

Atmospheric Composition, Global Cycles and Lifetimes

The major classification of the atmospheric species is the following:

- ⇒ *sulfur-containing* components
 - ⇒ *nitrogen-containing* components
 - ⇒ *carbon-containing* components
 - ⇒ *halogen-containing* components
 - ⇒ *particulate matter* (aerosols)
 - ⇒ *Ozone*
- every substance released into the atmosphere is eventually removed, so that we have a cycle of elements. This cycle is called
 - ⇒ the **biogeochemical cycle** of the element
 - an example for such cycle is water, which is continually circulating between the oceans, land and atmosphere.
 - **Air pollution** exists when a substance emitted from anthropogenic (man-made) sources exceeds the normal atmospheric background level and causes measurable effects on living species and/or material.
 - air pollution originated from *sulfur compounds and particles* is the result of coal and oil combustion. It is mainly connected with cold climate (heating).
 - air pollution due to the use of fuel and gasoline (traffic) is called
 - ⇒ *photochemical smog* (from smoke and fog)

Photochemical smog is the result of complex chemistry taking place when sunlight irradiates the atmosphere laden with organic gases and nitrous oxides. High temperatures and bright sun light favour photochemical smog. The secondary pollutants, formed from the organic gases and nitrous oxides, are more aggressive and dangerous as the first pollutants. Secondary pollutants are O₃, organic nitrates, oxidized hydrocarbons and aerosol.

The background mixing ratio for O₃ for instance is between 20 and 60ppb, whereas during a photochemical smog event the concentration can exceed 500ppb.

Atmospheric Residence Times

The average life time what all molecules of a species spent in the atmosphere is called the **residence time** of this species. In other words the residence time tells us how long a molecule spends on average in air.

A substance can be removed ultimately from the atmosphere in two ways:

- by precipitation \Rightarrow **wet deposition**
- by the Earth surface itself \Rightarrow **dry deposition**

Dry Deposition defines the direct transfer of a species (gaseous or particulate) to the Earth surface without precipitation.

Wet Deposition refers to all processes transferring airborne species in aqueous form to the Earth. This includes the dissolution of gases and particles in droplets, the removal of particles serving as cloud condensation nuclei (CCN) and the removal of molecules after collision with droplets.

Particulate matter are called all substances -except pure water - existing as liquid or solid under normal conditions with sizes larger than molecules. As soon as particles are released to the atmosphere they “age”. This means that they undergo reactions, which change their size, number and composition before they are ultimately removed. Particles have relatively short residence times in the lower atmosphere with a few weeks and there exist two main removal mechanisms:

- near the Earth’s surface (<100m) they settle and are removed by dry deposition
- above 100m precipitation scavenging is the main removal mechanism

Precipitation Scavenging:

When an air parcel ascends it passes through clouds and becomes supersaturated with water (>100% RH). Cloud droplets condense on tiny particles (this particles are called cloud condensation nuclei) and grow with further condensation and/or collision with each other. When they are large enough they become raindrops and fall out.

Calculation of Residence Times:

The fundamental principle in the atmosphere is the *conservation of mass*:

- the rate of accumulation of a species in a given volume (dQ/dt) is the rate of species flowing into this volume (F_{in}) minus the rate of species flowing out of this volume (F_{out}) plus the rate of introduction (P) minus the removal rate (R).

Mathematical expression:

$$\frac{dQ}{dt} = (F_{in} - F_{out}) + (P - R)$$

Under equilibrium conditions $dQ/dt = 0$

and $F_{in} + P = F_{out} + R$

For the entire atmosphere in equilibrium we have $F_{in} = 0$ and $F_{out} = 0$ and also $P = R$.
With this we can find the average residence time τ :

$$t = \frac{Q}{R + F_{out}} = \frac{Q}{P + F_{in}}$$

When we consider the entire atmosphere as reservoir:

$$t = \frac{Q}{R} = \frac{Q}{P}$$

The calculation of residence times is useful to estimate how far from its source a species is removed.

Mixing times T_M for species depend on the residence time of the species. When a substance has only short residence times it is poorly mixed throughout the atmosphere. Examples are radicals, which have often residence times of only a few minutes. They are hardly mixed in the atmosphere or even in mesoscales. Has a substance long residence times like the noble gases for instance ($\tau = \text{years}$) this substance can be considered as well mixed throughout the atmosphere.

Sulfur Containing Compounds

Sulfur has a mixing ratio in the Earth crust of <500ppm per mass and in the Atmosphere a mixing ratio of <1ppm per volume. It can be considered as trace element. Considering this low mixing ratios the role of sulfur-containing in atmospheric chemistry is rather big. The principal components in the atmosphere are:

- ⇒ H₂S
- ⇒ CH₃SCH₃ (DMS)
- ⇒ CS₂
- ⇒ OCS
- ⇒ SO₂

Sulfur is present in five different oxidation stages. The reduced sulfur compounds (-1;-2) are rapidly oxidized by hydroxyl radicals and other chemical species. This species occur preferably in the gas phase and due to their reactivity their residence times are rather short (few days). On the other hand sulfur compounds with the oxidation stage of +6 are often found in particles or droplets. Their residence times are determined by wet or dry removal.

The main emission sources for sulfur are anthropogenic and present about 75% of the current estimates. This estimates name a range between 98-120Tg/year (10¹²g) for total sulfur emissions. 75% are man made and 90% of the man made sources are found on the Northern Hemisphere. About 1981 Asia became the “leading” continent in sulfur emittance (>20Tg/year). One reason for this is the increased use of coal combustion in China.

Dimethylsulfide (DMS) CH₃SCH₃:

DMS is the dominant sulfur compound emitted from the oceans. It is produced in oceanic water by marine organisms: Phytoplankton produces dimethyl-sulfoniopropionate -a precursor to DMS- which is decomposed to DMS by certain algae species. The concentration of DMS varies strongly in the upper layer of the ocean and is in average ~100ng of S per Liter. The concentration is depending on diurnal, seasonal, sea depth and locational variations. Due to the high enrichment in the upper layer of the ocean there is a flux from the ocean surface to the atmosphere and the mixing ratio in the marine boundary layer (MBL) is 80-100ppt, but falls off quickly with altitude. Once in the atmosphere DMS reacts with the hydroxyl radical and also with the NO-radical. The fact the OH radical is formed during a photochemical cycle driven by sunlight effects the DMS concentration. During the day the DMS concentration is much lower than during the night, when DMS cannot react with OH. The oxidation of DMS is the only source for methan sulfonic acid (MSA) and the main source for SO₂ in the marine atmosphere.

Carbonylsulfide (OCS):

OCS is the most abundant sulfur species in the global background atmosphere due to its low reactivity and thus long residence time. In fact it is the only sulfur component which makes all the way through to the Stratosphere, where it is believed to be a main

compound of the stratospheric aerosol layer. The average tropospheric mixing ratio comprises 500ppt. The sources of OCS are CS₂ oxidation, ocean emissions and biomass burning. Its sinks are uptake by plants and soil as well as reactions with the hydroxyl radical. The total quantity of OCS in the atmosphere is estimated to be 5.2Tg, with approx. 4.63Tg in the Troposphere and 0.57Tg in the Stratosphere. The global atmospheric lifetime is compared with DMS rather long with 7years.

Sulfurdioxide (SO₂):

SO₂ has predominant anthropogenic sources and a background concentration of 20 – 1ppt in unpolluted regions. Its concentration can exceed several hundred ppb in urban environments.

Estimation of residence times for SO₂ and sulfate:

SO₂:

removal by dry deposition	removal by wet deposition	removal by chem. reaction	average residence time
60hrs	100hrs	80hrs	25hrs

Sulfate:

removal by dry deposition	removal by wet deposition	average residence
>400hrs	80hrs	80hrs

Nitrogen Containing Compounds

- Nitrogen (N₂) itself is very stable and not involved in the chemistry of the Troposphere and Stratosphere
- Other important nitrogen containing components in the atmosphere are N₂O, NO, NO₂, HNO₃, NH₃. In very low concentrations N₂O₅ and NO₃-radical can be found.

Nitrogen, the most abundant gas in the atmosphere, must be converted -“fixated”- in different forms to be useful for living species. The natural conversion happens by microorganisms, which convert N₂ to NH₄⁺, NH₃ and organic nitrogen compounds. Other natural fixation happens due to ionization phenomena like lightning or cosmic radiation. In this case nitrous oxides are formed. Anthropogenic fixation appears by cultivation of legumes and fertilizer use. The latter ones converts N₂ to NH₃, which is eventually oxidized to NO₂⁻ and NO₃⁻. This process is called *nitrification*. The opposite process – *denitrification* = reduction of NO₃⁻ to N₂, NO₂, N₂O, NO - is done by bacteria.

Nitrous oxide N₂O:

N₂O is a colorless gas and is almost totally emitted by natural sources (bacteria in soil). It is an extreme influential greenhouse gas due to its long lifetime and large energy absorption capacity. Its global warming potential is approx. 300 times that of CO₂. The most important sources are tropical soil and also the oceans. Other sources include biomass burning, degassing of irrigation water, agricultural activities and also industrial sources. Nitrous oxide is inert in the Troposphere and passes unchanged into the Stratosphere. There it is photodissociated (accounts to 90% as sink) or reacts with O(¹D) (10% as sink) yielding in NO. This pathway is the major source of NO in the Stratosphere. The lifetime of N₂O is estimated by models to about 120 ± 30 years. The level of this nitrogen containing gas rose from 276ppb in pre-industrial times to 311ppb today. This corresponds to an increase of about 15%.

Nitrogen oxides NO and NO₂:

NO is emitted by natural and anthropogenic sources, where for the latter ones high temperature combustion is the major source. NO₂ has its sources by oxidation of NO and in small quantities from combustion processes. The sum of NO and NO₂ is called NO_x.



NO_x are the most important nitrogen containing molecules in atmospheric chemistry. Their concentration increased significantly in the last century due to fuel combustion. Aircraft emissions account to a large amount in the free Troposphere in the Northern Hemisphere. This is expected to rise even more due to increase of aircraft transport.

The NO_x sources in the US are estimated as following: 40-45% from transportation, 30-35% from power plants and 20% from industrial sources.

Reactive “Odd” nitrogen NO_y :

Reactive “odd” nitrogen is the sum of NO_x plus all the compounds that form as products by atmospheric oxidation from NO_x . Products are: HNO_3 , HONO , NO_3 -rad., N_2O_5 , HNO_4 , peroxyacetyl nitrate (PAN) etc., with HNO_3 as the major oxidation product of NO_x . HNO_3 is rapidly deposited due to its water solubility and has therefore rather short lifetimes. The NO_3 radical is present especially during the nighttime. The conversion of NO_x to other NO_y needs around 4-20 hours. In urban location NO and NO_2 are the dominant NO_y constituents due to fuel combustion and other main sources. In rural and remote regions NO and NO_x are significantly lower, with the lowest concentration in isolated rural areas. In the marine atmosphere as well as the remote tropical rainforest atmosphere NO_x plays a minor role, with somewhat higher concentrations in the tropical forests (due to biogenic emissions from soil).

Ammonia (NH_3):

Ammonia is the primary basic gas in the atmosphere and after N_2 and N_2O the most abundant nitrogen containing compound. The ammonium ion – a reaction product for instance between NH_3 and HNO_3 – is an important part of the tropospheric aerosol. The residence times of NH_3 are about 10 days thus rather short, which is due to its easy absorption by surfaces like water and soil. Wet and dry deposition are the main removal path ways.

Carbon containing compounds

Methane CH₄:

Methane is the most abundant hydrocarbon in the atmosphere and has natural as well as anthropogenic sources. The major natural sources are wetlands emitting methane into the atmosphere. For the anthropogenic sources account fossil fuel combustion and, in the biospheric area, cultivation of rice and other species. Methane is primarily removed by reaction with the OH-radical and by microbial uptake in soil. The CH₄ concentration increased significantly in the last centuries from 700ppb in pre-industrial times to 1700ppb today.

Volatile Organic Compounds (VOC's):

VOC's are all non-natural organic components, which are volatile. About 600 of them are catalogized and differentiated. All of them have different effects in the atmosphere and their effects can vary substantially. The most dominant source in the US are motor vehicles, from which VOC's are emitted as the result of incomplete combustion of fuel or evaporated due to heat.

Biogenic Hydrocarbons:

The Earth vegetation releases organic compounds –the natural VOC's – into the atmosphere. The most abundant are isoprene and mono-terpenes, but the variety of species is large. All molecules consist of at least one olefinic double bond thus making the hydrocarbons extremely reactive. Isoprene is emitted by deciduous trees as a byproduct of photosynthesis and/or photorespiration. Its concentration is temperature and light dependent with increasing temperatures and more light resulting in higher isoprene concentration. Terpenes are emitted by conifers by biophysical processes connected to the terpenoid material present in the plant. Compared to the isoprene it is not strongly depending on light but depends on temperature. The largest biogenic hydrocarbon emission happens in the tropical rainforests with its enormous biological mass.

Carbonmonoxide CO:

CO is formed by oxidation of CH₄ with OH as well as by technological processes and biomass burning. Two third of its sources are anthropogenic with most of them due to fuel combustion. The lifetime of CO is about 30-90days. Due to higher human activities more CO exists in the Northern Hemisphere as in the Southern Hemisphere. Its maximum lays in the northern midlatitudes and decreases with altitude. On the Southern Hemisphere CO appears to be more uniformly mixed in the troposphere.

Carbondioxide CO₂:

The levels of CO₂ increased in the last 150 years due to fossil fuel combustion, land use and cement production. Between 1000 and 1800AD the CO₂ mixing ratio was rather stable at about 280ppm before increasing in the last 150 years to an amount of 358ppm. This corresponds to a 30% increase. Important sinks for CO₂ are the oceans and fresh water lakes as well as plants (photosynthesis and photorespiration).

Because of the great carbon mass exchanges between the different pools (oceans, Earth surface and atmosphere) it is difficult to estimate the net exchange of this three pools. It is estimated at about 7.1Gt of C/year. Since a large amount of carbon is stored in plant material deforestation and forestation influences the balance of CO₂ emissions.

Halogen-Containing Compounds

Terminology:

<i>Halocarbons:</i>	general term referring to halogen-containing organic carbons
<i>Chlorofluorocarbons (CFC's)</i>	halocarbons containing C, Cl, F
<i>Hydrochlorofluorocarbons (HCFC's)</i>	halocarbons containing H, Cl, F, C
<i>Hydrofluorocarbons (HFC's)</i>	halocarbons containing H,F,C
<i>Perhalocarbons</i>	halocarbons with every C-bond containing halogen
<i>Halons</i>	bromine-containing halocarbons

Halocarbons have natural and anthropogenic sources. For the natural sources account the oceans, where halocarbons are formed by biological processes and sea spray. Biomass burning and industrial processes are the primary man-made sources.

CFC's are very inert in the Troposphere and are transported into the Stratosphere, where they are photolytically destroyed. The destruction releases Cl atoms, which support catalytically the O₃ destruction in the Stratosphere. This destruction mechanism is the only relevant sink for CFC's.

Halocarbons containing one or more H are reacting with OH-radicals in the Troposphere and thus reach only to a small extent the Stratosphere, where they undergo the same mechanism as the CFC's. Some (10-15%) of the HCFC's react with sea water accounting another sink.

The lifetimes of halocarbons can vary from month's to decades.

CHCl_3 is the dominant halogen compound with 600ppt mixing ratio and has its source mostly in the oceans by biological reactions. Its life time is about 2years and it can therefore be considered as considerably mixed throughout the atmosphere.

Ozone

Ozone is a reactive oxidant and produced naturally in the atmosphere. About 90% is found in the Stratosphere between 20-30km altitude. O_3 absorbs efficiently UV radiation between 240-290nm and this property made life on Earth only possible - this radiation is harmful for living species. The longer UV-B radiation (290-320nm) is screened as well, but the decreasing concentration of O_3 in the Stratosphere lead to an increase of UV-B on the Earth surface. Only 10-15% of total Ozone in the atmosphere is found in the Troposphere. The mixing ratios for the clean marine troposphere are 10-40ppb and for the Stratosphere between 25-30km are 10ppm.

Dobson Units (DU): Ozone is often measured in Dobson Units. The Dobson units refer to the total amount of O_3 integrated from the Earth surface to the top of the atmosphere (TOA). 100 DU would correspond to a 1mm thick layer of pure Ozone. Total column units range from 290-310 DU.

The Stratospheric ozone decreased since about 1970 with losses most marked in the regional winter and spring. Ozone can be exchange between Stratosphere and Troposphere during tropopause folding events, but only approx. 0.1% of the stratospheric ozone is transported to the Troposphere. In the Troposphere the O_3 concentration is increasing with 1-2% per year over the past 30 years. See photochemical smog.