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## Some general facts about the Earth's Atmosphere

- atmosphere is contains 78% $N_2$, 21% $O_2$, 1% Ar, up to 3% water vapor in the lower part and less than 1% of other various constituents.
- approximately 30% of solar radiation is reflected back to space by clouds, the remaining part is absorbed by the atmosphere or the earth surface.
- the earth emits radiation in the IR range back to space
- clouds present a cooling effect for the earth as they reflect sun light back and prohibit it to reach the surface
- due to the tilt of the earth axis with respect to the sun, the polar regions have much less energy absorption as the equator. As a result, energy is transported by wind, wet and dry air masses, and ocean currents to other regions of the earth.
- the earth temperature increased at about 0.5C over the past century due to the manmade greenhouse gases (GHG).

## Layers of the Atmosphere

- they are characterized by temperature behavior

- **Troposphere**: 0-~10 to 15km altitude; characterized by temperature decrease (positive lapse rate) of about 5-10C per 1000m depending on humidity (9.7K/km for dry air), most of chemistry happening there, high and variable humidity, fast vertical mixing. Troposphere contains approx. 80% of the atmospheric mass and almost all water vapor. Distribution in a) Planetary Boundary Layer (PBL or BL) from 0-1000m altitude and b) Free Troposphere (FT) > 1000m altitude.
- **Tropopause**: ~10 to 15km altitude; marks the border between Troposphere and Stratosphere, temperature at 217K or –56C, Tropopause is at ~18km height at the equator and ~8km at the poles.
- **Stratosphere**: ~10 to 15km - ~45-55km altitude; characterized by temperature increase (negative lapse rate) due to presence of $O_3$, which absorbs UV-radiation, low humidity, slow vertical mixing
- **Stratopause**: ~45 to 55km altitude; marks the border between Stratosphere and Mesosphere, temperature at 271K
- **Mesosphere**: ~45 to 55km - ~80 to 90km altitude; characterized by temperature decrease, fast vertical mixing
- **Mesopause**: ~80 to 90km altitude: marks the border between Mesosphere and Thermosphere; coldest point of the atmosphere
- **Thermosphere**: >80 to 90km altitude: characterized by high temperature due to absorption of short wave radiation by $N_2$ and $O_2$, fast vertical mixing
- **Exosphere**: >500km altitude: outermost region of the atmosphere, gas molecules can escape gravitation when sufficient energy.

Interesting for us: TROPOSPHERE & STRATOSPHERE

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# Pressure in the Atmosphere:

- the pressure changes by six orders of magnitude from the surface to the exosphere and decreases approx. exponentially:

$$\frac{p(z)}{p_0} = e^{\frac{-z}{H}}$$

p(z): pressure at point z; $p_0$: standard pressure at Earth surface; z: altitude

$$H = \frac{RT}{M_{air} g}$$

H: Scale height, approx. 8km for the lower atmosphere at 273K, R: gas constant; $M_{air}$: mol. Weight of air; g: gravitation constant

$$H_i = \frac{RT}{M_i g}$$

$H_i$: Scale height for species i

# General Circulation in the Atmosphere

- exchange of moisture, momentum and energy between the atmosphere and the earth surface
- only small mass exchange with space, but direct energy exchange due to solar radiation
- the average total dry mass of the atmosphere per year is $5.15 * 10^{18}$kg
- uneven energy distribution at the Earth surface due to latitudinal variations – higher latitudes receive less energy than lower latitudes - and differences from the absorptivity of the earth surface
- the uneven energy distribution leads to large scale air motions to redistribute the energy:
    - warm tropical air rises with poleward direction
    - cold polar air sinks with equatorial direction
- **Coriolis force** influences air:
    - air moving south experiences a velocity component in westward direction
    - air moving south on the NH appears to lag behind the Earth
    - in the Planetary Boundary Layer (0-1km altitude) the effects of the earth surface are influencing the air motion: wind speed and direction are governed by horizontal pressure gradients, shear stresses and the Coriolis force
    - in the Geostrophic Layer (>1km altitude) only horizontal pressure and the Coriolis force influence the air flow

## Circulation of air

- air rises at the equator in poleward direction, it sinks at about 30° due to radiative cooling. This cold sinking air moves back to the equator. The Coriolis force acting on it leads to easterly winds. This circulation cell is called “Hadley Cell”.
- in the polar region (>55°) the same situation happens: warm air from the mid-latitudes rises and sinks at the poles whereas the cold polar air is transported in equatorial direction. The Coriolis force produces again easterly winds the so-called polar easterlies. This circulation cell is called “Polar Cell”.
- in the mid-latitudes between 40° and 55° the temperate regions are placed. In this regions large scale weather systems are occuring; polar air competing with equatorial systems. The main wind direction is west.
- at the equator, 30° and 55° calm regions are present. The air is rising or sinking at this points. At 30° air is sinking because it loses its moisture, while at the equator air is rising and takes moisture from the oceans.

## Cyclones and Anticyclones

- **Cyclone:**
  - air rising (converging) at low levels towards low pressure regions experiences a circular motion due to the Coriolis force. The winds are directed inward and spiral toward the low pressure region, which produces a vortex-like motion. The center of a cyclone is usually a column of warm rising air. Cyclones have on the Northern Hemisphere (NH) a counterclockwise direction and on the Southern Hemisphere (SH) a clockwise direction.
- **Anticylcone:**
  - low-level air from a high pressure systems converges and will spiral outward. An Anticyclone is clockwise at the NH and counterclockwise at the SH.

## Exchange of air in the lower Atmosphere

- **Interhemispheric exchange:**
  - a species needs around 1-2 months until it is mixed within one hemisphere
  - a species needs around 1-2 years until it is mixed within the complete atmosphere
  - the mixing between the two hemispheres happens mainly in the upper troposphere.
  - the reason for the long time needed for the global mixing is the so-called Inter tropical Convergence Zone (ITCZ), where almost no exchange between the two hemisphere exists due to the absence of winds with North-South direction. Air rises almost perpendicular at this regions.

- **Tropospheric-Stratospheric exchange:**
  - the vertical transport in the Troposphere happens in time scales of hours by large convective updrafts via clouds
  - the vertical transport in the Stratosphere takes about months to years due to the lack of humidity.
  - as a result appears the Troposphere well mixed whereas in the Stratosphere exists a mixing gradient – most of the species are concentrated near the Tropospause.
  - an exchange between Troposphere and Stratosphere happens when the Tropospause breaks up during an tropospheric folding event. A tropospheric folding event marks a situation when stratospheric air intrudes into the Troposphere. Only at such situations air can be exchanged and the lower most part of the stratosphere receives material from the Troposphere along a surface of constant potential temperature.
  - clouds can reach the Stratosphere by deep convection in the tropical regions. The air is “pumped” along a surface of constant potential temperature in poleward direction, where it finally sinks back into the Troposphere.
  - long lived species have their highest mixing ration in the Stratosphere immediately above the tropical Tropopause

## Temperature and Water Vapor in the Atmosphere

- temperature decrease from the tropics to the polar regions, is leveled out by altitude. The mean surface temperature difference between the Tropics and the polar regions is about 35ºC.
- water vapor is distributed throughout the lower Troposphere with highly variable values. Generally the gradient is similar as the temperature gradient. The maximum of water vapor in the Troposphere lays in the Tropics with approx. $16g_{H2O}/kg_{air}$.

## Useful Units in Atmospheric Chemistry

**Mixing Ratio:**

Ratio of amount (or mass) of the substance in a given volume to the total amount (or mass) of all constituents of interest in that volume. It is usually for dry air measured as the water vapor is variable.

**Volume Mixing Ratio** x**:**

$$x_i = \frac{c_i}{c_{total}}$$

$c_i$: mol.conc. of species i; $c_{total}$: total mol.conc.of air

$$c_{total} = \frac{p}{RT}$$ at any point of the atmosphere

$$x_i = \frac{c_i}{p/RT} = \frac{p_i/RT}{p/RT} = \frac{p_i}{p}$$ $p_i$: partial pressure of species i

Mixing ratios are molar fractions and very useful to describe abundances of substances.

**Units:**

| | |
|---|---|
| ppm | µmol/mol |
| ppb | nmol/mol |
| ppt | pmol/mol |

Sometimes also $ppm_v$ or $ppm_m$ found. The index "v" stands for volume and "m" for mass.

**Conversion** between ppm and µg/m3 for a species i:

$$i(ppm) = \frac{8.314T}{pM_i} c_i\left[mg/m^3\right]$$ $M_i$: mol. weight of i.

**Measurements of water vapor in the atmosphere:**

*Specific humidity*: proportion of water vapor in total air = $g_{H2O}/kg_{air}$.

*Relative humidity (RH)*: ratio of the specific humidity to the maximum specific humidity at a given temperature and pressure. Expressed in pressure it is defined as the ratio of partial pressure of water to its saturation vapor pressure at the same temperature.

$$RH = 100\frac{p_{H_2O}}{p^0_{H_2O}}$$

or expressed in molar fractions y: $$RH = 100\frac{y}{y_s}$$ y: actual mole fraction of water vapor; $y_s$: mole fraction of water vapor at saturation

*Mixing ratio of water vapor*: mole (or volume mixing ratio): mole of water vapor/mole of air

*Amount of water vapor to dry air by mass*: $g_{H2O}/kg_{dry\ air}$

*Mass concentration*: $g_{H2O}/m^3_{air}$

*Mass mixing ratio*: $g_{H2O}/g_{air}$

## Composition of the Atmosphere

- the atmosphere is a dynamic system and most gases are continuously exchanged with the vegetation, oceans and organisms
- in a cycle gases are produced and removed from the atmosphere by chemical reaction, biological activity and physical processes. The lifetime of gases is highly variable and can range from seconds to $10^6$years.
- a substance can alter in the air by photochemical processes (UV radiation can break up molecular bonds) or by interaction with other molecules (homogeneously and heterogeneously)
- atmosphere is oxidizing due to the presence of radicals such as OH and also $O_3$ as well as other substances have oxidizing properties.
- noble gases as well as $N_2$ and $O_2$ have long life times and are well mixed throughout the atmosphere
- water vapor, $CO_2$, $O_3$ etc. are influencing in the transmission of solar and terrestrial radiation. They are key components of biogeochemical cycles. They determine the oxidizing capacity of the atmosphere and therefore the lifetime of biogenic and anthropogenic trace gases.
- the spatial and temporal distribution of chemical species in the atmosphere is determined by several processes:
  - surface emissions: volcanic eruptions, biological activity (land and oceans), biomass burning, agriculture, industry…
  - transport: large scale advective (=horizontal) motions; convective (vertical) motions; boundary layer exchange; mixing associated with turbulence
  - wet deposition: rain, snow etc.
  - dry deposition on surfaces
  - chemical processes: oxidation, radical reactions…
- substances are transported upward to the Stratosphere when they are not destroyed or removed. In the Stratosphere they are destroyed to radicals due to UV radiation.
- Oceans provide $CO_2$, $CH_4$ and reduced sulfuric components to a large extend.