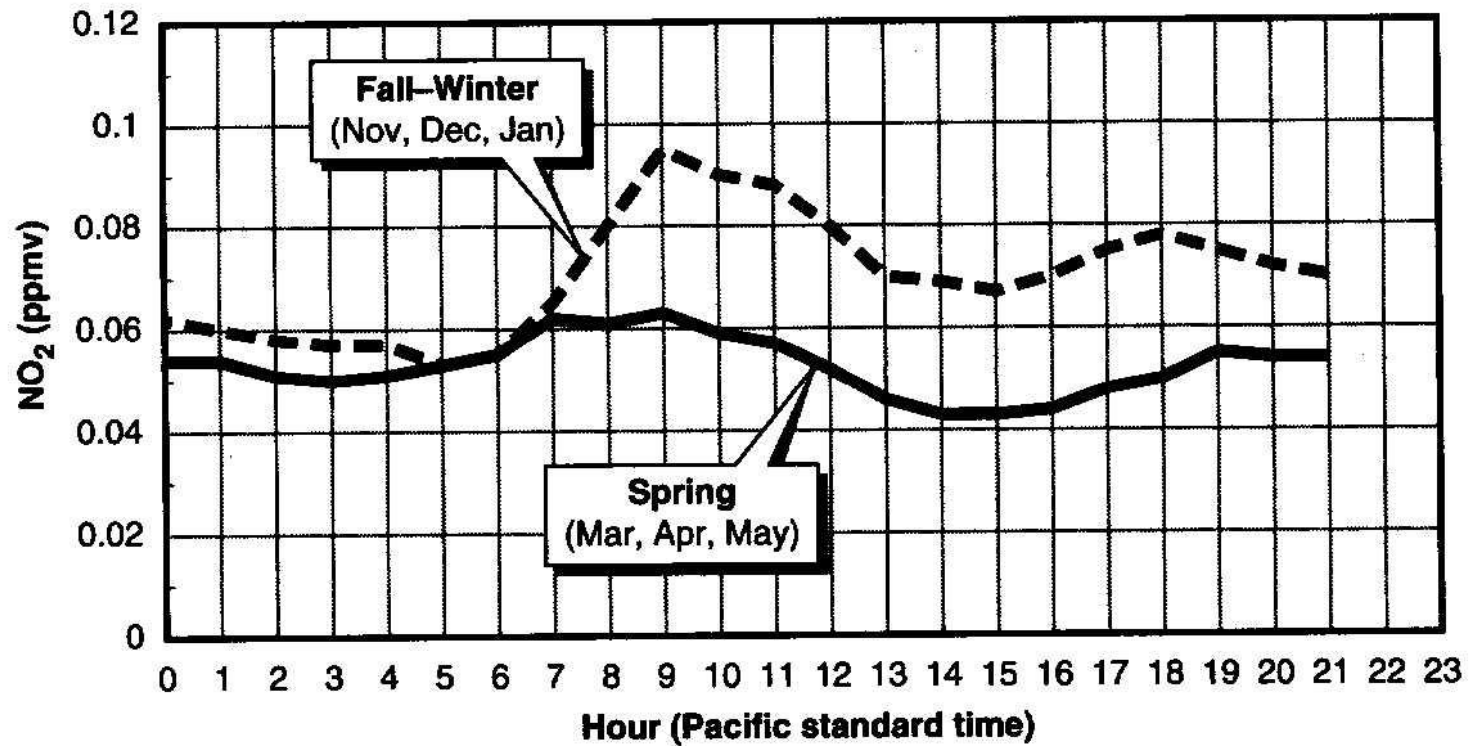
Diurnal Behavior of Various Species

Ozone (O₃)

Let's look at CO – it's a bit different than most hydrocarbons

Because it lacks a hydrogen atom, CO prefers (energetically) to become CO_2, which means that it abstracts an oxygen atom from OH, leaving a bare hydrogen atom (note that reactions of OH with HCs resulted in the formation of water, leaving the carbon species at the radical)

$$CO + OH \rightarrow CO_2 + H$$
$$H + O_2 + M \rightarrow HO_2 + M$$
$$HO_2 + NO \rightarrow OH + NO_2$$
$$NO_2 + h\nu \rightarrow NO + O$$
$$O + O_2 + M \rightarrow O_3 + M$$

$$\text{net: } CO + 2O_2 + h\nu \rightarrow CO_2 + O_3$$

The key to this reaction is that the first step is very slow – the rate constant is about $2x10^{-13}$ cm^3 molecule^{-1} s^{-1} at ~300 K. For an average [OH] in the polluted urban atmosphere of ~$2x10^6$ molecules cm^{-3}, the lifetime of CO is about $2.5 x 10^6$ seconds, or 28 days (note, this value is even smaller in the free troposphere because [OH] and k are both smaller).
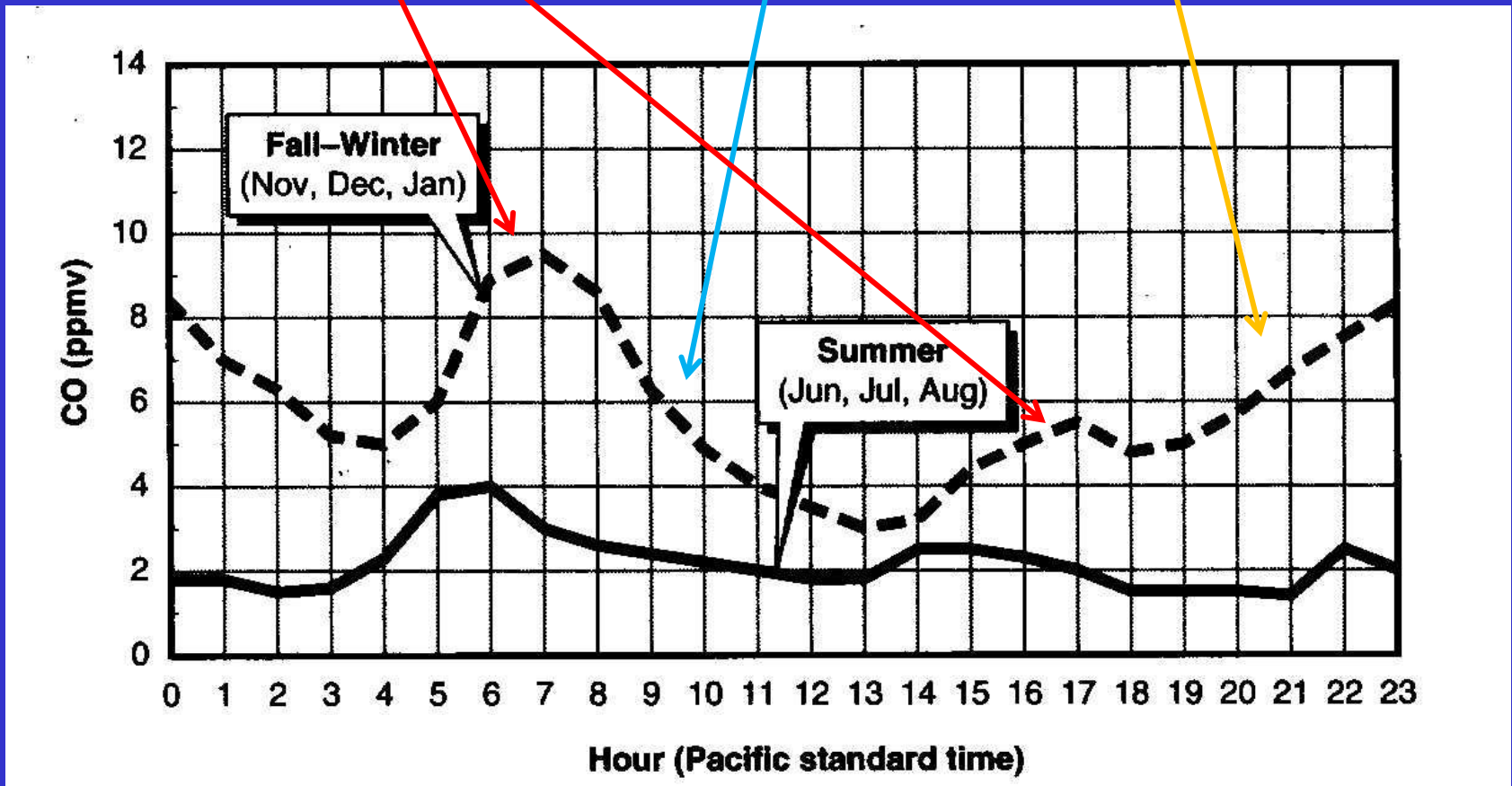
So we can use measurements of CO as an indication of the amount of ventilation or mixing in the boundary layer – if we see CO increase, we know there are emissions, if CO decreases, we can deduce that there is a source of fresh air (either a breeze that is bringing in fresher air that has less pollutants or that our 'box' is increasing in size – that is, the height of the boundary layer is increasing due to convection as the surface warms during the day).

Note also that NO emissions from combustion will react with O_3, and in the absence of sunlight to photolyze NO_2, this may eventually titrate (remove) the O_3, forming NO_2, which gives the false impression that the air is cleaner, when, in fact, there has just been a shift from O_3 to NO_2.

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

One more piece of the puzzle before we summarize the simple behavior of pollutants in the urban troposphere.

Note – earlier, when we talked about oxidation of methane, we stopped at the formation of formaldehyde (CH_2O) – we didn't take the next logical steps of oxidizing CH_2O with OH to eventually form CO_2 and H_2O. The main reason is that in the urban atmosphere which is high in NO_x (NO and NO_2) oxidized organic compounds can react with NOx to form organo-nitrates which may live long enough to be convectively transported to higher altitudes where temperatures are low enough that reactions of these species become slow, and their lifetimes become longer, allowing for much more distant transport.
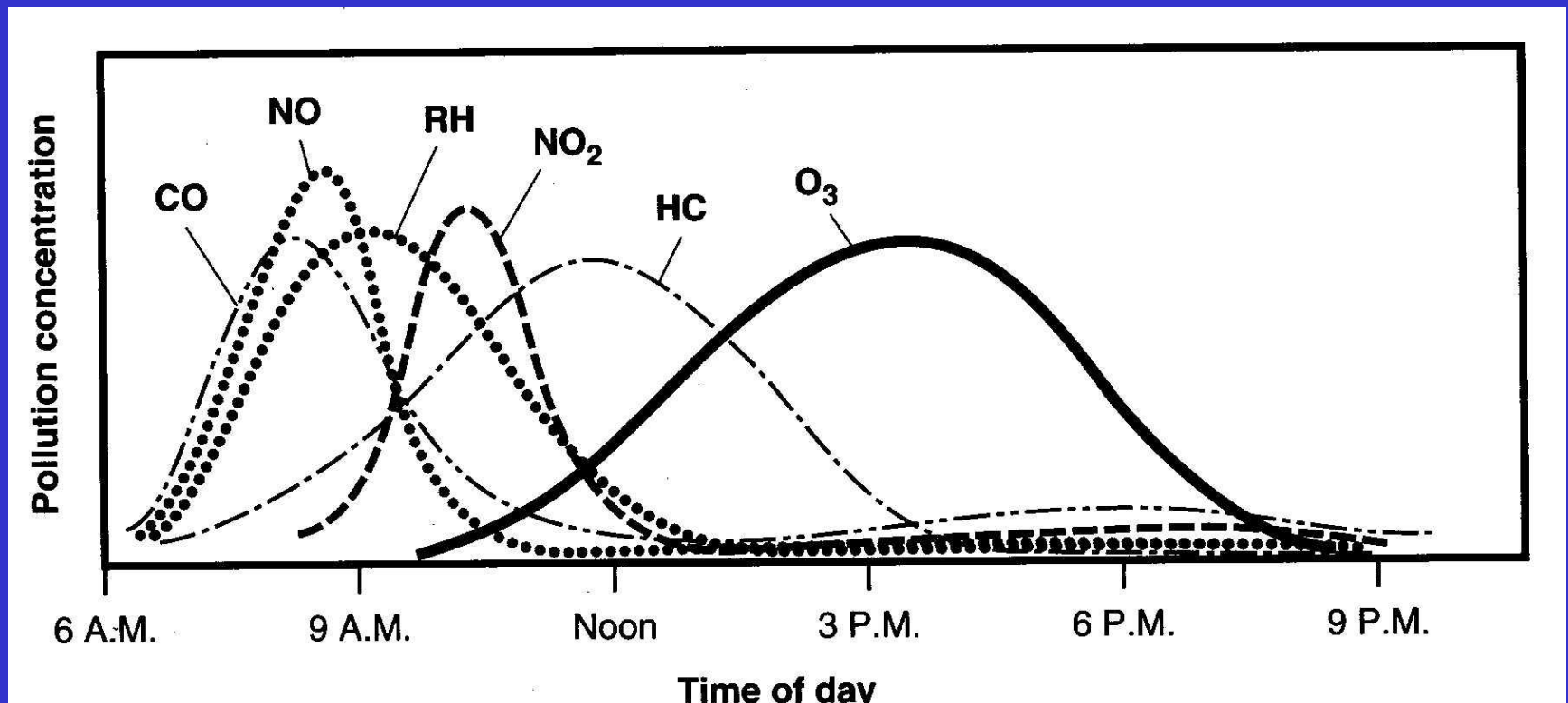
Recall our generic hydrocarbon oxidation initiation reaction:

$$R\text{-}H + OH \rightarrow R + H_2O$$
$$\text{or} \quad R\text{-}CH_3 + OH \rightarrow R\text{-}CH_2 + H_2O$$
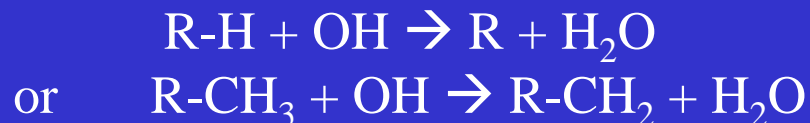
where R = $C_xH_yO_z$

Diurnal Behavior of Various Species

Putting it all together (schematically):

There are a few observations of RH behavior in the atmosphere that are worth noting:

(1) Typically, the more carbons there are in the hydrocarbon, the smaller the concentration in the atmosphere. This is largely because there are more sources of smaller compounds than there are for larger ones, and also because larger organic compounds tend to be less volatile, making them more likely to partition into the particulate (i.e., aerosol) phase.

(2) The rate constants for reactions of OH with HCs typically increase with a larger number of H atoms (consequently, C atoms) in the hydrocarbon. So larger compounds typically have shorter lifetimes.

(3) As hydrocarbons become more oxidized (fewer H's and a larger number of O's), they become more acidic and more water-soluble, so that they tend to stick and dissolve when they collide with wet particles.

(4) As the lifetime of a species in the atmosphere increases, its mixing ratio (especially far away from sources) tends to be less variable.

Here is an example of some measurements of the variability of different short-lived hydrocarbons versus their lifetimes
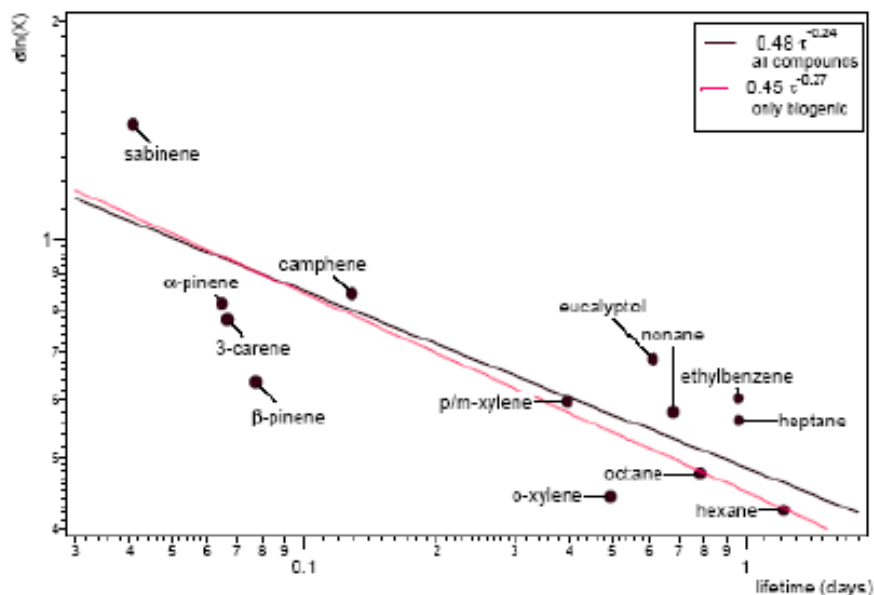

Fig. 6. Logarithmic graph showing the variability of measured short-lived VOCs. The black line is a fit through all VOCs, the dotted line with biogenically emitted compounds only. Assumed concentration for HO is 1.7×10^{6} molecules cm^{-3} (0.071 pmol mol^{-1}) and for O_3 1.0×10^{12} molecules cm^{-3} (42.0 nmol mol^{-1}).
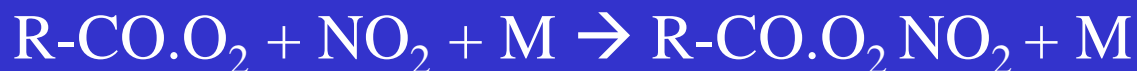
S. Bartenbach[1], J. Williams[1], C. Plass-Dülmer[2], H. Berresheim[2], and J. Lelieveld[1]

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So – back to organo-nitrates (see pages 336-339)

Back to our generic hydrocarbon oxidation reaction – what could happen to our aldehyde?

$$R\text{-}CHO + OH \rightarrow R\text{-}CO + H_2O$$
$$R\text{-}CO + O_2 + M \rightarrow R\text{-}CO.O_2 + M$$
$$R\text{-}CO.O_2 + NO_2 + M \rightarrow R\text{-}CO.O_2\,NO_2 + M$$

If R = CH_3 (the smallest possible hydrocarbon that can form a semi-stable $R\text{-}CO.O_2$ adduct), the nitrate product is called "PAN" for peroxy acetyl nitrate, which isn't a proper systematic name (it might be better named "ethane peroxoic nitric anhydride," but this is even a bigger mouthful!

So why all this detail? They all factor into strategies to best deal with urban pollution.

(1) In high NO_x, low-sun, adding pollution (HCs + NO) will actually remove ozone and form NO_2 and higher oxides of NO_x (NO_3 and N_2O_5). If one is simply measuring ozone, it could appear as though the air is getting cleaning (e.g., ozone will actually decrease in these conditions). Seeing ozone values smaller than about 35-40 ppb, the normal 'clean' background value is probably a bad sign that there's a lot of NOx pollution around!

(2) In sunlight, adding HCs (also called VOCs for volatile organic compounds) and NOx will tend to produce very high amounts of ozone as oxidation initiated by OH takes place.

(3) If temperatures are low (e.g., winter), high NOx and HCs can also produce exotic compounds like PAN, which is far more toxic than either ozone or NOx, and so there needs to be a special concern for these kinds of pollutants.

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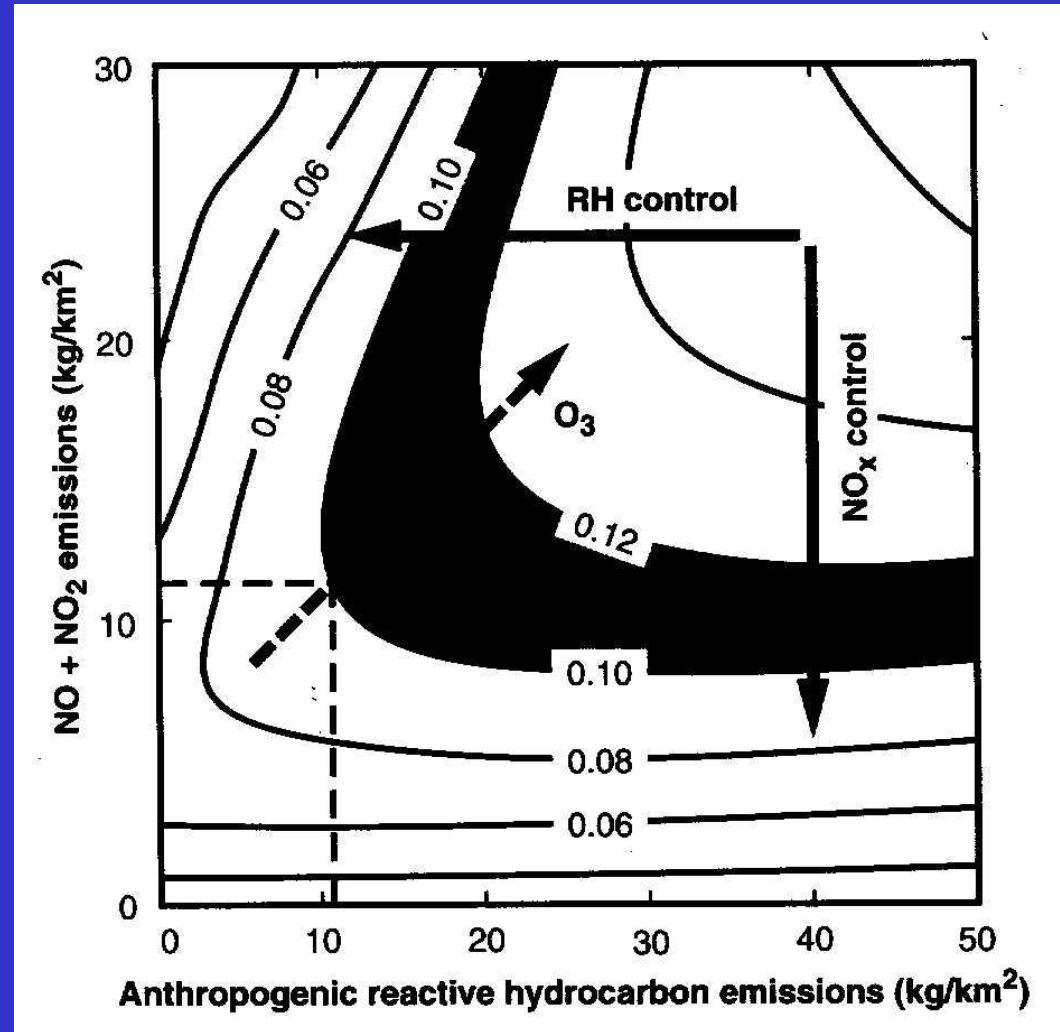
Unlike acid rain, can't really fix or forestall damage once pollutants are emitted. Instead, need to control emissions (sources)

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