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Tropospheric Chemistry

Oxidation rates of trace gases in the troposphere depend on species-specific rate coefficients and are predominantly governed by the concentration of the hydroxyl radical (OH), the most important oxidizing molecule in the troposphere. The concentration of OH is in local photochemical steady state; it is, however, dependent on the concentration of trace gases such as ozone, water vapor, volatile organic compounds, and oxides of nitrogen. Diffusive and advective transport processes influence and change the concentrations of these trace gases. Oxidative and transport time scales are often of similar magnitude, which leads to coupling between tropospheric chemistry and transport.

Structure and Composition of the Troposphere

For study and reference, scientists have separated the atmosphere into four regions, very different in their structure, thermodynamics, photo-chemistry and dynamics. This partition is best reflected by the atmospheric vertical temperature profile, whose points of inflection are used to distinguish the four regions (Figure 1). Starting from the ground, they are called the 'troposphere', the 'stratosphere', the 'mesosphere' and the 'thermosphere', and the boundaries separating them the 'tropopause', the 'stratopause' and the 'mesopause'.

The atmospheric thermal structure is ultimately defined by a combination of dynamic and radiative transfer processes. The troposphere is heated from the ground, which absorbs solar radiation and releases heat back up in the infrared. The temperature of the air in this region therefore decreases linearly with altitude, at a lapse rate of 5 to 7 K km^{-1}, or a little over half a degree per 100 m, as common knowledge suggests. The tropopause, situated between 8 km (at high latitudes) and 15 km (at the equator), marks the end of this linear decrease and the beginning of the stratosphere, where lies the bulk of atmospheric ozone (the 'ozone layer'). The presence of ozone is vital for life on Earth, as it absorbs the dangerous part of incoming ultra-violet radiation. As a result, the stratosphere heats up and has a positive temperature gradient. The temperature peaks at the stratopause at approximately 50 km in altitude, then falls linearly again in the mesosphere, as ozone heating diminishes. The region of the atmosphere above the mesopause is called the thermosphere and is radically different from the three lower regions. It cannot be treated as an electrically neutral medium because energetic solar radiation ionizes the molecules and atoms to form a plasma of free electrons and ions that interact with the Earth's magnetic field.

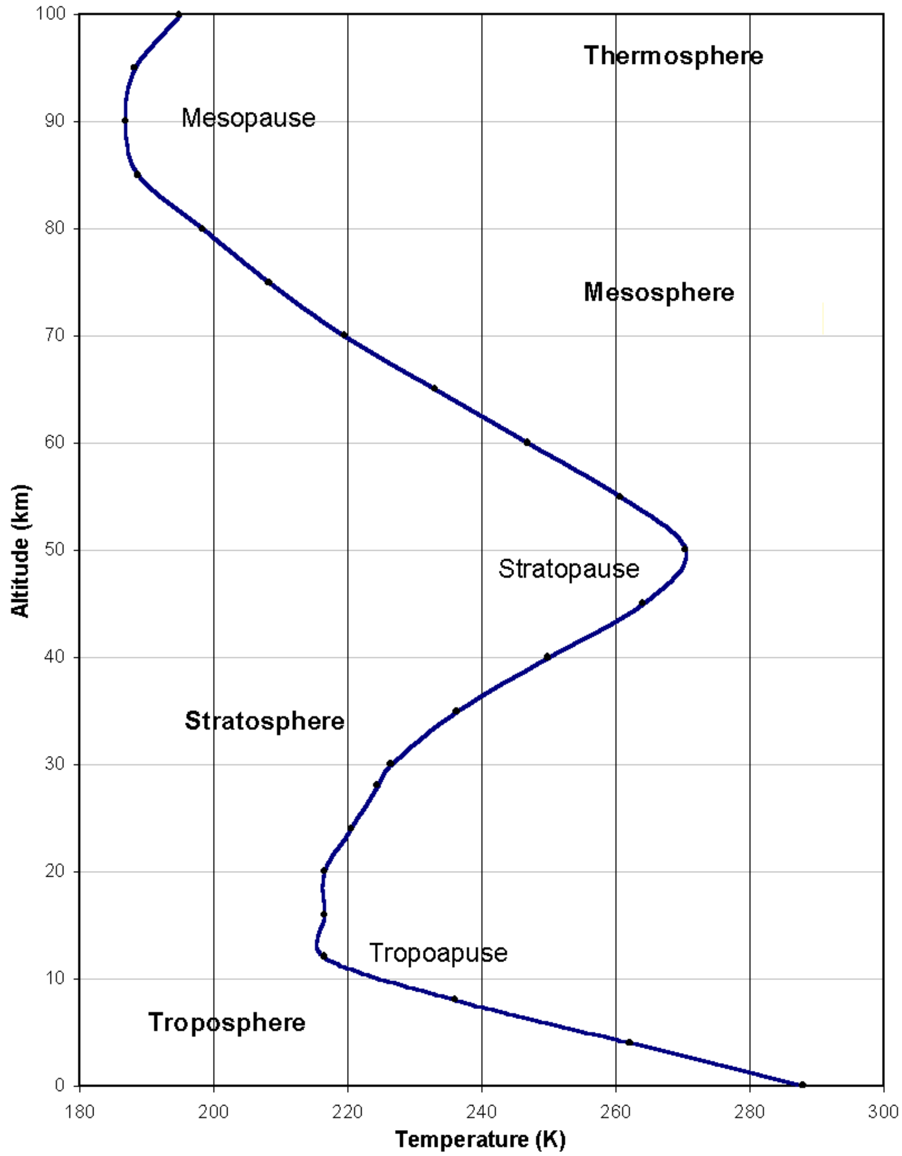


Figure 1: The atmospheric temperature profile (US Standard Atmosphere, 1976). To the four regions correspond very different temperature gradients.

The word troposphere means ‘turning sphere’, which symbolizes the fact that, in this region, convective processes dominate over radiative processes. The troposphere is indeed marked by strong convective over-turnings, whereby large parcels of warm air travel upwards to the tropopause, carrying water vapor and forming clouds as they cool down (the stratosphere, on the other hand is a very stable a stratified environment where heat transfer is mainly radiative). The troposphere contains the bulk of atmospheric water vapor, the majority of clouds and most of the weather, both on a global and a local scale. Because pressure decreases exponentially with altitude, it also contains over 75% of the total mass of the atmosphere. Most importantly, however, it is in contact with the Earth’s surface and therefore interacts directly with other climate subsystems, such as the biosphere (the land and vegetation), the hydrosphere (the oceans), the cryosphere (the ice caps), the lithosphere (the topography), and most all, with the human world (Peixoto and Oort, 1992).

Constituent	**Tropospheric mixing ratio**
N_2 (Nitrogen)	78.08%
O_2 (Oxygen)	20.95%
H_2O (water vapor)	<3.00%
A (Argon)	0.93%
CO_2 (carbon dioxide)	345 ppmv
O_3 (ozone)	10 ppmv
CH_4 (methane)	***1.6 ppmv***
N_2O (nitric oxide)	350 ppbv
CO (carbon monoxide)	***70 ppbv***
CFC=s 11-12	0.2-0.3 ppbv

Table 1: The composition of the atmosphere (adapted from Salby, 1996). All values are mean tropospheric values.

The bulk of dry air is made up of nitrogen (78% by volume) and oxygen (21% by volume). Noble gases, carbon dioxide and a large number of other minor gases constitute the remaining 1% of the atmosphere. Although they are in very small concentrations, these trace constituents play a vital role in all aspects of atmospheric physics and chemistry (in contrast with nitrogen: inert and uninteresting). Table 1 gives the average tropospheric abundance of a selected number of species. Note that the gases of interest in this work, namely methane and carbon monoxide, have mixing ratios expressed in ppmv and ppbv. Most constituents are distributed fairly evenly up to the mesopause, with the exception of water vapor, which is mostly confined to the troposphere, and ozone which is concentrated in the stratosphere (Figure 2).

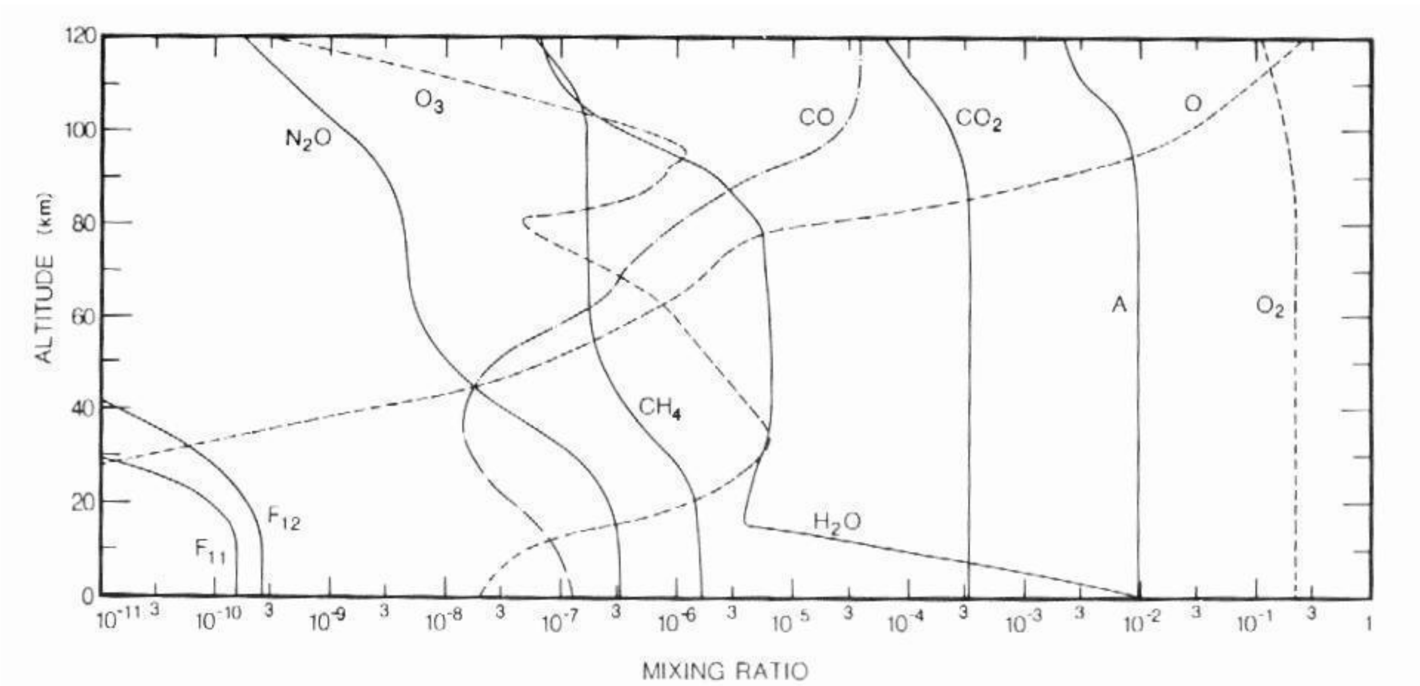


Figure 2**:** Vertical profiles of the mixing ratios of selected species at the equinox (from Goody and Yung, 1989).

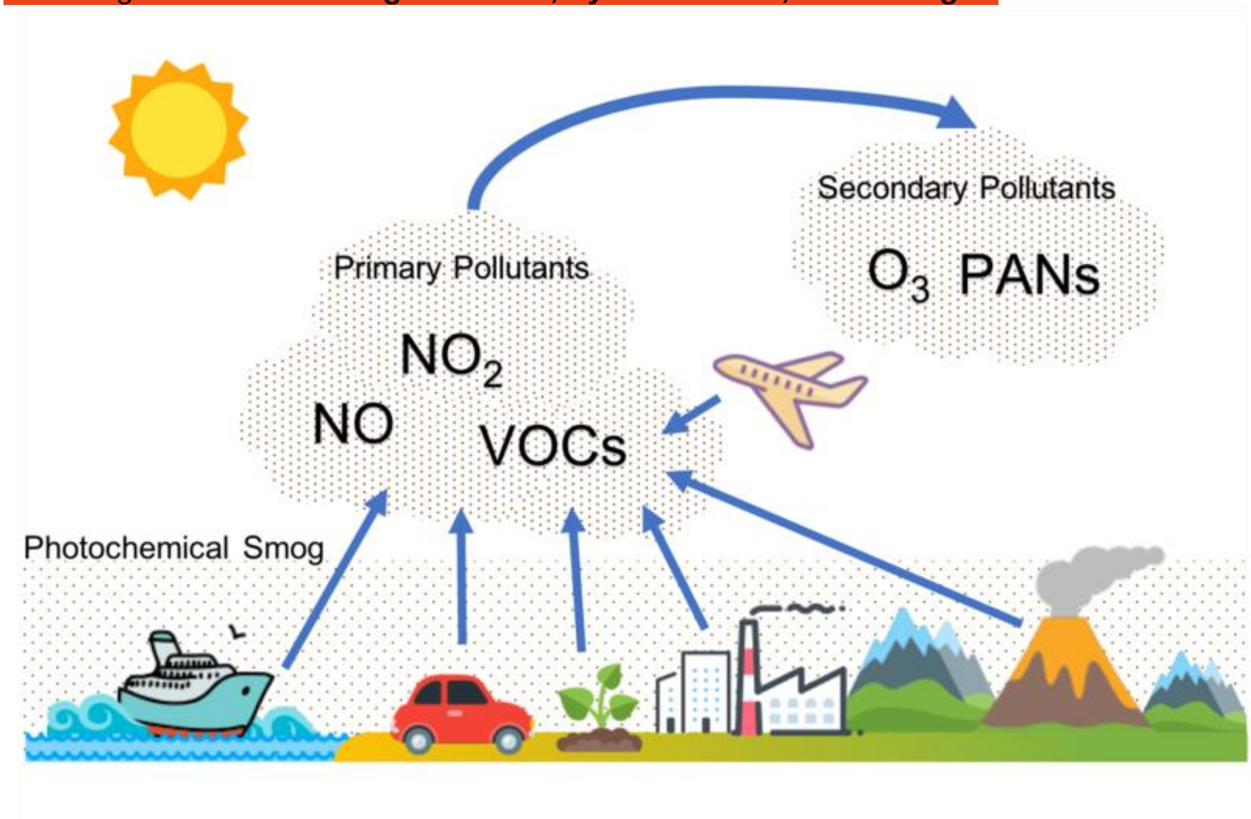
Photochemical smog

Photochemical smog is a mixture of pollutants that are formed **when nitrogen oxides and volatile organic compounds (VOCs) react to sunlight**, creating a brown haze above cities. It tends to occur more often in summer, because that is when we have the most sunlight

The major undesirable components of photochemical smog are **nitrogen dioxide (NO_2), ozone (O_3), PAN (peroxyacetylnitrate), and chemical compounds that contain the –CHO group (aldehydes)**. PAN and aldehydes can cause eye irritation and plant damage if their concentrations are sufficiently high.

Photochemical smog is created by the interaction of sunlight with certain atmospheric chemicals. Ozone is the principal component of air pollution of this kind. Ozone in the stratosphere protects us from harmful ultraviolet radiation but it is detrimental to human health when it is present on the ground level.

The formation of photochemical smog consists of three main ingredients. Moreover, these ingredients are **nitrogen oxides, hydrocarbons, and sunlight**.



Tropospheric Air Pollution: Ozone, Airborne Toxics, Polycyclic Aromatic Hydrocarbons, and Particles

Tropospheric air pollution has impacts on scales ranging from local to global. Reactive intermediates in the oxidation of mixtures of volatile organic compounds (VOCs) and oxides of nitrogen (NO_x) play central roles: the hydroxyl radical (OH), during the day; the nitrate radical (NO_3), at night; and ozone (O_3), which contributes during the day and night. Halogen atoms can also play a role during the day. Here the implications of the complex VOC-NO_x chemistry for O_3 control are discussed. In addition, OH, NO_3, and O_3 are shown to play a central role in the formation and fate of airborne toxic chemicals, mutagenic polycyclic aromatic hydrocarbons, and fine particles.