

Module 4: Tropospheric gas-phase species

Topics to be covered

- Local, regional and global pollutants
- The oxidizing capacity of the atmosphere
 - The importance of the OH radical
- CO, CH₄ and NO_x – sources and trends
- The production of tropospheric O₃
 - Regimes and policy controls
- Photochemical smog – a case study of USA
- Dry and wet deposition – an overview
- Acidic deposition – a case study of USA

Required reading

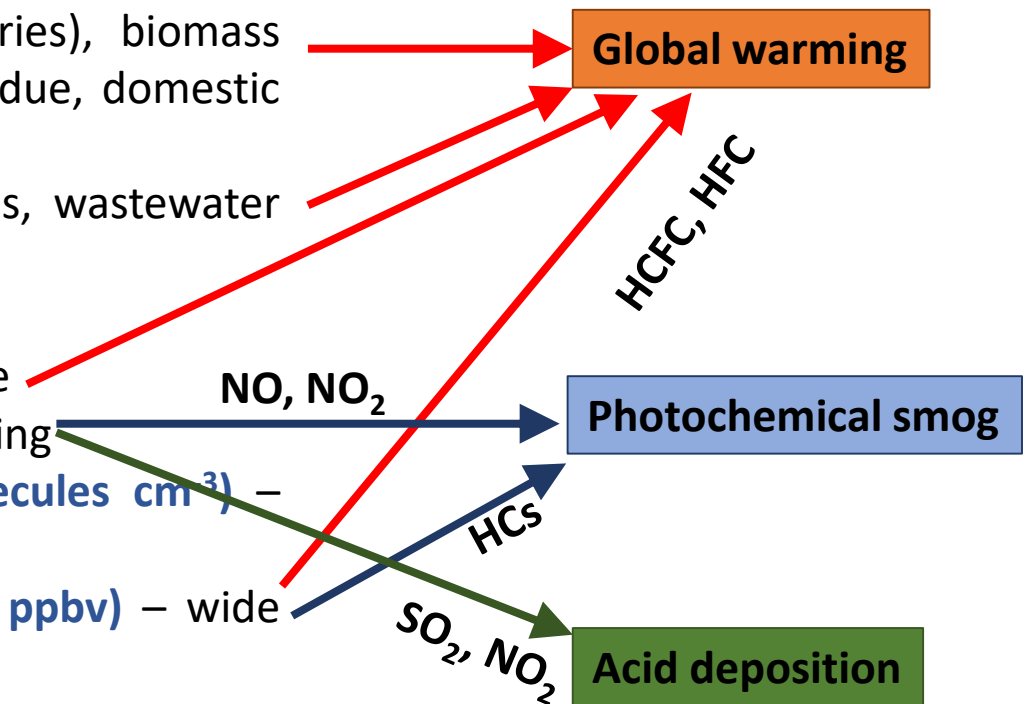
- Jacob, 1999 – Introduction to atmospheric chemistry
(<http://acmg.seas.harvard.edu/publications/jacobbook/index.html>)
 - Chapters 11 and 12

Gas-phase species in the troposphere – Sources, processing, effects

Reading: Jacob, Chapters 11 and 12

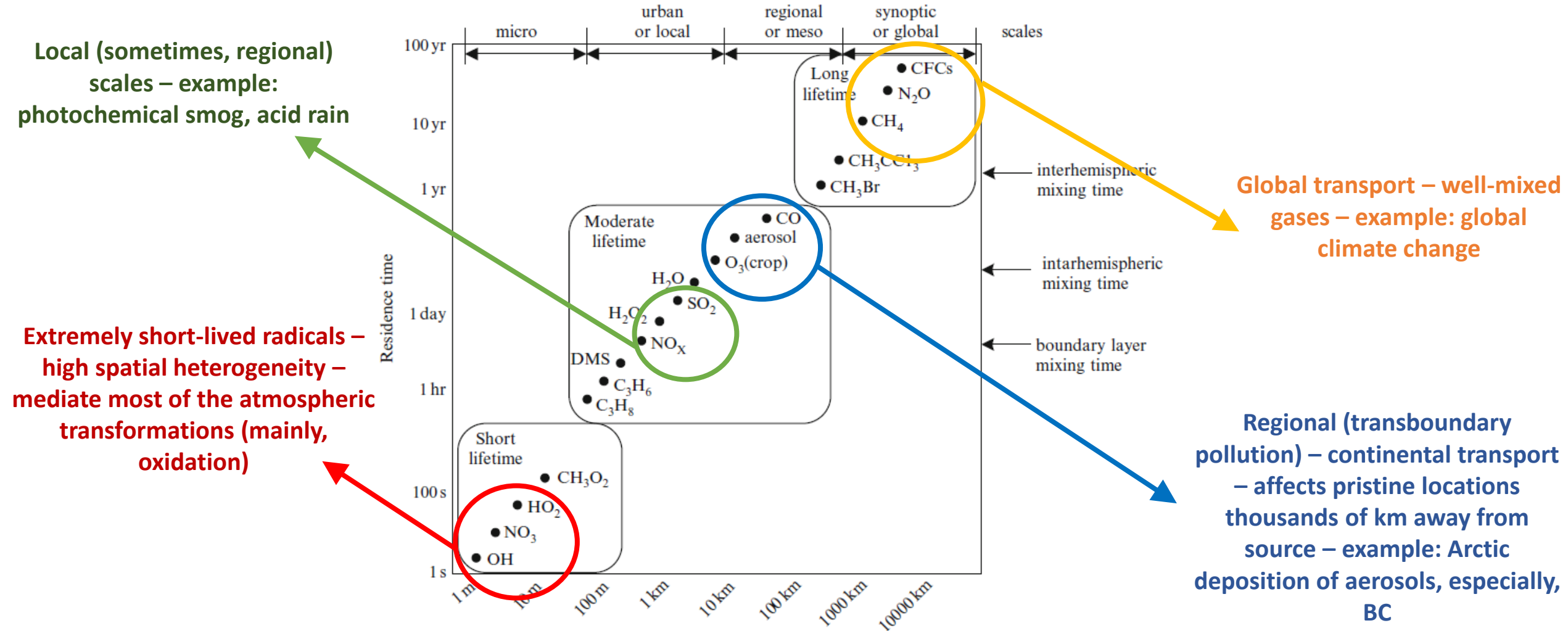
Gas-phase species in the troposphere

- **Major components of air**
 - **N_2 (78%), O_2 (21%)** – natural
- **Minor and trace components of air**
 - **Water vapor (~1%)** – varies widely by location
 - **CO_2 (~410 ppmv)** – fossil fuel combustion (vehicles, industries), biomass burning (prescribed wildfires, open burning of agricultural residue, domestic combustion of low-efficiency fuels)
 - **CH_4 (~1900 ppbv)** – livestock rearing, rice agriculture, landfills, wastewater treatment, biomass burning, natural gas distribution
 - **CO (0.1-1 ppmv)** – vehicles, biomass burning
 - **O_3 (10-100 ppbv)** – photochemical production in the atmosphere
 - **NO, NO_2 , SO_2 (10-200 ppbv)** – vehicles, industries, biomass burning
 - **OH radical (0.01-1 pptv; note: preferably expressed in molecules cm^{-3})** – photochemical production in the atmosphere
 - **Halocarbons, other VOCs (aliphatic, aromatic) (few pptv-few ppbv)** – wide variety of sources



The OH radical mediates many of the atmospheric transformations that lead to these effects

Spatial scales and residence times of atmospheric constituents



In terms of policy, which is easier to implement? Local (city/federal), regional (multiple states/federal) or global (multiple countries)?

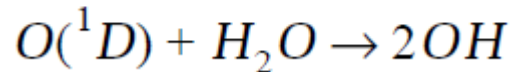
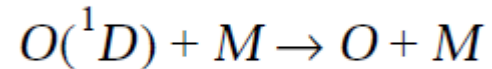
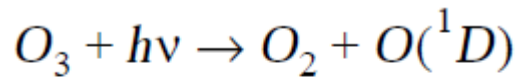
The oxidizing capacity of the troposphere

The most abundant oxidants in the atmosphere are O_2 and O_3 . But both are relatively unreactive except toward radicals.

In terms of reactions with non-radicals, the predominant atmospheric oxidant is the hydroxyl radical (OH) (along with the intermediate HO_2)

The hydroxyl radical (OH)

Source: reaction of water vapor with $O(^1D)$ generated from the photolysis of O_3 (we'll discuss the source of this O_3 shortly)



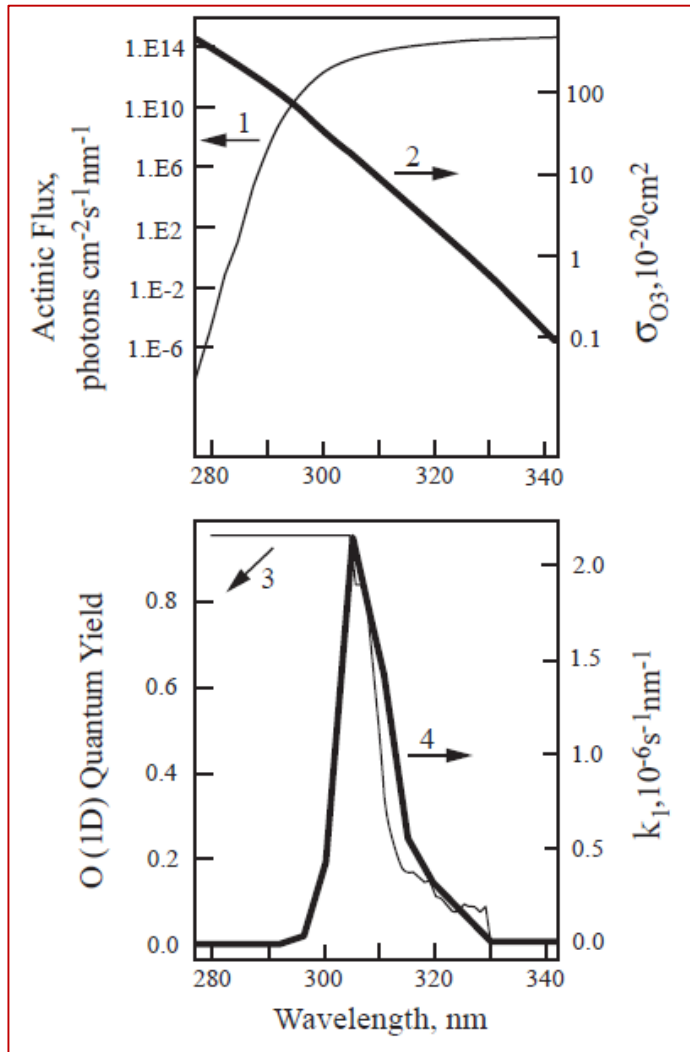
- The wavelength needed is $\lambda \leq 310$ nm – but remember, $\lambda \leq 310$ nm is absorbed by the stratospheric O_3 layer.
- So, how does this photolysis happen in the troposphere? **Next slide.**

Previous understanding: $O(^1D)$ production in the troposphere is negligible due to near-total absorption of $\lambda \leq 310$ nm in the stratosphere.

Implication: CO (which is oxidized by OH) would need to be transported to the stratosphere (timescale: 5-10 y) for breakdown, leading to build-up in the troposphere.

OH radical – the “detergent” of the troposphere

We know now that $O(^1D)$ production in the troposphere generates sufficient quantity of OH that allows oxidation of CO and CH_4



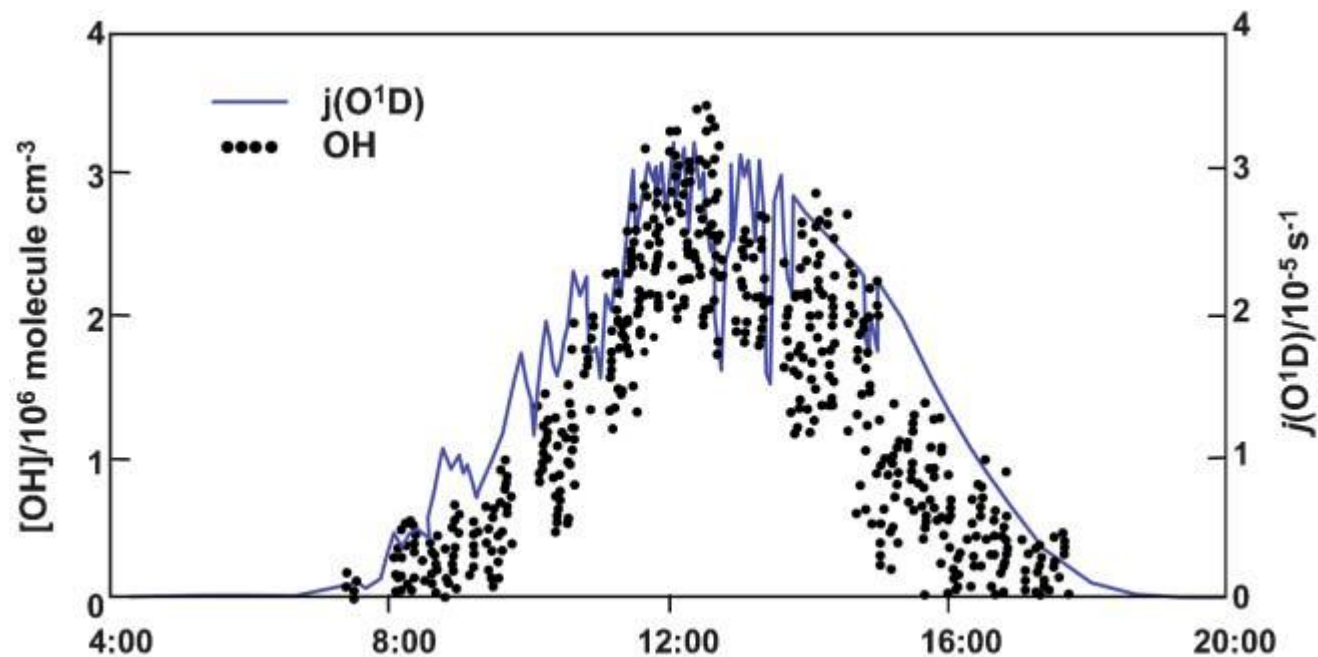
Rate constant of O_3 photolysis to $O(^1D)$ as a function of wavelength

- **Line 1:** Solar actinic flux; **Line 2:** Absorption cross-section of O_3 ; **Line 3:** $O(^1D)$ quantum yield; **Line 4:** Rate constant of O_3 photolysis
- **Two competing factors**
 - Lower $O(^1D)$ production due to less intense light of $\lambda \leq 310$ nm
 - Compensated by much higher mixing ratios of H_2O in the troposphere as compared to the stratosphere (10^2 - 10^3 times)
 - **Net result:** sufficient quantities of OH is produced in the troposphere to ensure oxidation of CO
- **Atmospheric concentrations and lifetime**
 - Model calculations in the 1970s showed that OH concentrations were in the order of 10^6 molecules cm^{-3}
 - Lifetime: **<1 second** – extremely short-lived

Implication?

Measurement is extremely difficult. Instrumental accuracy is often only around 50%!

OH radical – diurnal variation and implications



Solar radiation is needed for the production of the OH radical. So, it is a “daytime oxidant.”

Implication:

- Oxidative power of the troposphere is most enhanced in the daytime due to the presence of the OH radical.
- Formation of tropospheric O_3 and photochemical smog therefore happens during the day (**we'll come to these soon**).
- But does that mean there's no oxidative processes happening in the troposphere at night?
- Nighttime oxidative capacity of the troposphere is weaker and is driven by other species, e.g., the NO_3 radical