Air pollution and climate change
ENV-409

Ozone chemistry
(abridged version)

Overview

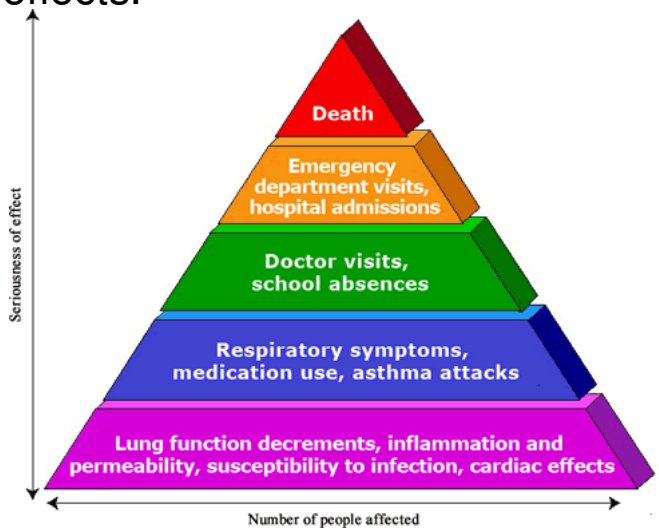
Chemical transformations:

- convert harmful pollutants to innocuous forms
- convert harmful pollutants to other harmful pollutants (e.g., SO_2, NO_2 converted to acids; CO converted to CO_2)
- produce harmful pollutants (e.g., O_3)

We will briefly review the *nonlinear* chemistry of O_3 as it pertains to interpretation of air pollution measurements.

Tropospheric O_3

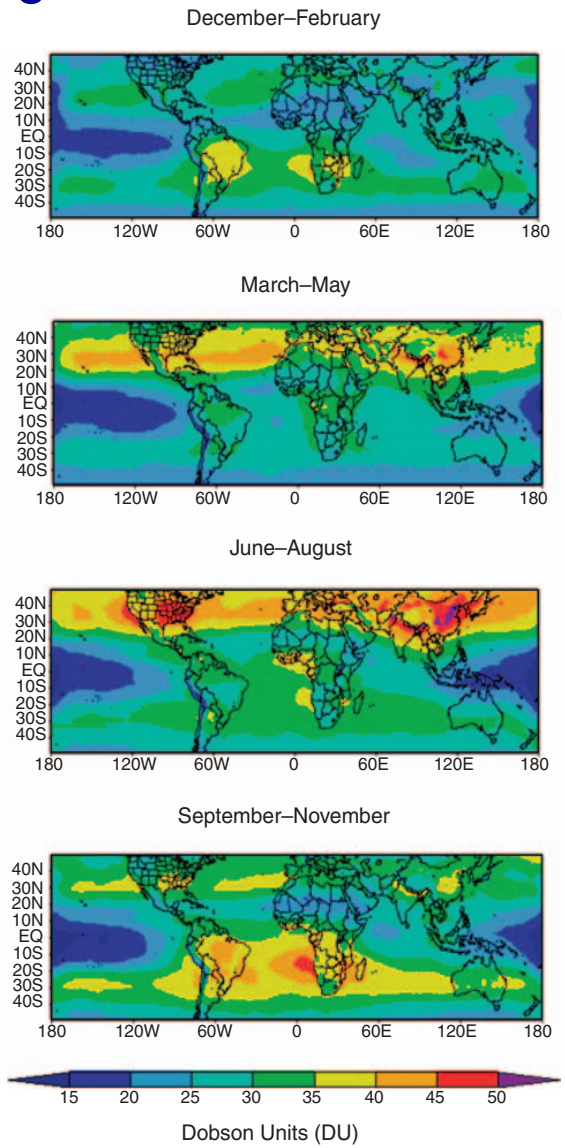
Atmospheric concentrations of tropospheric O_3 are monitored and regulated on account of its health effects.



source: US EPA

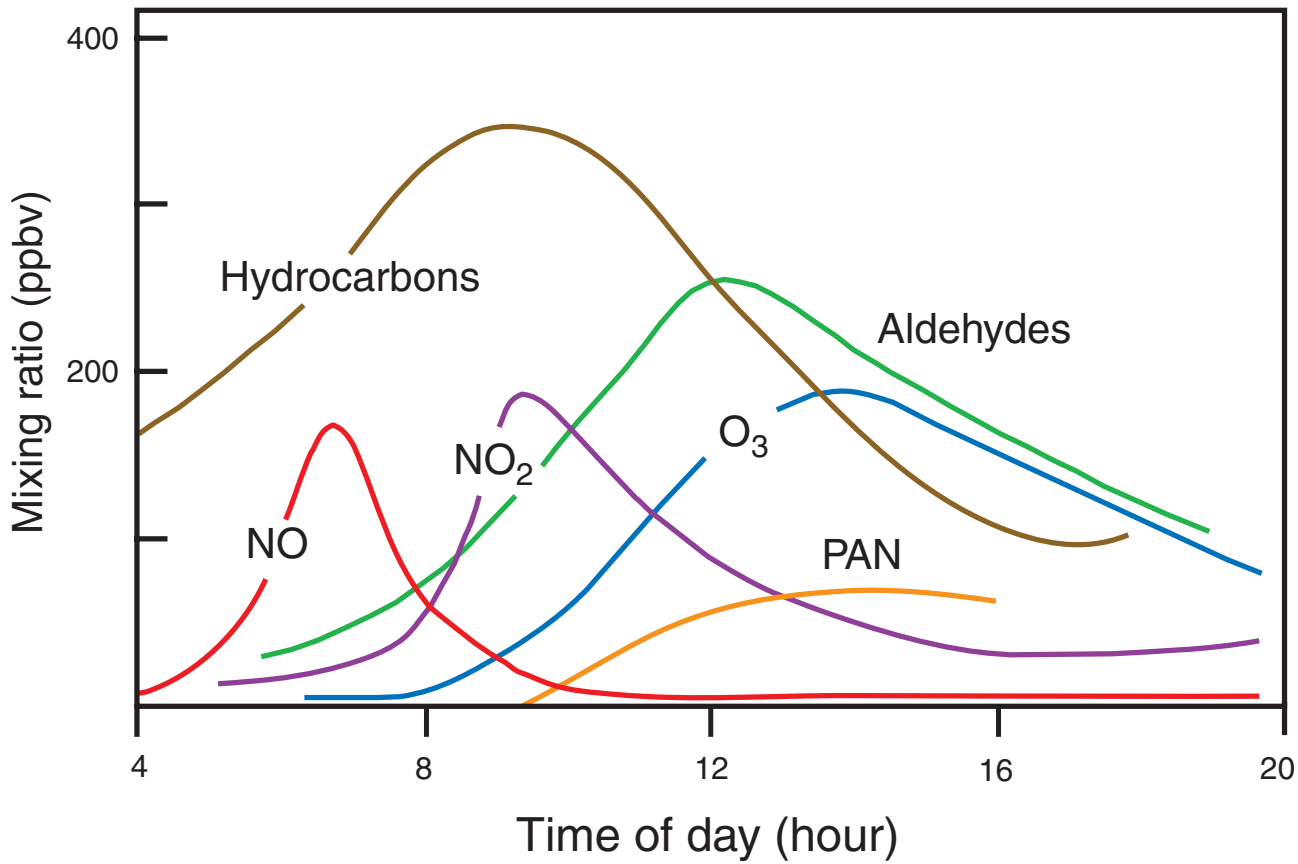
Concentrations dependence on

- Emissions/concentrations of precursor species
- Solar radiation
- Temperature



Wallace and Hobbs, 2006: Composite seasonal distribution of the atmospheric ozone column determined from satellite measurements from 1979 to 2000. [from *Atmos. Chem. Phys.*, 3, 895 (2003).]

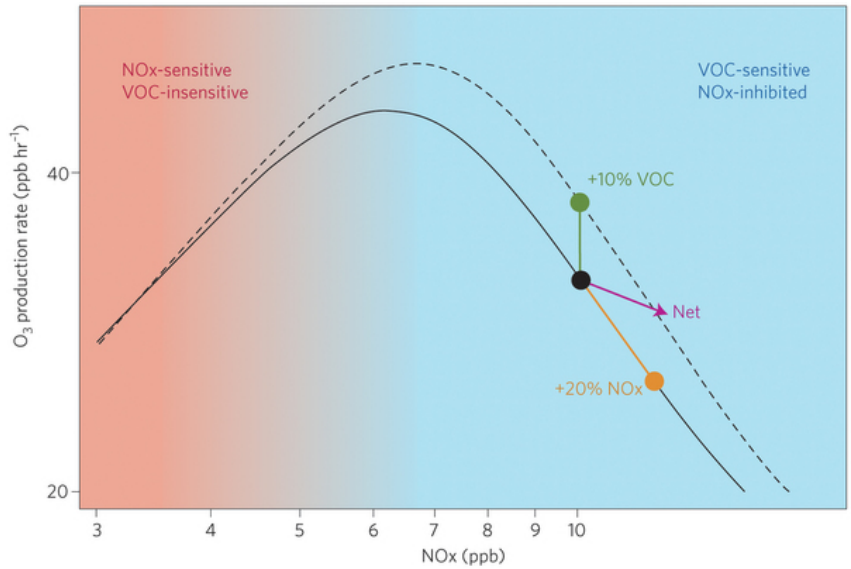
Los Angeles smog



Wallace and Hobbs, 2006: Typical variations during the course of a day of some important pollutants in photochemical smogs in Los Angeles. [Adapted from P. A. Leighton, Photochemistry of Air Pollution, Academic Press, New York, 1961, p. 273, with permission of Elsevier.]

Nonlinear chemistry of ozone

- Presence of weekly cycle and higher concentrations of an ozone *weekend* effect, in which concentrations of O_3 increase due to the decrease in NO_x concentrations.
- Reductions in NO_x due to emission controls may increase average ozone concentrations.
- With sufficient reduction in NO_x, dO_3/dNO_x may become positive.

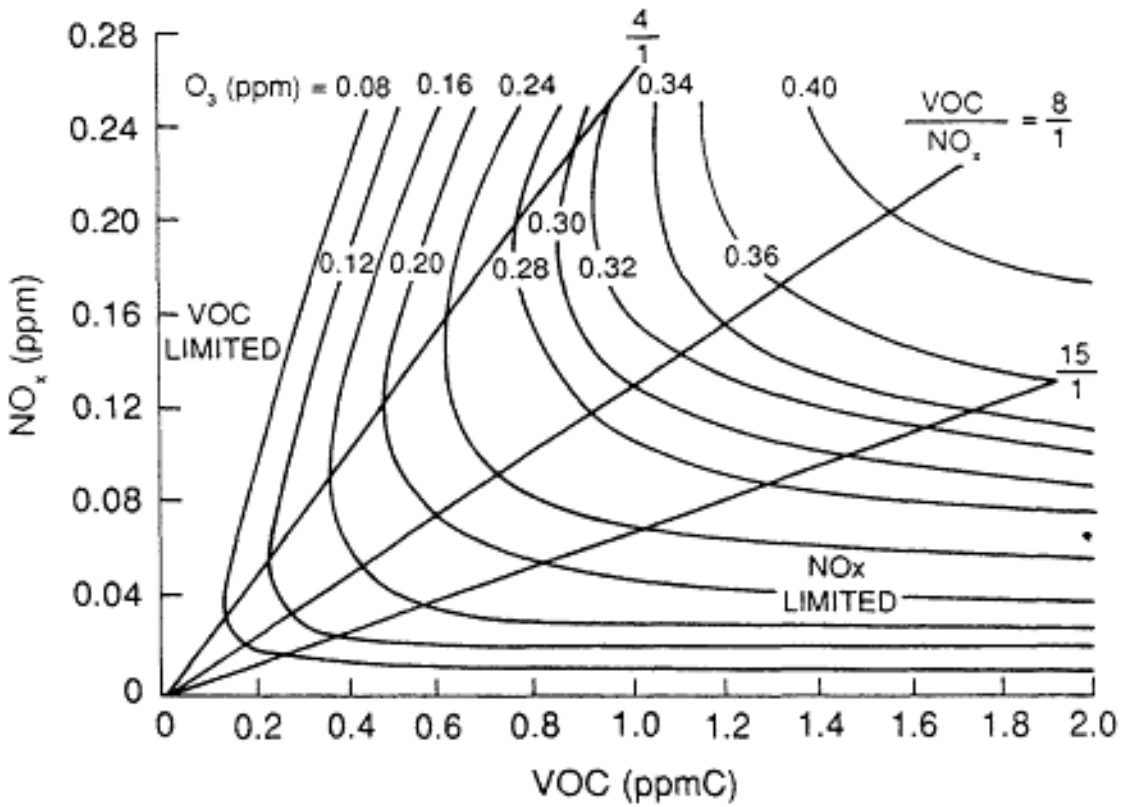


"Ozone production rates rise in line with NO_x concentrations up to a certain point, beyond which further additions of NO_x start to inhibit ozone formation (solid line). The addition of volatile organic compounds (dotted line) starts to stimulate it at about this point. In this example, the effects of a 10% and 20% increase in VOC and NOx concentrations (green and orange lines, respectively) on ozone production rates (green and orange circles) are shown. The net effect is a small reduction in ozone production rates. Salvo and Geiger show that ozone levels fell in São Paulo following a switch from ethanol to gasoline use, and therefore suggest that ozone production in São Paulo lies on the part of the curve that is inhibited by NO_x but stimulated by the addition of VOCs. Values are illustrative only, as actual rates depend on time and location, mixtures of emitted VOCs and NO_x, solar radiation and other meteorological factors. [...]"

Madronich, *Nat. Geosci.*, 2014

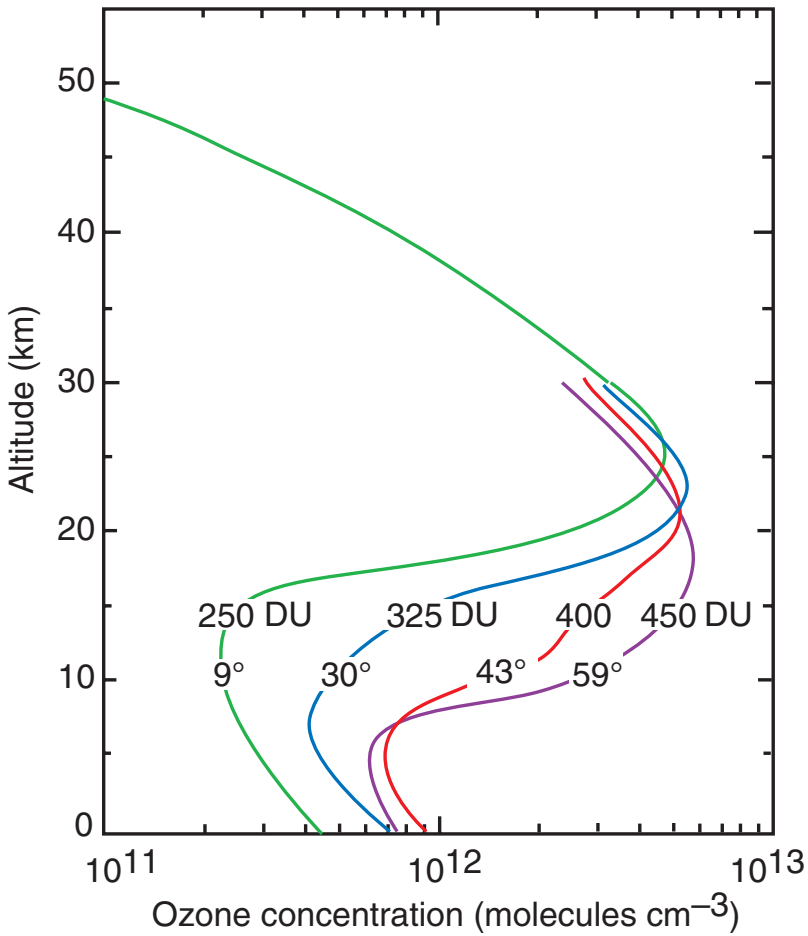
Ozone isopleth

- Contour plot of maximum O_3 concentrations resulting from a set of initial VOC and NO_x concentrations.
- Generated by contour plotting the predicted ozone maxima obtained from a large number of simulations with an atmospheric VOC/NO_x chemical mechanism with varying initial concentrations of VOC and NO_x (all other variables held constant).
- Highlights non-linear response to NO_x in the VOC-limited region. Understanding the O_3 response to NO_x concentrations in this region is a major objective of this lecture.



National Academies Press, 1993

Atmospheric O_3



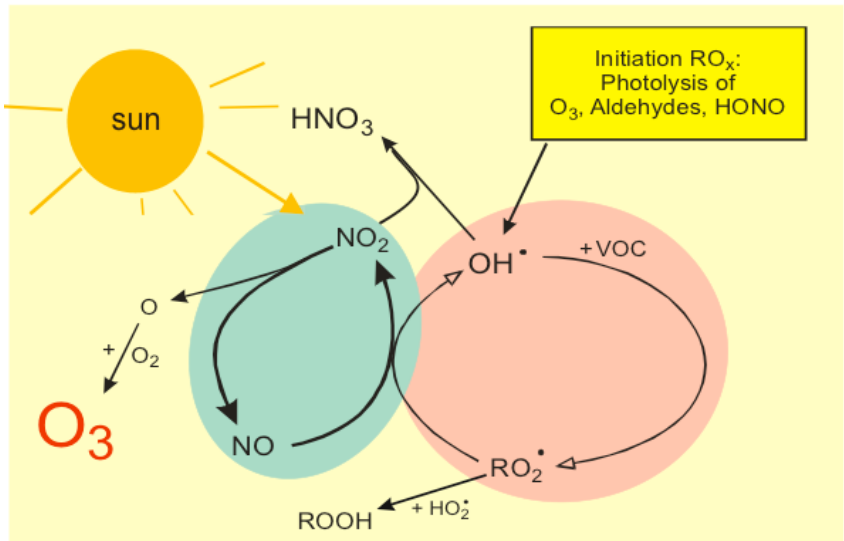
Wallace and Hobbs, 2006

Approximately 90% of the O_3 in Earth's atmosphere is found in the stratosphere. The flux from the stratosphere to the troposphere accounts for less than $\sim$1/5 of the tropospheric ozone budget.

Tropospheric O_3 formation

Dependence on NO_x and VOC

Ozone chemistry is complex and may be nonlinear, depending on relative concentrations of VOC and NO_x.



Prevot and Staehelin, ETHZ.

There are many pathways for transformation of NO $\rightarrow$ NO_2. The Leighton relationship considers an atmosphere polluted with NO_x.

Leighton cycle (production of O_3):

$$NO_2 + h\nu \xrightarrow{j} NO + O$$

$$O + O_2 \underset{k_1}{\overset{M}{\rightarrow}} O_3$$

$$NO + O_3 \xrightarrow{k_2} NO_2 + O_2$$

M is a chaperone molecule, N_2 or O_2. Note that this is a *null cycle*: no net O_3 is created.

However, the ratio of NO_2 to NO will determine the O_3 concentration according to the photostationary state relation:

$$\frac{d[NO_2]}{dt} = -j[NO_2] + k_2[O_3][NO] \approx 0$$

$$[O_3] = \frac{j[NO_2]}{k_2[NO]}$$

This relation is established within a few minutes.

Simplified chemistry

Oxidation of CO and Volatile organic compounds (VOCs) by OH radicals will produce hydroxy radicals (HO_2) and peroxy radicals (RO_2):

$$CO + OH \xrightarrow{O_2} HO_2 + CO_2$$

$$R_iH + OH \xrightarrow{O_2} R_iO_2 + H_2O$$

R_i is a hydrocarbon fragment

These peroxy radicals will convert NO to NO_2 by further oxidation:

$$NO + HO_2 \xrightarrow{k_3} NO_2 + OH$$

$$NO + R_iO_2 \xrightarrow{k_4} NO_2 + R_iO$$

VOC contributions can lead to deviation between the $[NO_2]/[NO]$ and $[O_3]$ otherwise observed under photostationary state conditions.

$$\frac{[NO_2]}{[NO]} = \frac{k_2[O_3]}{j} + \frac{1}{j}\left(k_3[HO_2] + \sum_i k_{4,i}[R_iO_2]\right)$$

At high concentrations of NO, reaction with OH forms HNO_3 (a sink for reactive nitrogen in the atmosphere, and a source of particulate matter) and removes NO_x from the system, reducing ozone production rates:

$$OH + NO_2 \xrightarrow{M} HNO_3$$

Useful metrics for analyzing data

Sum of oxidants $[O_x] = [O_3] + [NO_2]$ is a conserved quantity in the "NO titration" reaction:

$$NO + O_3 \longrightarrow NO_2 + O_2$$

If O_3 concentrations are "suppressed" locally by NO, O_x should not exhibit depressed trend.

Photostationary state ratio:

$$\begin{aligned}\Phi &= \frac{j[NO_2]}{k_2[NO][O_3]} \\ &= 1 + \frac{1}{k_2[O_3]}\left(k_3[HO_2] + \sum_i k_{4,i}[R_iO_2]\right)\end{aligned}$$

Note that j is dependent on the radiation intensity.