Chapter 2

CONTAMINANTS IN AIR

Reference textbook*:* A. Tiwary, I. Williams – *"Air pollution – Measurement, Modelling and Mitigation",* Taylor&Francis Group (2019)

2.1 CLASSIFICATION OF ATMOSPHERIC POLLUTANTS

Earth atmosphere

The atmosphere (from Greek atmòs, “vapor” and sphàira, “sphere”) is a layer of gas and suspended solids extending from the Earth's surface up many thousands of miles, becoming increasingly thinner with distance but always held by the Earth's gravitational pull. **This layer of gas is what is generally called “air”.**

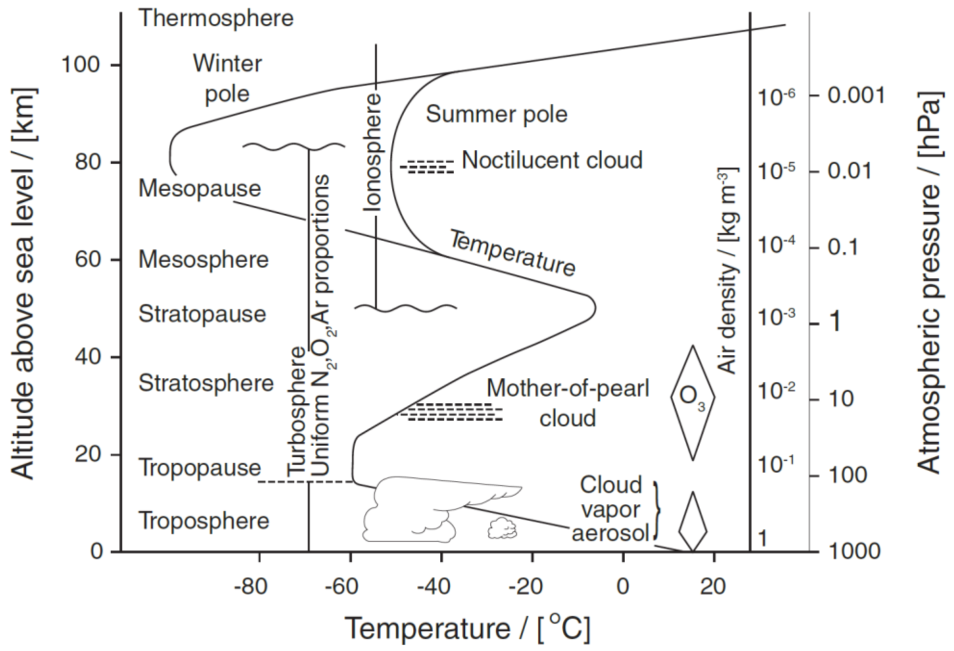
The atmosphere is a mixture of gases that surrounds the Earth. It helps make life possible by providing us with air to breathe, shielding us from harmful ultraviolet (UV) radiation coming from the Sun, trapping heat to warm the planet, and preventing extreme temperature differences between day and night.

2.1 CLASSIFICATION OF ATMOSPHERIC POLLUTANTS

The structure of atmosphere

The Earth atmosphere has no abrupt cut-off. It slowly becomes thinner and fades away into space. There is no definite boundary between the atmosphere and outer space.

The atmosphere extends horizontally with a scale in the order of the circumference of the Earth, which is 40000 km. The vertical scale is much smaller, about 100 km.

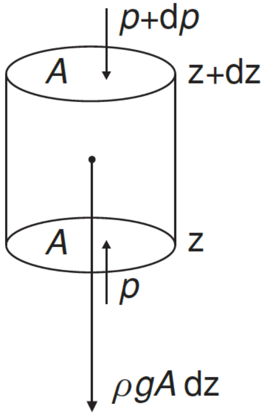


The fall or rise of temperature with altitude defines in order the **troposphere**, **stratosphere**, **mesosphere** and **thermosphere**. The regions separating these ‘spheres’ are called the tropopause, stratopause and mesopause. Their altitude varies with latitude.

The troposphere is the scene of strong vertical motion of air caused by the heating of the Earth’s surface. This heating warms air masses, which then rise to release latent heat as sensible heat that further uplifts the air mass.

2.1 CLASSIFICATION OF ATMOSPHERIC POLLUTANTS

Pressure change in troposphere



Let’s consider a parcel of air is in **hydrostatic equilibrium with the air above and below**. In vertical equilibrium the force upwards must be equal to the force downwards:

$$pA = (p + dp)A + g\rho A\,dz \qquad (2.1)$$

Which becomes:

$$dp = -g\rho\,dz \qquad (2.2)$$

This is called the **hydrostatic equation**. In the lower troposphere the gravity acceleration *g* can be assumed as constant, while the density *ρ* has a strong exponential decrease with increasing altitude and it may not be taken constant.

However, **the relation between *ρ* and *p* as the thermodynamic behavior of the air in the atmosphere can be approximated rather well by the equation of state of an ideal gas.**

2.1 CLASSIFICATION OF ATMOSPHERIC POLLUTANTS

Pressure change in troposphere

The equation state of ideal gas is:

$$pV = nRT \tag{2.3}$$

The number of moles *n* in a volume *V* can be related to the mass of air by its molar weight (28.9647 g/mol)

$$m = nM\ 10^{-3}\ [kg] \tag{2.4}$$

The specific gas constant for air is defined as:

$$R' = \frac{10^3}{M} R \tag{2.5}$$

Substituting *n* from Eq. 2.4 and *R* from Eq. 2.5 in Eq. 2.2 we have:

$$p = \frac{m}{V} R'T = \rho R'T \tag{2.6}$$

Following the hydrostatic equation, results:

$$\frac{dp}{dz} = -g\rho = -\frac{g}{R'T} p \tag{2.7}$$

2.1 CLASSIFICATION OF ATMOSPHERIC POLLUTANTS

Pressure change in troposphere

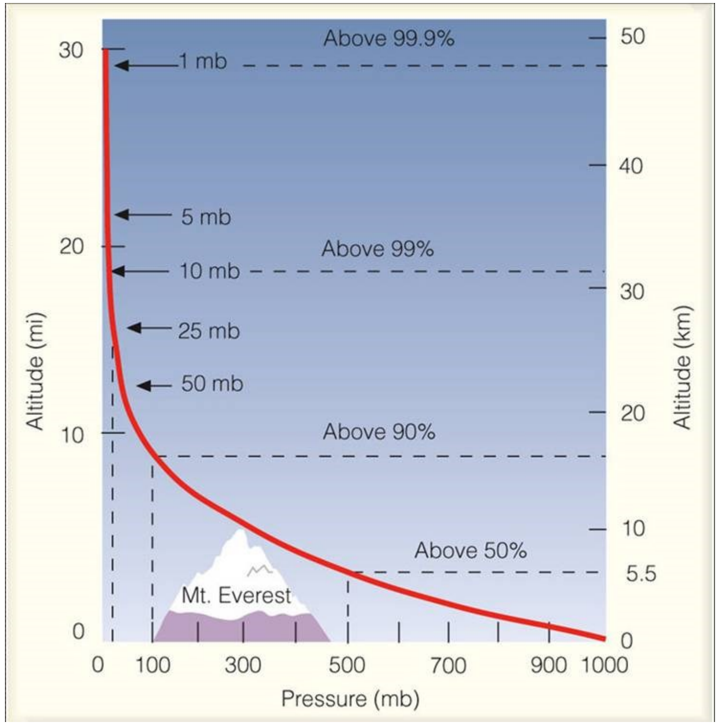
In most of the atmosphere the temperature T varies between 200 and 300 K. Taking some average value T_{av} for T one may define an effective scale height H_e as:

$$H_e = \frac{R' T_{av}}{g} \ [\mathrm{m}] \qquad (2.8)$$

Therefore, the hydrostatic equation can be solved as:

$$p = p_0 e^{-\frac{z}{H_e}} \qquad (2.9)$$

For T = 250 K results $H_e \approx 7.3$ km and a decrease of a factor of 10 in pressure for an increase of altitude with 16.8 km.
At sea level (z = 0) the atmospheric pressure is **1013.25 hPa (=1 atm, = 1.01325 Bar)**



2.1 CLASSIFICATION OF ATMOSPHERIC POLLUTANTS

Earth atmosphere

What we experience today as our atmosphere is a transient snapshot of its evolutionary history.

The planet Earth was formed around 4600 million years ago by the gravitational accumulation of relatively small rocks and dust, called planetesimals, within the solar nebula. There was probably an initial primordial atmosphere consisting of nebula remnants, but this was lost to space because the molecular speeds exceeded the **Earth's escape velocity of 11.2 km s^{-1}**.

A combination of impact energy and the radioactive decay of elements with short half-lives raised the temperature of the new body. The atmosphere of Earth derived primarily by thermal outgassing of volatile substances from virgin planetary material during and subsequent to the formation of the planet. **The same heating caused dissociation of hydrated and carbonate minerals with consequent outgassing of H_2O and CO_2.**

As the Earth cooled, most of the H_2O condensed to form the oceans, and most of the CO_2 dissolved and precipitated to form carbonate rocks.

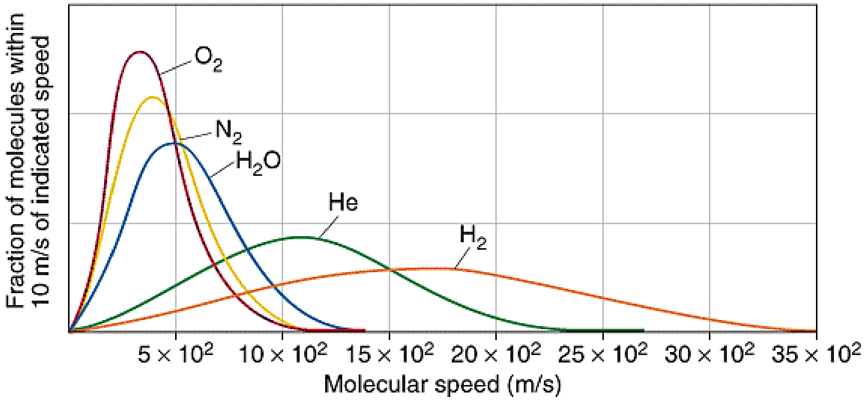
2.1 CLASSIFICATION OF ATMOSPHERIC POLLUTANTS

Earth atmosphere

About one hundred times more gas has been evolved into the atmosphere during its lifetime than remains in it today.

The effect of atomic mass makes a huge difference to the likelihood of molecules escaping from the Earth. The Maxwell distribution means that there is a most likely velocity, which is relatively low, and a long tail of reducing probabilities of finding higher speeds.

$$f(v) = \left(\frac{m}{2\pi kT}\right)^{\frac{3}{2}} 4\pi v^2 e^{-\frac{mv^2}{2kt}} \tag{2.10}$$



For example, a hydrogen atom at 600 K (typical temperature at the top of the atmosphere) has a 10^{-6} chance of exceeding escape speed, while the corresponding value for an oxygen atom is only 10^{-84}. This process results in a steady attrition of lighter atoms.

2.1 CLASSIFICATION OF ATMOSPHERIC POLLUTANTS

The composition of atmosphere – dry, clean air

Air consists of a number of constituent gases that have **fairly constant average proportions**, both at different horizontal and vertical positions and at different times. These are called “natural constituents”

Gas	Symbol	Concentration
Nitrogen	**N_2**	**78.084%**
Oxygen	**O_2**	**20.947%**
Argon	**Ar**	**0.934%**
Carbon Dioxide	**CO_2**	**0.041%**
Neon	Ne	18.182 parts per million
Helium	He	5.24 parts per million
Methane	CH_4	1.70 parts per million
Krypton	Kr	1.14 parts per million

Gas	Symbol	Concentration
Hydrogen	H_2	0.53 parts per million
Carbon monoxide	CO	0.47 parts per million
Nitrous oxide	N_2O	0.31 parts per million
Xenon	Xe	0.09 parts per million
Sulphur dioxide	SO_2	0.08 parts per million
Ozone	O_3	0.07 parts per million
Nitrogen dioxide	NO_2	0.02 parts per million
Ammonia	NH_3	0.01 parts per million

These values refer to the so called **clean, dry air**, which is a hypothetical construct and excludes the small but exceptionally important amounts of particulate matter and water vapor. **This composition has not changed much over time except for methane, nitrous oxide and carbon dioxide**, which have increased significantly since the Industrial Revolution, and are still rising.

2.1 CLASSIFICATION OF ATMOSPHERIC POLLUTANTS

The composition of atmosphere – dry, clean air

- **Nitrogen (N_2)** is the most dominant gas in air. It is a primary outgassing product, which enters the biosphere by bacterial nitrogen fixation, which is a process that reduces N_2 to amino compounds and incorporates it directly into the living cell. The biosphere eventually releases nitrogen to the atmosphere by anaerobic bacterial denitrification.

- **Oxygen (O_2)**, which is the second most abundant gas in air, is not a planetary outgassing product but a by-product of the assimilation of carbon dioxide (CO_2) by phytoplankton and green plants. Oxygen gas has evolved over time in conjunction with the development of the biosphere. On a geological short time scale, the production and consumption of O_2 are nearly balanced. The present amount of atmospheric oxygen is understood to represent an excess over that used up in the oxidation of organic carbon and other reduced chemical compounds.

2.1 CLASSIFICATION OF ATMOSPHERIC POLLUTANTS

The composition of atmosphere – dry, clean air

- **Carbon dioxide (CO_2)** is readily absorbed by seawater. On a time-scale of approximately 1000 years, atmospheric CO_2 is in equilibrium with that residing in the ocean. The majority of CO_2 released by thermal outgassing has entered sediments in the form of limestone deposits. The exchange of CO_2 with the biosphere via photosynthesis and reoxidation of organic material occur on a time scale of 10–100 years. The **increase of CO_2** in the atmosphere since the Industrial Revolution is caused by the **combustion of fossil fuels** that are taken from deposits of sedimentary organic carbon.

- **Rare gases** in the atmosphere have resulted from planetary outgassing. The dominant isotope of argon, ^{40}Ar, is a product of the radioactive decay of potassium-40.

- **Trace gases** include all those gaseous components in the atmosphere that, because of their low concentrations, do not affect the bulk composition of air. This makes it convenient to quantify the local abundance of a trace gas by its molar mixing ratio. Because the major components of air are chemically rather inert, **atmospheric chemistry is for the most part driven by trace gases**.

2.1 CLASSIFICATION OF ATMOSPHERIC POLLUTANTS

The composition of atmosphere – dry, clean air

The concentrations of atmospheric trace gases can be shown to adjust to a **steady state** (a situation in which all state variables are constant in spite of ongoing processes that strive to change them) between the sources and sinks and their global distributions.

For trace gases that are **long-lived**, with residence times of 2 years or longer, the general circulation of the atmosphere guarantees a **fairly uniform mixing ratio**.

For trace gases that are **short-lived**, the **mixing ratio is determined by the local sources and sinks**, and it may undergo substantial variations. In this case, the global distribution of sources and sinks as well as advection (a transport mechanism of a substance or conserved property due to the atmosphere’s bulk motion) with the winds becomes important.

2.1 CLASSIFICATION OF ATMOSPHERIC POLLUTANTS

Water vapor in the atmosphere

The gases listed as "natural constituents" of Earth's atmosphere have long residence times in the atmosphere and are well mixed, and their concentrations are broadly the same everywhere in the atmosphere.

Water is very different, due to its unusual properties at normal Earth temperatures and pressures. It is the only material that is present in all three phases, i.e., solid (ice), liquid and gas (water vapor), and there is continuous transfer between the three phases depending on the conditions.

The proportion of water vapor in the atmosphere depends both on the local conditions and on the history of the air. More specifically, water vapor concentration depends on **air temperature,** determining the maximum amount of water vapor that can be present. The water vapor pressure at this point is called the **saturated vapor pressure** (**P_{ws}**), and it varies roughly exponentially with temperature.

$$P_{ws}(T) = 611 \times e^{\left(\frac{19.65T}{273+T}\right)} \; [Pa] \tag{2.11}$$

2.1 CLASSIFICATION OF ATMOSPHERIC POLLUTANTS

Water vapor in the atmosphere

The local, ambient vapor pressure (P_w) may be any value between zero and P_{ws}. The ratio of actual to saturated vapor pressure is called the **relative humidity RH**, often expressed as a percentage.

$$RH = 100 \times \frac{P_w}{P_{ws}} \tag{2.12}$$

If water vapor is evaporated into dry air, then the vapor pressure increases towards P_{ws} but cannot exceed it. If air is cooled, for example, by being lifted in the atmosphere, then a temperature will be reached at which the air is saturated due to its original water content. Any further cooling results in the excess water being condensed out as **cloud droplets**. If the cooling occurs because the air is close to a cold ground surface, then dew results.

The complexity of this sequence for any air mass is responsible for the variability of water vapor concentration in space and time.

2.1 CLASSIFICATION OF ATMOSPHERIC POLLUTANTS

The composition of atmosphere – wet air

The highest vapor concentrations occur in the humid tropics, with temperatures of 30°C and relative humidity of near 100%. In this condition, the vapor pressure will be 4300 Pa (see Eq. 2.11), corresponding to a mixing ratio of 4.3/101 = 4.3%.

At the low end, an RH of 50% at a temperature of –20°C would correspond to a mixing ratio of around 0.1%. The **global average mixing ratio is around 1%**, so the abundance of water vapor is similar to that of argon.

Water vapor	Nitrogen	Oxygen	Argon
0%	78.084%	20.947%	0.934%
1%	77.30%	20.70%	0.92%
2%	76.52%	20.53%	0.91%
3%	75.74%	20.32%	0.90%
4%	74.96%	20.11%	0.89%

2.1 CLASSIFICATION OF ATMOSPHERIC POLLUTANTS

Atmospheres outside our planet

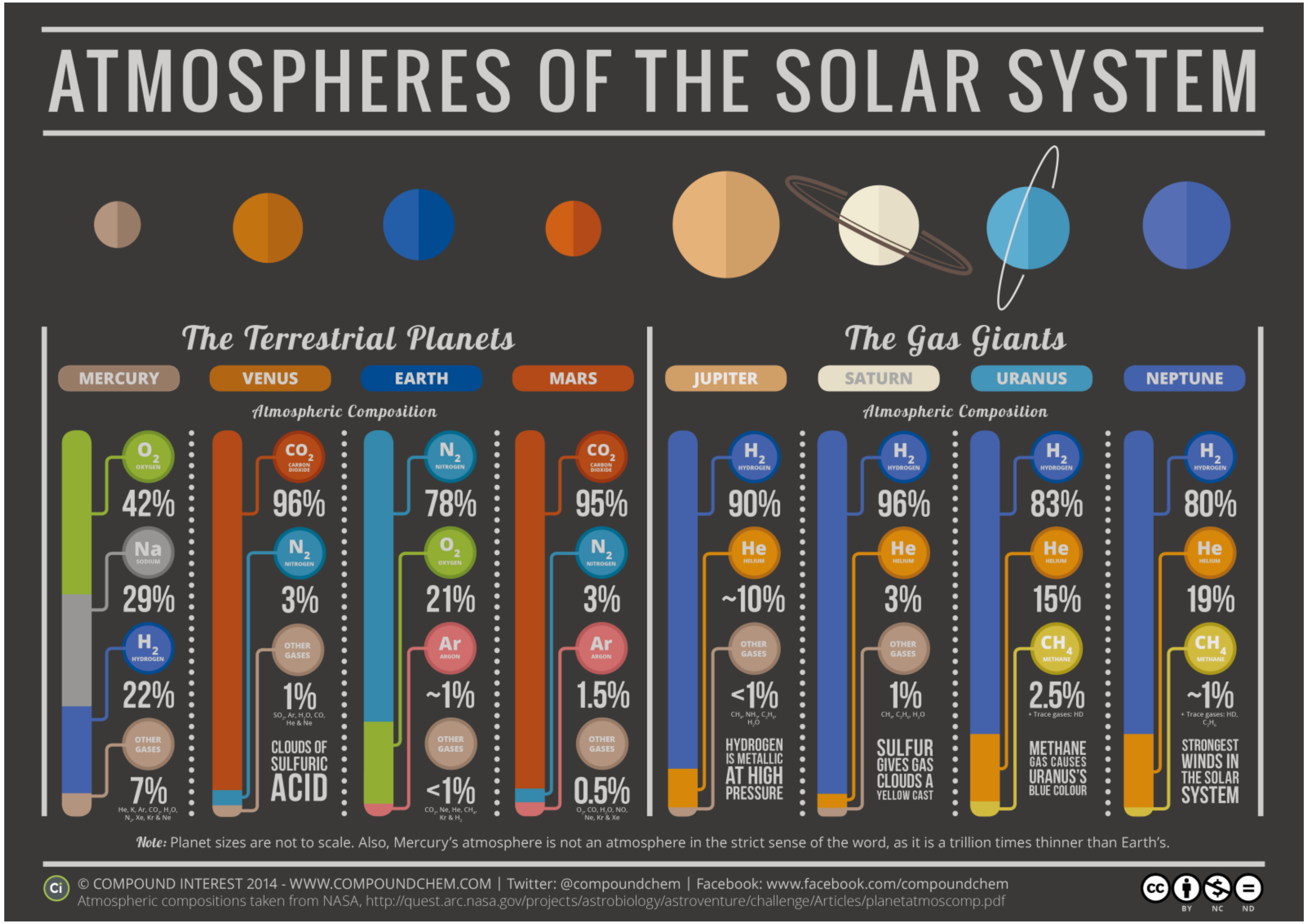
Earth is not the only world with an atmosphere. Each of the planets - and even a few moons - in our solar system have an atmosphere. Some planets have active atmospheres with clouds, wind, rain and powerful storms (like the Great Red Spot on Jupiter).

Each of the planets in our solar system has a uniquely structured atmosphere. The atmosphere of Mercury is extremely thin and is not very different from the vacuum of space. The gas giant planets in our solar system (Jupiter, Saturn, Uranus and Neptune) each have a thick, deep atmosphere. The smaller, rocky planets (Earth, Venus and Mars) each have thinner atmospheres, hovering above their solid surfaces. The moons in our solar system typically have thin atmospheres, with the exception of Saturn's moon, Titan, where the air pressure at the surface is higher than on Earth. Pluto has a thin atmosphere that expands and collapses seasonally, and Ceres has an extremely thin and transient atmosphere made of water vapor.

Only Earth's atmosphere has a **layered structure** that traps enough of the Sun's energy for warmth while also blocking much of the harmful radiation from the Sun. This **important balance** is necessary to maintain life on Earth.

2.1 CLASSIFICATION OF ATMOSPHERIC POLLUTANTS

The composition of atmosphere – comparison with other planets



Note: Planet sizes are not to scale. Also, Mercury's atmosphere is not an atmosphere in the strict sense of the word, as it is a trillion times thinner than Earth's.

Atmospheric compositions taken from NASA, http://quest.arc.nasa.gov/projects/astrobiology/astroventure/challenge/Articles/planetatmoscomp.pdf

2.1 CLASSIFICATION OF ATMOSPHERIC POLLUTANTS

Characterization of atmospheric pollutants

Air pollution is defined as the presence in the atmospheric environment of natural and artificial substances that affect human health or well- being, or the well-being of any other organism is air pollution. This is a term used to describe any **unwanted chemicals or other materials that contaminate the air we breathe**, resulting in the reduction of its life-supporting qualities (commonly referred to as air quality). In principle, an air pollutant is any chemical species that exceeds the concentrations or characteristics of the natural constituents of air, with particular attention of the human induced changes (anthropogenic sources).

Pollutants in air can be divided in two main categories:

- **Gaseous pollutants**: can have either biogenic or anthropogenic origins, but the major sources over the last century have been dominated by anthropogenic fossil fuel combustion. However, non-combustion sources are particularly important for volatile organic compounds and methane.

- **Particulate matters**: also commonly known as aerosols, are an important environmental pollutant, being responsible for loss of visual range, soiling of surfaces and health effects on people.

2.1 CLASSIFICATION OF ATMOSPHERIC POLLUTANTS

Gaseous pollutants

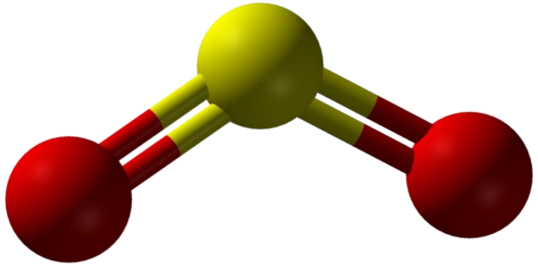
Pollutant gases in the atmosphere may be released directly from sources (**primary pollutants**) or may be formed in the atmosphere after chemical reaction (**secondary pollutants**).

- **Primary pollutants**: sulphur dioxide (SO_2), carbon dioxide (CO_2), carbon monoxide (CO), nitrous oxide (N_2O), methane (CH_4), nitric oxide (NO), ammonia (NH_3), and VOCs.
- **Secondary pollutants**: nitrogen dioxide (NO_2), nitrous acid (HNO_2), nitric acid (HNO_3), and ozone (O_3)

Several gas pollutants can be **either primary or secondary**, including CO_2, CO, and NO_2.

2.1 CLASSIFICATION OF ATMOSPHERIC POLLUTANTS

Sulphur dioxide



Sulphur dioxide (SO_2) is a colorless gas with a penetrating, choking odor. It dissolves readily in water to form an acidic solution (sulphurous acid). SO_2 (generally expressed as SO_x) has long been recognized as a pollutant because of its role, along with particulate matter, in forming **winter-time smog.**

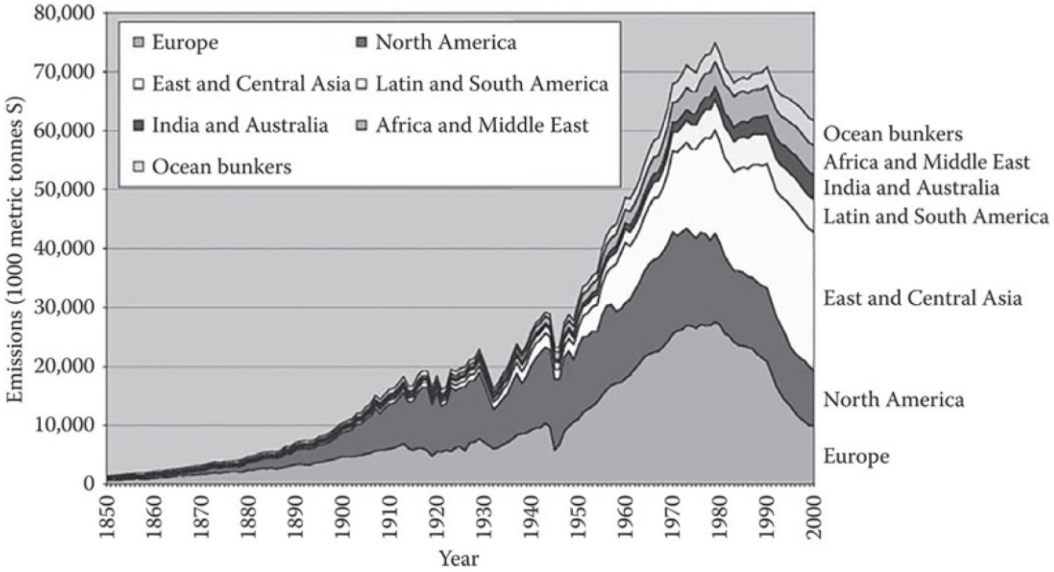
Sulphur is present in all hydrocarbon fuels to some degree and has especially high concentrations in coal, up to 7% sulphur by weight. **SO_2 is formed as a primary pollutant when coal is burnt**. The major natural sulphur emissions are in the reduced forms of H_2S (hydrogen sulphide), CS_2 (carbon disulphide) or OCS (carbonyl sulphide).

SO_2 can affect both **health and the environment**. Short-term exposures to SO_2 can harm the human respiratory system and make breathing difficult. People with asthma, particularly children, are sensitive to these effects of SO_2. At high concentrations, gaseous SO_x can harm trees and plants by damaging foliage and decreasing growth. SO_2 and other sulfur oxides can contribute to acid rain which can harm sensitive ecosystems.

2.1 CLASSIFICATION OF ATMOSPHERIC POLLUTANTS

Sulphur dioxide

A global estimate of sulphur dioxide SO_2 emissions can be calculated from the knowledge of the sulphur content of the fuel and from the information on the amount of sulphur retained in the ash. The natural sources are now heavily outweighed by human ones, principally fossil fuel combustion. It suggests that global sulphur dioxide emissions peaked about 1980 and since then have been declining.



In industrialised countries, emissions have been falling in recent decades, mainly from application of efficient tail-pipe cleaning technologies and from investment in alternative combustion technologies. In western country, a decline in urban SO_2 concentrations to an average concentration of ~10 ppb, was observed. This is not true in developing country, where coal burning is still widely employed for energy production.

2.1 CLASSIFICATION OF ATMOSPHERIC POLLUTANTS

Sulphur dioxide

Exposition to gaseous emissions is regulated according to the gas concentration and the period of exposition.
The **National Institute for Occupational Safety and Health (NIOSH)** defines two main parameters for exposition to harmful gases:

- **Immediately dangerous to life or health air concentration (IDLH)**, whose exposure leads to a "condition posing an immediate threat to life or health or a conditions that pose an immediate threat of severe exposure to contaminants, which are likely to have adverse cumulative or delayed effects on health".
- **Recommended exposure limit (REL)** which is reported both as time-weighted average (TWA) concentration for up to a 10-hour workday during a 40-hour workweek and as short-term exposure limit (STEL) a 15-minute TWA exposure that should not be exceeded at any time during a workday.

SO_2 is characterized by an IDLH of **100 ppm**, a TWA-REL of **2 ppm** (5 mg/m^3) and a ST-REL of **5 ppm** (13 mg/m^3).

2.1 CLASSIFICATION OF ATMOSPHERIC POLLUTANTS

Nitrogen oxides (NO_x)

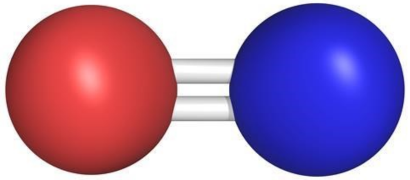
Nitrogen oxides are acid gases and ozone precursors.

The two principal oxides of nitrogen are **nitric oxide (NO) and nitrogen dioxide (NO_2).** The directly emitted NO_2 (also known as primary NO_2) immediately influences the ambient concentration. However, the emitted NO eventually reacts with ozone (O_3) to form additional NO_2 (known as secondary NO_2), thereby increasing their effective human health concerns. The sum of these two is known as NO_x.

Despite their quite different physical properties, chemical affinities and environmental impacts, they are often lumped together. **Combustion always produces a mixture of NO_2 and NO**, although typically more than 90% of combustion NO_x production is in the form of NO. However, as the NO can all potentially be converted to NO_2, it is usual to express all of the NO_x as NO_2 when making mass emission estimates.

2.1 CLASSIFICATION OF ATMOSPHERIC POLLUTANTS

Nitric oxide (NO)



Nitric oxide is typically formed from thermal process and from fuels.

Thermal NO is formed from reactions between the nitrogen and oxygen in the air. This is highly endothermic, so that thermal NO production is at a maximum in the highest-temperature regions of a combustion chamber.

$$N_2 + O \rightarrow NO + N$$

$$N + O_2 \rightarrow NO + O$$

Fuel NO is formed from nitrogen in the fuel. Typically, fuel nitrogen contents are 0.5%–1.5% in oil and coal, and rather less in gas.

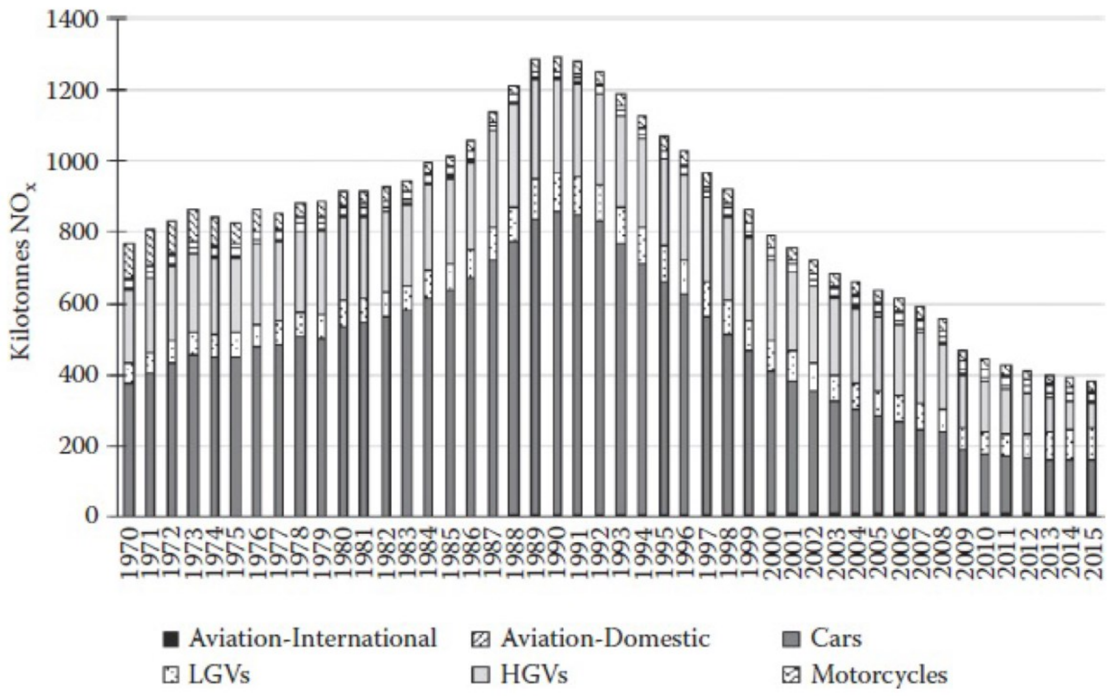
Nitric oxide is also emitted from soils, but it has proved harder to quantify the source strength. Nitrifying bacteria produce both nitric and nitrous oxide – anaerobic production of NO is thought to dominate overall. Estimation based on rather sparse data in UK suggest that soil production of NO may be equivalent to 2%–5% of the production from fuel combustion.

2.1 CLASSIFICATION OF ATMOSPHERIC POLLUTANTS

Nitric oxide (NO)

The figure shows the estimated historical UK NO_x emissions from different transport options between 1970 and 2015.

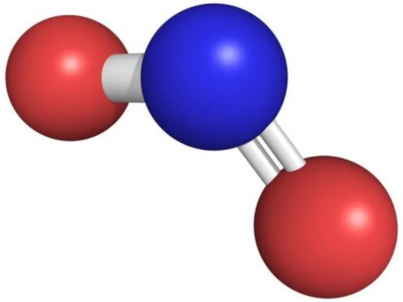
Road vehicle emissions rose steadily between 1970 and 1989. During this period emission from total petrol consumption, mainly by cars, rose by 106% from the 1970 level and emission from diesel consumption rose by 38%.



However, since 1989 there has been a steady decline in emissions due to the introduction of three-way catalytic converters on petrol cars and stricter regulations on truck emissions. By 2015, the cumulative emissions from all transport categories reached almost half their corresponding level in 1970.

2.1 CLASSIFICATION OF ATMOSPHERIC POLLUTANTS

Nitrogen dioxide (NO_2)



Nitrogen dioxide is a reddish-brown gas with a pungent odor mainly produced as secondary pollutant.

The nitric oxide from fossil fuel combustion reacts with ozone as follows:

$$NO + O_3 \rightarrow NO_2 + O_2$$

During daylight, the NO_2 absorbs blue and UV radiation <420 nm and **decomposes back to NO and O_3**, resulting in a photochemical equilibrium between the four gases. In rural areas, away from the NO sources, the NO_2 concentration is usually considerably higher than that of NO. In urban areas, the O_3 becomes depleted, and the balance moves in favor of NO. In atmosphere, NO_2 reacts with other molecules (e.g., water vapor), resulting in a lifetime of about a day.

As primary pollutants, NO_2 is emitted from the **burning of fuel**. NO_2 forms from emissions from cars, trucks and buses, power plants, and off-road equipment (in particular, from diesel engine).

2.1 CLASSIFICATION OF ATMOSPHERIC POLLUTANTS

Nitrogen dioxide (NO_2)

High levels of nitrogen dioxide affect both human health and environment.

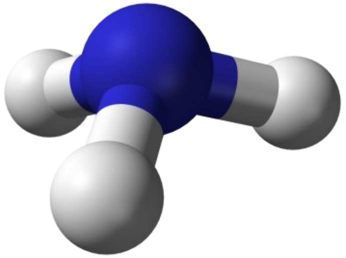
Breathing air with a high concentration of NO_2 can irritate airways in the human respiratory system. Such exposures over short periods can aggravate respiratory diseases, particularly asthma, leading to respiratory symptoms. NIOSH **IDLH is 13 ppm**, while the **ST-REL is 1 ppm**.

NO_2 and other NO_x interact with water, oxygen and other chemicals in the atmosphere to form acid rain. Acid rain harms sensitive ecosystems such as lakes and forests. High levels of nitrogen dioxide are also harmful to vegetation, damaging foliage, decreasing growth or reducing crop yields.

NO_2 is one of the main responsible for the so-called "**photochemical smog**" (to be discussed later).

2.1 CLASSIFICATION OF ATMOSPHERIC POLLUTANTS

Ammonia (NH_3)



Ammonia (NH_3) is a primary pollutant, often grouped with ammonium (NH_4). The three main sources of atmospheric ammonia are **livestock farming and animal wastes**, with emissions primarily due to the decomposition of urea from large animal wastes and uric acid from poultry wastes.

The overall total emission from these sources has increased with the intensification of agriculture, which has also changed the nature of the emissions from area to point sources. Emissions from housed and field animals are relatively steady in nature, while operations such as slurry and manure spreading result in more intense short-term emissions. **Globally, animal emissions are roughly equal to the combined emissions from other sources.**

Additional sources with small contributions to NH_3 emissions are from the industrial plants where ammonia and fertilizers are produced, human sweat and breath (around 0.2 kg person^{-1} a^{-1}) and wastes from domestic pets. However, these emissions are negligible compared to those resulting from agricultural activities.

NIOSH **IDLH is 300 ppm**, while **TWA-REL is 25 ppm** and **ST-REL is 35 ppm**.

2.1 CLASSIFICATION OF ATMOSPHERIC POLLUTANTS

Non-methane volatile organic compounds (NMVOCs)

Dealing with air pollution, the class of **non-methane volatile organic compounds** is usually labelled to include organic compounds different from methane, which is characterized by different emission sources and different effects in the atmosphere.

The category of **NMVOCs** includes different organic compounds. Hydrocarbons make up the majority, although smaller quantities of partially oxidized compounds such as alcohols, aldehydes, ketones and acids are also emitted. Altogether, **around 1000 different compounds** are known to be emitted.

Historically, NMVOCs are grouped under one label because the majority of them **display similar behavior in the atmosphere**. NMVOCs are mainly emitted as combustion products, as organic vapors from gasoline and solvent use. Within the NMVOCs, **hydrocarbons** have received the most attention for their role in ozone photochemistry (**BTEX** group).

NMVOCs can undergo many transformations in the atmosphere, most of which involve **reactions with** NO_3 or OH radicals, or with $\mathbf{O_3}$. During these reactions, the NMVOC may form more stable or soluble species, or may become converted from gas to particle or vice versa.

2.1 CLASSIFICATION OF ATMOSPHERIC POLLUTANTS

Non-methane volatile organic compounds (NMVOCs)

The major emission categories are **solvent use and industrial processes**. Substantial VOC emissions occur during processes such as painting (evaporation of solvents), oil production and refining, distribution of oil, use of aerosol sprays (both in the product and from the propellant), production of alcoholic drinks (breweries and distilleries) and arable farming.

Additional natural **NMVOC emissions occur from forests**. However, we know far less about biogenic VOC emissions than we do about the anthropogenic ones. Plants synthesize many organic molecules as an integral part of their biochemistry. Some of these VOCs are released to the atmosphere and are responsible for some **characteristic smells**: pine forests (*α-pinene* and β-*pinene)*, mint (monoterpenes, $C_{10}H_{16}$), and mown grass (multiple aldehydes and alcohols).

Once released, the VOCs are involved in a great multiplicity of oxidation reaction pathways, although there is much uncertainty about the details of these at present. In addition, hundreds of photoreactive organic species are present in the polluted atmosphere, each with a different reaction rate coefficient **contributing to formation of secondary gaseous and particulate pollutants.**

2.1 CLASSIFICATION OF ATMOSPHERIC POLLUTANTS

Persistent organic pollutants

Persistent organic pollutants (POPs) are a common label for a group of **organic compounds that are persistent in the environment**, with half-lives of **years in the soil** or sediment and **days in the atmosphere**. Hence concentrations may still be increasing decades after emissions have started.

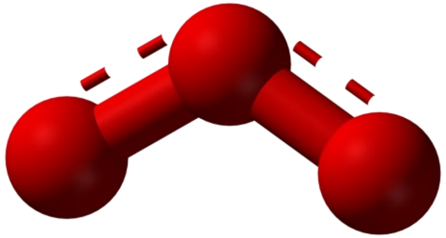
POPs include:

- **Dioxins and furans**, mainly due to incomplete combustion of plastics such as PVC.
- **Polychlorinated biphenyls**, mainly released from production in the electrical industry as dielectric insulating media.
- **Polycyclic aromatic hydrocarbons** (PAHs), formed by incomplete combustion of fossil fuels, such as occurs in vehicle engines (especially diesel), furnaces, coke ovens, bonfires and barbecues.

These substances accumulate in living organisms and pose a risk to health and environment. Due to their long lifetime, they can be transported by air, water or migratory species reaching regions where they have never been produced or used

2.1 CLASSIFICATION OF ATMOSPHERIC POLLUTANTS

Ozone (O_3)



Ozone is a gas composed of three atoms of oxygen. Ozone occurs both in the Earth's upper atmosphere and at ground level. Ozone can be good or bad, depending on where it is found.

The “**good” ozone** occurs naturally in the **stratosphere**, where it forms a protective layer shielding from the sun's harmful ultraviolet rays. This beneficial ozone has been partially destroyed by manmade chemicals, causing what is sometimes called a "hole in the ozone."

The “**bad” ozone** occurs as a secondary pollutant in the **troposphere** (commonly known as the tropospheric ozone), formed from photochemical disintegration of nitrogen oxides and VOCs.

Even at low concentrations, tropospheric ozone is considered to impair the ability of plants to produce and store food and is harmful for the human respiratory tract and the lungs. Ozone is the main component of **photochemical smog** (also known as “summer smog”) and has a background concentration of 10–20 ppb.

2.1 CLASSIFICATION OF ATMOSPHERIC POLLUTANTS

Ozone (O_3)

The major pathway for yielding tropospheric ozone is the result of photochemical disintegration of natural NOx in presence of UV photons:

$$\boldsymbol{NO_2 + h\nu \; (280\, nm < \lambda < 400\, nm) \; \rightarrow NO + O} \tag{2.13}$$

This is referred to as **NO_2 photolysis**. Photons with a wavelength greater than 400 nm do not have enough energy to break up the NO_2 molecule, while those having a wavelength shorter than 280 nm have been absorbed so effectively in the stratosphere that their tropospheric flux is negligible.

Then, ozone is formed combined **molecular oxygen and an additional molecule**, known as a *chaperone* (N_2 or O_2), which is required for energy absorption but doesn't take part in the reaction.

$$\begin{gathered}\boldsymbol{O + O_2 \leftrightarrow O_3^*} \\ \boldsymbol{O_3^* + M \rightarrow O_3 + M}\end{gathered} \tag{2.14}$$

The buffer gas atom or molecule M removes excess internal energy from the excited complex and thereby stabilizes it.

2.1 CLASSIFICATION OF ATMOSPHERIC POLLUTANTS

Ozone (O_3)

Under ambient conditions, the generated ozone reacts readily with NO, which oxidizes to form NO_2

$$NO + O_3 \rightarrow NO_2 + O_2 \tag{2.15}$$

In the **unpolluted atmosphere**, equilibrium between the above-mentioned three reactions gives low and **stable O3 concentrations**.

Additional ozone can be formed in the troposphere as a secondary pollutant when there are **increased concentrations of NO_2.**

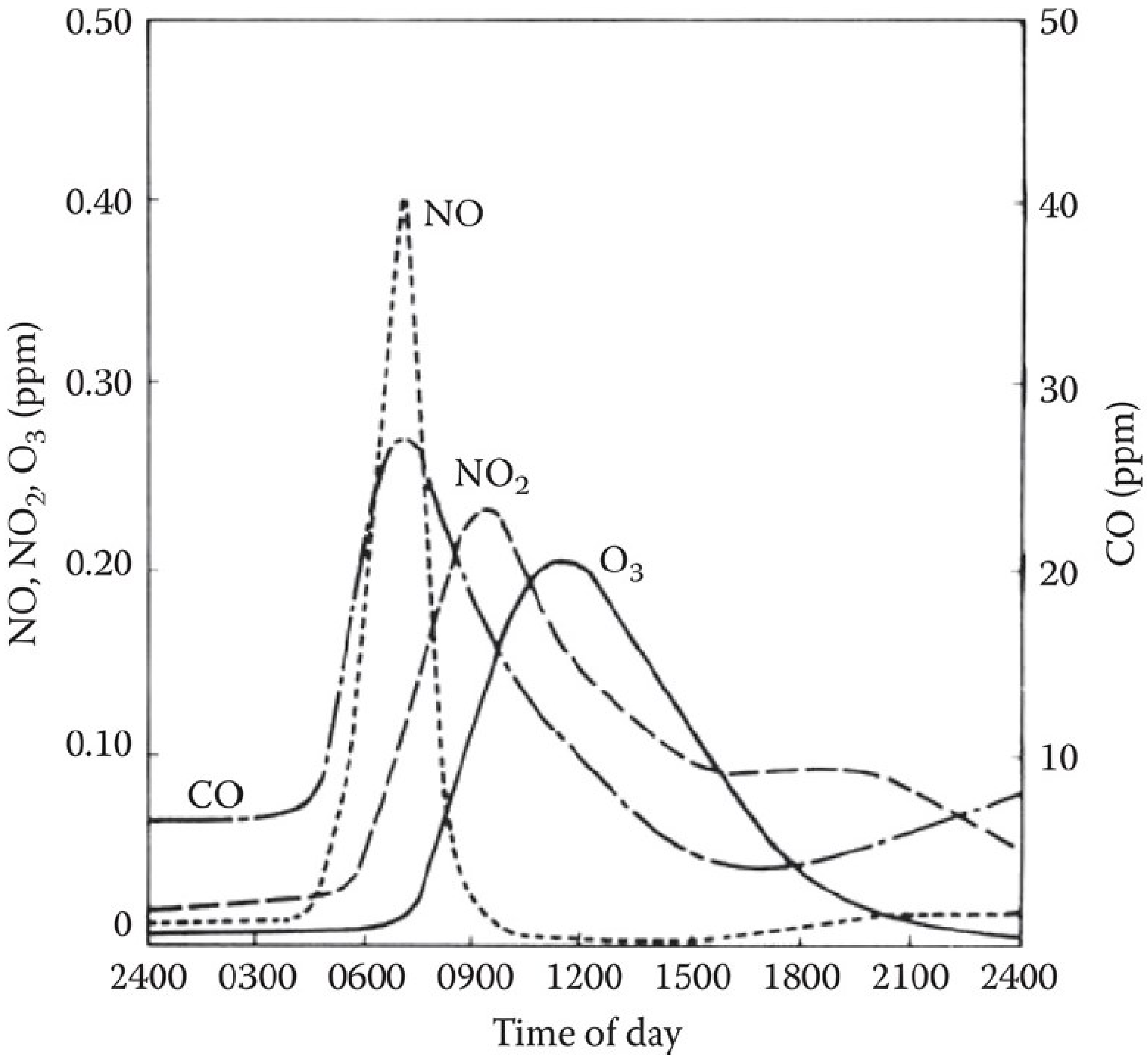
Other mechanisms to be considered for ozone production by means of NO_2 photolysis involve **organic radicals** (molecule characterized by at least one unpaired valence electron and thus strongly reactive). These molecules react easily with NO to form NO_2, depleting NO from Equation 2.15 thus shifting the equilibrium towards O_3 production. Then, the radicals are re-emitted in the atmosphere, thus even small concentrations can exert a powerful influence.

2.1 CLASSIFICATION OF ATMOSPHERIC POLLUTANTS

Ozone (O_3)

The requirement for UV photons and the short lifetime of O_3 molecules in the atmosphere combine to create a **characteristic diurnal cycle** of **ozone concentrations** in the lower troposphere.

The morning rush hour is marked by an increase in the primary emissions of NO and CO.



2.1 CLASSIFICATION OF ATMOSPHERIC POLLUTANTS

Particulate matters

Airborne particulates, also commonly known as **aerosols**, are an important environmental pollutant, being responsible for loss of visual range, soiling of surfaces and health effects on people.

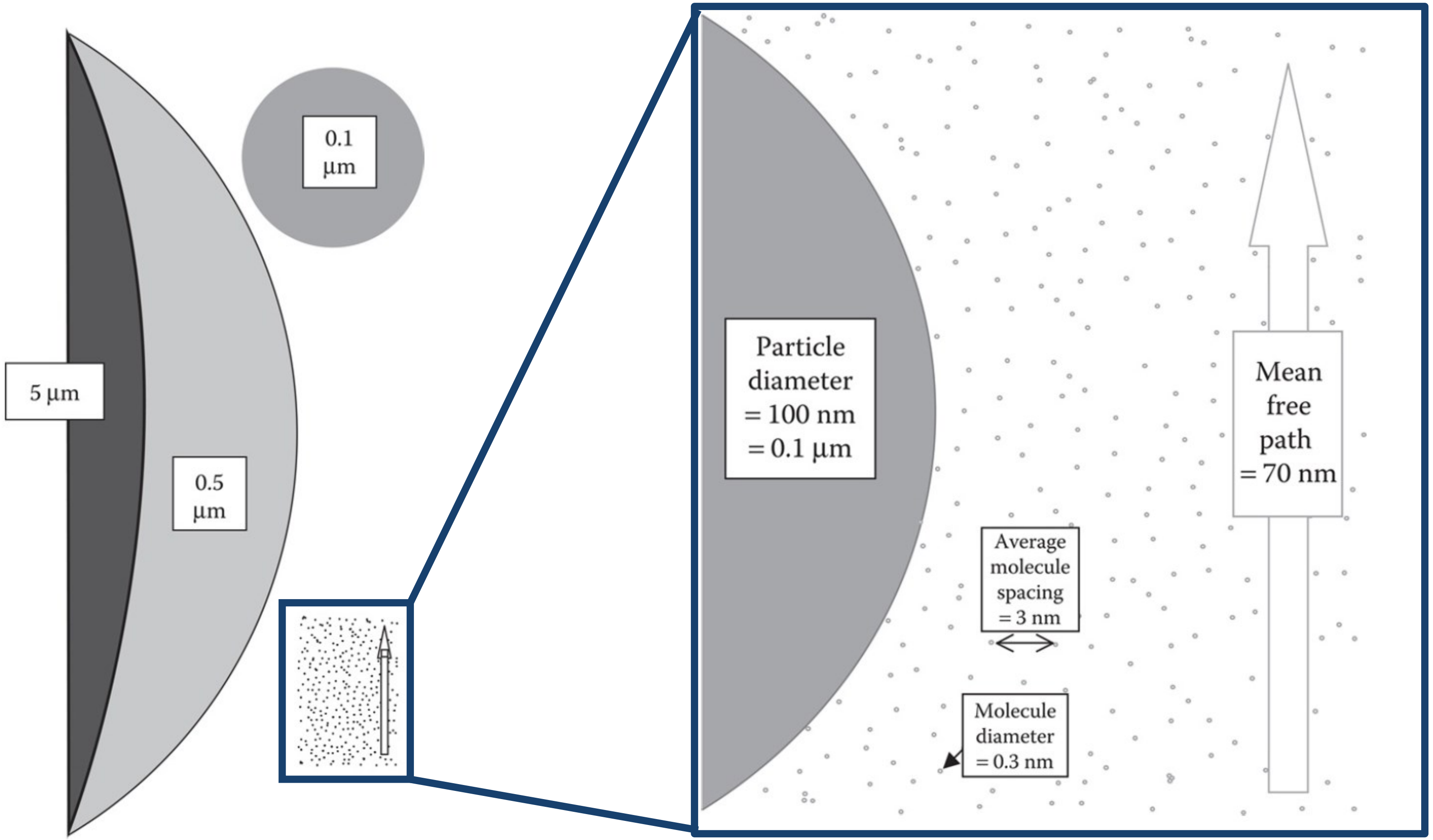
Atmospheric particles come in a very **wide range of size**, from clusters of molecules only a few tens of nanometers in diameter, up to several micrometers in diameter. They are maintained in suspension in air by atmospheric turbulence. Particles also have a very wide range of chemical composition and may act as the vectors for less volatile gases adsorbed to their surface.

Differently from gaseous pollutants, particles with less than 10 µm in diameter have **very low sedimentation speeds** under gravity and may **remain in the air for days** before eventually being washed out by rain or impacted out onto vegetation or buildings.

2.1 CLASSIFICATION OF ATMOSPHERIC POLLUTANTS

Particulate matters

Air molecules have an average diameter of 0.3 nm, with an average separation of 3 nm. The mean free path is estimated around 70 nm. These length scales are much shorter compared to those of particulate matters.



2.1 CLASSIFICATION OF ATMOSPHERIC POLLUTANTS

Particulate matters

Many different terms are used to describe the origins and characteristics of particles.

- **Particulate matter (PM)**: Sometimes used in this form as an abbreviation, but more commonly as PM10 or PM2.5. PM10 is the mass concentration of particulate matter (PM) from those particles that can pass through a size-selective inlet with 50% efficiency at an aerodynamic diameter of 10 µm. PM2.5 is the corresponding concentration for a cut diameter of 2.5 µm.

- **Fine particles**: In general, those smaller than a few µm. Often used synonymously with PM2.5.

- **Ultrafine particles or nanoparticles**: Those smaller than about 0.2 µm, for which the size is normally expressed in nm.

- **Aerosol**: Any solid or liquid particles of aerodynamic diameter ranging from submicron to several microns that remain suspended in the air. Common usage refers to the aerosols as the particulate component only and throughout this book the terms aerosols and particles have been used interchangeably to refer to airborne particulates.

2.1 CLASSIFICATION OF ATMOSPHERIC POLLUTANTS

Particulate matters

The primary sources of direct particle injection into air are **natural withering, sandstorms, smoke and soot from combustion sources**. However, the residence time of these particles can vary, largely depending on the particle size characteristics, compositions and the microenvironment where they are airborne.

The main **natural source** of particulate is erosion of soil by wind. These processes are intermittent and can generate highly episodic erosion fluxes, concentrated into short periods when strong winds over bare soil follow extended dry periods. Volcanoes, forest fires, spores and pollen also contribute to particulate emissions.

Several **anthropogenic sources** contribute to particles emission. **Combustion, melting, grinding, ploughing or spraying produce particles**. Diesel engines (cars and vans) emit around 5 g particles per liter of fuel, while this figure rises to around 12 g for heavier duty vehicles. In contrast, petrol-engined vehicles without catalysts emit only around 0.5 g.

2.1 CLASSIFICATION OF ATMOSPHERIC POLLUTANTS

Particulate matters

Natural sources of particulate contribute for 90% of total emissions. Nevertheless, anthropogenic particles have had a strong effect on the atmosphere, both because their production is concentrated in urban and heavily inhabited areas, and because they are mostly formed as small secondary particles with long atmospheric residence times.

Reducing ambient PM levels is difficult due to the large contribution of **secondary particles** formed in the atmosphere from **a range of gaseous pollutants.** The same summertime photochemical conditions that can generate ozone in the troposphere from pollutant precursors can also generate particles.

The main source of secondary particles is the **atmospheric oxidation of SO_2** by the hydroxyl radical to form sulphur trioxide (SO_3). The latter reacts with water vapor to form sulphuric acid (H_2SO_4) vapor, which in turn nucleates to form a sulphuric acid mist. As with gas phase photochemistry, the OH radical is recycled and small concentrations can exert a powerful influence. The other major player in secondary particle formation is **ammonia** (NH_3).

2.1 CLASSIFICATION OF ATMOSPHERIC POLLUTANTS

Particulate matters – black carbon

Black carbon (BC) is the most strongly light-absorbing component of particulate matter, mainly formed by incomplete combustion of fossil fuels, biofuels, and biomass. BC is emitted directly into the atmosphere in the form of fine particles (PM2.5).

BC is the most effective form of PM, by mass, **at absorbing solar energy**: per unit of mass in the atmosphere, BC can absorb a million times more energy than carbon dioxide. BC is a major component of "**soot**", a complex light-absorbing mixture that also contains some organic carbon.

The largest share of BC emissions come from mobile sources as especially **diesel engines and vehicles**. In fact, in 2005, 93% of all mobile source emissions came from diesels. However, BC emissions in the are projected to decline substantially by 2030, largely due to controls on new mobile diesel emissions.

Another source domestically is open biomass burning (including wildfires), although residential heating and industry also contribute.

2.1 CLASSIFICATION OF ATMOSPHERIC POLLUTANTS

What is smog?

Smog, a term coined by Des Voeux in 1905, is a mixture of smoke and fog (**sm[oke and f]og**).

Smog can be formed during either **summer or winter months** respectively arising due to oxidizing and reducing chemistry of airborne pollutants under adverse weather and seasonal conditions

Winter smog is formed by mixing of fog with pollutant smoke during cold periods. It forms when the ground cools rapidly, often on clear calm winter nights.

It is composed of NOx, SOx, O_3, smoke and other particulates trapped at ground level when a thin layer of the atmosphere near the Earth's surface becomes cooler than the air above it (meteorologically termed as a **temperature inversion**). The **atmospheric pollution** has been found to be significantly increased by such inversion that traps pollution close to the ground. Smog severity is often aggravated by stubble burning in neighboring agricultural areas.

2.1 CLASSIFICATION OF ATMOSPHERIC POLLUTANTS

Winter smog

In winter smog, smoke and particulates play a pivotal role. The smoke is mainly formed from the combustion of fuels. Normally, a hydrocarbon is burnt to produce carbon dioxide and water:

$$C_mH_n + O_{2(g)} \rightarrow CO_{2(g)} + H_2O_{(g)} \tag{2.16}$$

Smoke is also composed of unoxidized/reduced fuel particles and carbon monoxide and oxidized impurities, such as sulphur dioxide. The sulphur dioxide is soluble in water and so it dissolves in the water droplets of the fog. Other contaminants in the smoke, for example, iron (Fe) or manganese (Mn), then catalyze the reaction of dissolved sulphur dioxide to sulphuric acid:

$$\begin{gathered} SO_{2(g)} + H_2O_{(l)} \leftrightarrow H^+_{(aq)} + HSO_{3^-(aq)} \\ 2HSO_{3^-(aq)} + O_{2(aq)} \rightarrow 2H^+_{(aq)} + 2SO_{4^{2-}(aq)} \end{gathered} \tag{2.17}$$

2.1 CLASSIFICATION OF ATMOSPHERIC POLLUTANTS

Winter smog

The **sulphuric acid makes the smoke a very low pH**, which has many effects. One of these is to **increase the size of the water droplets** as it has a great affinity for water; this creates a thicker fog.

The addition of smoke to the fog to make smog can **increase the thickness of the fog** in two additional ways. First, the addition of material (the smoke) can increase thickness. Second, the more pollution in the fog, the more nuclei for the water droplets to condense around. This increases the number of small fog droplets.

All these factors, the collecting caused by light winds and valleys, the presence of sulphuric acid, the addition of material and the creation of more nuclei, help to make the fog thicker, which **helps the smog to persist through the daylight when normally the sun would cause the water droplets to evaporate.**

2.1 CLASSIFICATION OF ATMOSPHERIC POLLUTANTS

Great London Smog

The **Great London Smog of 1952**, also known as the Big Smoke, was a severe air pollution event that affected London in December 1952. A period of **cold weather**, combined with an **anticyclone and windless conditions**, collected airborne pollutants mostly from the use of coal to form a thick layer of smog over the city.

The smog lasted from Friday to Tuesday, 5–9 December 1952, and then quickly dispersed after a change in the weather. This represented a major event of the London's infamous *pea soupers,* which were regular occurrences starting from 1880. Pea soup fog (also known as a pea souper, black fog or killer fog) is a thick fog, characterized by yellowish, greenish or blackish color depending on the concentration of **soot particulates and sulphur dioxide**.

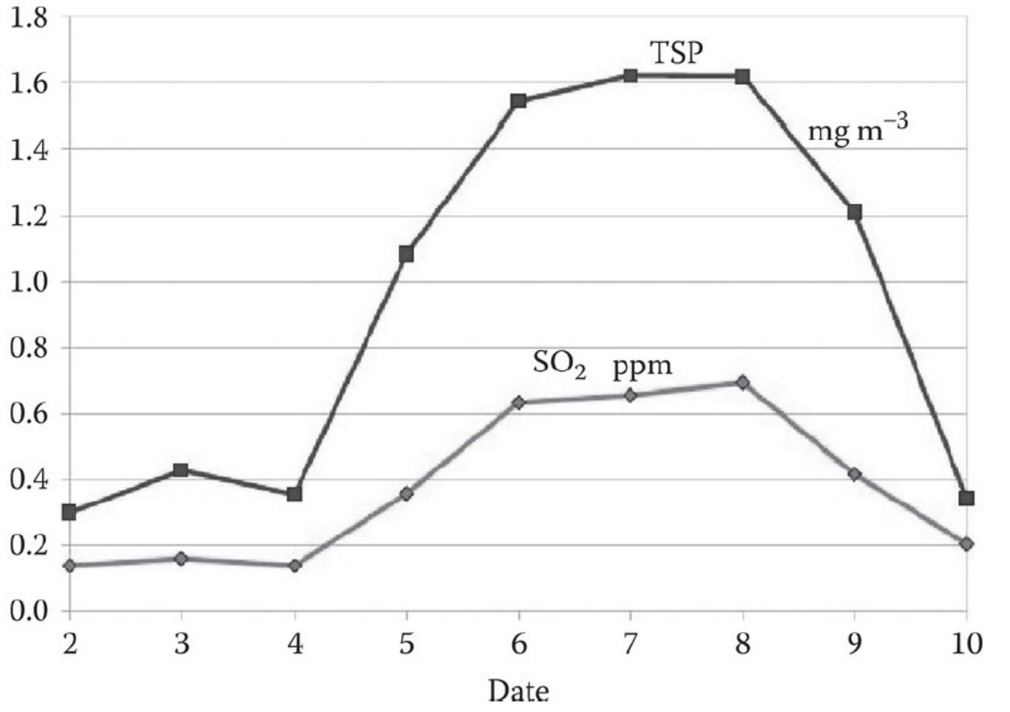
2.1 CLASSIFICATION OF ATMOSPHERIC POLLUTANTS

Great London Smog

Although it caused major disruption due to the effect on visibility and even penetrated indoor areas, it was not thought to be a significant event at the time. In the following weeks, medical reports estimated that 4,000 had died prematurely and 100,000 more were made ill because of the smog's effects on the human respiratory system. More recent research suggests that the number of fatalities was considerably higher, at around 12,000.

The extreme levels of fatalities and health effects during the London Smog incident could have resulted from a cocktail of harmful pollutants generated over that period, mainly **SO_2, CO and acid particulates and fumes.** Effects on the environment were mainly due to deposition of sulphuric acid generated by the high level of SO_2.

Following this events, in 1956 the British government ultimately passed the **Clean Air Act**, generally considered a major event in the history of environmentalism.



2.1 CLASSIFICATION OF ATMOSPHERIC POLLUTANTS

Photochemical smog

Summer smog (also known as **photochemical smog**) is another form of secondary pollution caused by chemical reactions in the exhaust fumes of cars in the presence of sunlight on warmer days.

Photochemical smog occurs in **warm weather and peaks around midday, whereas the winter smog occurs during early winter mornings**. Most important, **photochemical smog does not occur in the presence of fog** and represent a direct effect of air pollution.

The main visible effect is the **yellowish/brownish haze** that can be seen above many cities. The brown tinge is caused by very small liquid and solid particles scattering the light.

2.1 CLASSIFICATION OF ATMOSPHERIC POLLUTANTS

Photochemical smog

The exact **formation mechanisms is complex**, involving reactions between hundreds of different hydrocarbons, radicals, NOx and VOCs. These primary pollutants recombine due to sunlight in a series of chemical reactions to create secondary pollutants as ozone and other hazardous substances as **peroxyacetyl nitrate (PAN).**

O_3 formation by means of NOx was described in Eqs. 2.13-2.14, while chemical products as PAN are formed by the **interaction among NO_2 and different VOCs.** Similarly, oxygenated organic and inorganic compounds react with nitric oxide to produce more nitrogen oxides.

In these last two reactions, **VOCs play a pivotal role**. Ozone is normally consumed by nitric oxide (see Eq. 2.15). However, when VOCs are present, nitric oxide and nitrogen dioxide are consumed allowing the build up of ground level ozone.

Hence, a typical **summer smog is a mixture of NO, NO_2 and O_3** in concentrations and proportions that depend not only on the source strengths of the precursors but also on the availability of the reactive components, mixing conditions, life histories and weather conditions.

2.2 SAMPLING PROCEDURES AND ANALYSIS

Sampling philosophy

In setting out to monitor air pollution , **the aims must be clearly identified** before an effective sampling strategy can be designed.

Which characteristics of the target gases, particles or dissolved pollutants **are of greatest importance**?

It may be that an overall picture of the behavior of a particular pollutant is required, **either in time or in space,** or there may be particular times of day or areas of the country that are of special importance. Both time and space scales need to be considered.

For characterization of a pollutant over time, a decision must be made on whether the **statistical distribution of concentration over time is required , or some long-time integrated average value**.

2.2 SAMPLING PROCEDURES AND ANALYSIS

Sampling philosophy

The **great temporal variability of all forms of air pollution** makes it very difficult to design sampling strategies based on non-continuous measurements, because of the very large contribution to the average concentration of a few 'extreme' events.

In most cases, therefore, some form of **continuous sampling is applied**, often with relatively long integration times, that includes all the 'extreme' events but gives little information about the magnitude of a short-lived episode of high concentration.

Different strategies may be employed, depending on the inherent variability at the monitoring site. A site close to a primary source of pollution, for example, would require greater time resolution in order to characterize completely the statistical distribution of gas concentrations than would a site remote from local sources, where variations have been smoothed to some extent during the time taken for the pollutant to reach the site.

2.2 SAMPLING PROCEDURES AND ANALYSIS

Sampling philosophy

Although much of the temporal variability in pollutant concentrations in air can be encompassed by time integration, such an approach is not easily applied to the problem of **spatial heterogeneity**. The distribution of pollutants over the landscape is a **complex function of sources, weather patterns and chemistry**.

Continuous monitoring of pollutants in air is expensive, so that high-density networks of measurements are usually impracticable. Ideally, a stratified sampling regime should be employed, within the constraints of suitable sampling locations, to make **representative measurements at a well-defined range of sites** that cover the major variables in the landscape (elevation, exposure, proximity to sources, land use, etc.).

In practice, however, the constraints on the availability of electrical power and access to operators determine to a large extent where measurements are made. As a result, **all monitoring networks require some form of spatial interpolation or extrapolation to estimate concentrations** between monitoring sites, and a large effort has been made in finding the best ways of achieving this.

2.2 SAMPLING PROCEDURES AND ANALYSIS

Sampling philosophy

Inevitably, however, **simple interpolation is not always appropriate**.

For example, the O_3 concentrations estimation at the top of a mountain from measurements made in the valleys on either side need some form of **model to make reasonable predictions**.

Such models may be based on fundamental processes known to influence pollutant concentrations or may be partly or wholly empirical in nature, relying on the application of relationships derived from other places where measurements have been able to show the spatial variation of concentration with altitude.

The processes of **interpolation and extrapolation**, and the use of process-based models, can produce very detailed maps of the spatial distribution of a pollutant, but it must be remembered that these maps are no more than the **best available estimate of concentrations at given point**.

2.2 SAMPLING PROCEDURES AND ANALYSIS

Gas sampling methods

Most measurement methods require the pollutant, or the air containing the pollutant, to be sampled. The purpose of sampling is to get some air to the analyzer without changing the concentration of the gas to be measured, and in a condition that the analyzer can accept.

We can divide the available methods into three categories:

- **pumped systems**
- **pre-concentration**
- **grab samplers**

There are also combinations of these.

2.2 SAMPLING PROCEDURES AND ANALYSIS

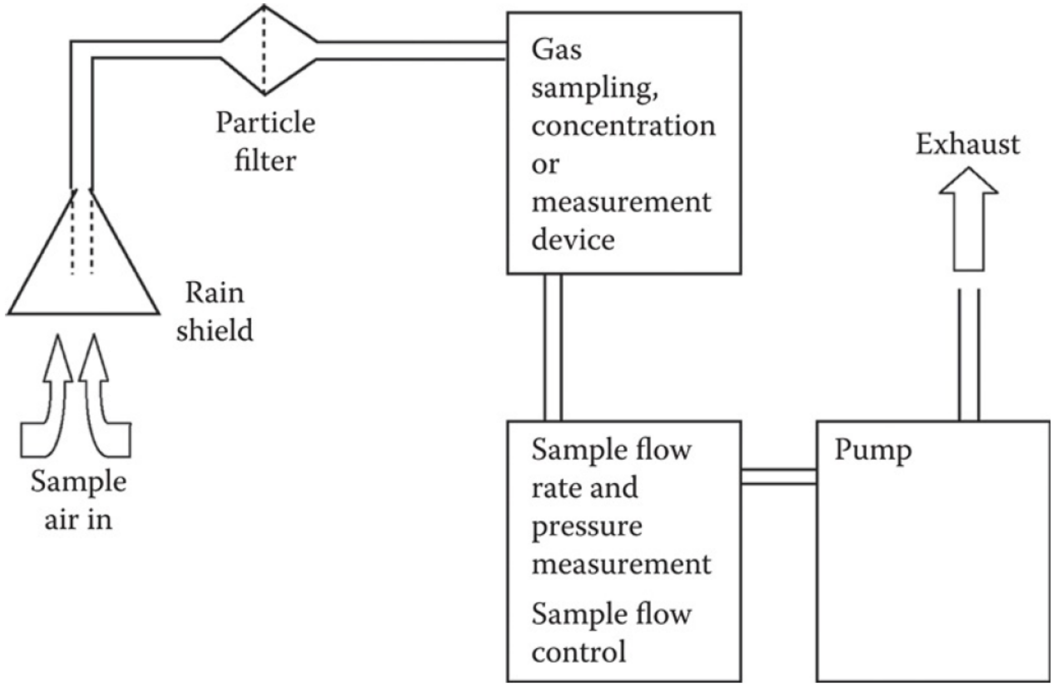
Pumped systems

In pumped systems, the sample is drawn continuously from the ambient air and delivered directly to the analyzer.

Sampling the gas will involve the **inlet** itself (normally shrouded to protect the sensor), **tubing**, the **analyzer**, **flow measurement** and a **pump**.

This method allows for a **continuous-sampling** of the gas target, thus ideally representing the best methodology for environmental monitoring.

However, several potential sources of error in this combination may occur.



2.2 SAMPLING PROCEDURES AND ANALYSIS

Pumped systems

When designing a monitoring platform based on pumped system is crucial to consider the influence of interferent factors.

- **There are always particles in the air.** Gas species other than the target one may produce spurious signals (cross-sensitivity), or they can decompose and release a measurable gas concentration. The particles are therefore usually trapped on a filter close to the sample inlet. However, the filter selection should avoid additional interferences or undesired absorption.
- **Air sample can be adsorbed in transit.** This effect varies with the gas and the tubing material. The contact time is also important here as samples taken down long lengths of tube must have high flow rates to minimize the residence time.
- **The gas of interest may react with other species.** For example, O_3 and NO and NO_2 are in a dynamic photochemical equilibrium in the atmosphere. As soon as they are sampled, the conditions are changed, and the concentrations will start to change in consequence.

2.2 SAMPLING PROCEDURES AND ANALYSIS

Pumped systems

- **Pumped systems operate under atmospheric pressure.** The pump will usually come last in the flow path to avoid interfering with the air sample before measurement. Hence there is a risk of leaks occurring, in which air from other locations, having a different gas concentration to that of the original sample, is drawn into the sample line and delivered to the analyzer.
- **Ambient air always contains water vapor**. This means that reaction with H2O should always be considered, as well as potential interferences from water vapor itself. Moreover, if the sampling system allows the air to cool below the dewpoint temperature, then the vapor will eventually become saturated, and the excess water will condense out in the sample lines. One possible solution is to remove some of the water vapour by passing the air sample through an adsorbent such as silica gel. This works well only for relatively unreactive gases present at ppm concentrations. An alternative, but usually more complex solution is to heat the sample lines so that the air is about 10°C above ambient temperature.

2.2 SAMPLING PROCEDURES AND ANALYSIS

Preconcentration

Several detection techniques are not feasible for continuous monitoring, **thus the sample are collected and to be then quantitatively analyzed in the laboratory.**

The main preconcentration methods include:

- **Absorption**
- **Adsorption**

These methods are characterized by different collection efficiency, strongly dependent on the target analytes and on the sample's composition.

2.2 SAMPLING PROCEDURES AND ANALYSIS

Preconcentration - absorption

The common theme is that a specific chemical reaction between the gas and captive absorbing molecules retains all the gas from the sample air.

There are many different practical arrangements:

- **Bubblers.** The sample is bubbled through an absorbing chemical solution; the gas is absorbed by the solution which is selected to produce irreversible chemical reactions which prevents it from being subsequently desorbed.

- **Impregnated filters.** The sample is drawn through a filter paper that has been impregnated with a chemical that reacts with the gas. Multiple filters are typically used: the first is a high-efficiency untreated particle prefilter reducing interference from other particles, the second and third filters might be impregnated with two different chemicals to absorb two different gases.

2.2 SAMPLING PROCEDURES AND ANALYSIS

Preconcentration - absorption

- **Passive samplers**. Passive samplers rely on diffusion of the sample rather than pumped flow. This device are usually cheap and do not require electrical power, so they are useful for large-area surveys. On the other hand, these devices have a long acquisition time and provide average concentrations over days to weeks. Therefore, the sample is then to be analyzed to give the average concentration during the period. In the simplest type of diffusion tube, a linear molecular diffusion gradient is set up between the atmospheric concentration at the lower end of an inert plastic tube and zero concentration at an absorbent-coated substrate at the upper end. The rate of diffusion depends only on the near-constant molecular diffusivity of the gas, as the long as turbulent transport is avoided.

- **Denuder tubes.** The air sample is drawn through a hollow tube, whose inside walls are coated with an absorbent for the gas. Operating in laminar flow (according to tube geometry), the molecular diffusivity of the gas is thousands of times greater than the Brownian diffusivity of the particles, so that the gas moves to the walls quicker. The length of the tube is selected so that when the air leaves the tube most of the gas has been absorbed and most of the particles remain suspended.

2.2 SAMPLING PROCEDURES AND ANALYSIS

Preconcentration - adsorption

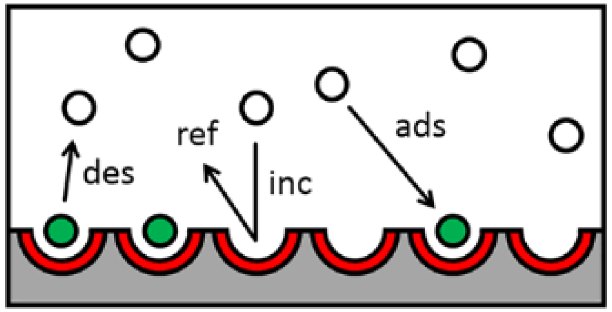
Adsorption is a surface process that leads to transfer of a molecule from a fluid bulk to solid surface. This can occur because of **physical forces or by chemical bonds**. Usually it is **reversible**, and the reverse process is called desorption. Then it is responsible not only for a subtraction of substances but also for release.

The target gas molecules are bound to the surfaces of a solid collecting substrate and subsequently they are stripped off, typically by heating the substrate itself or by solvent extraction. Then, the molecules delivered into the selected gas analysis system.

In most of the cases, this process is described at the equilibrium by means of some equations that **quantify the amount of substance attached on the surface given the concentration in the fluid**. These equations are called isotherms because of the dependence of their parameters on the temperature, which is one of the most important environmental factors affecting adsorption. The most famous are the Langmuir and the Freundlich equations.

2.2 SAMPLING PROCEDURES AND ANALYSIS

Preconcentration - adsorption



Langmuir model described gas adsorption at a solid interface as bearing a mechanistic similarity to gas-phase condensation at a liquid surface. As gas molecules strike the surface, they are held near the surface by attractive intermolecular forces for some short but finite time until leaving into the bulk gas phase again. This is a **purely kinetic view of adsorption**, linking the **equilibrium site occupancy, θ**, and the **pressure of the gas phase, P**. Langmuir model relies on three fundamental assumptions:

i. The rate of incidence of the molecules in a bulk gas phase on a unit area of adsorbent surface, r_{inc}, is proportional to the pressure at constant temperature via the kinetic theory of gases.

ii. The rate of adsorption, r_{ads} , depends not only on the rate of incidence of molecules on the surface, r_{inc} , but also on the probability of adsorption, p_{ads} , and the probability of incidence at a vacant adsorption site, p_{vac} .

iii. The rate of desorption is equal to the rate of desorption at maximum surface coverage, $r_{des,sat}$, multiplied by the fractional occupancy of the surface sites by adsorbed molecules, θ (thereby neglecting any role of adsorbate−adsorbate interactions)

2.2 SAMPLING PROCEDURES AND ANALYSIS

Preconcentration - adsorption

These three assumptions can also be summarized by stating that both the gas phase and adsorbed phase behave ideally, i.e., with no intermolecular interactions, and that every binding site is identical. Combined, they yield the following expression for the equilibrium fractional occupancy of adsorption sites under a gas phase at pressure P:

$$\boldsymbol{\theta = \frac{r_{inc}p_{ads}}{r_{des,sat} + r_{inc}p_{ads}} = \frac{KP}{1+KP}} \tag{2.18}$$

The Langmuir constant, K, is independent of pressure and hence depends only on temperature. When the temperature is invariant, the isotherm can be measured and K can be experimentally determined, which from this kinetic model is defined as:

$$\boldsymbol{K = \frac{1}{\sqrt{2\pi mRT}}\frac{p_{ads}}{r_{des,sat}}} \tag{2.19}$$

The Langmuir constant has units of inverse pressure. It is useful to recognize that the surface is precisely half-occupied at the pressure corresponding to K^{-1} and so represents a “characteristic inverse pressure of adsorption.”

2.2 SAMPLING PROCEDURES AND ANALYSIS

Grab sampling

For various reasons, it may be impracticable to either measure the concentration continuously or extract the pollutant gas from an air sample for subsequent analysis. In these cases, the alternative technique is to **capture a sample of the air itself** and take it back to the laboratory. There are several different ways in which this is put into practice:

- **Evacuated bottles**: A stainless steel, glass or inert plastic bottle is evacuated in the laboratory and sealed securely. The bottle is opened in the ambient air and fills with the sample.
- **Syringes**: The plunger on an empty syringe is pulled out, drawing in a sample of ambient air.
- **Bags**: A bag made of an inert material is filled by pumping the air sample into it. The major disadvantage of this method is that the air must pass through the pump before entering the bag, so that reactive gases may be corrupted. In order to avoid this limitation, the bag can be held inside a bottle. The space outside the collapsed bag can then be evacuated by pumping out the air. This draws an air sample into the bag. The sample cycle can be repeated many times.

2.2 SAMPLING PROCEDURES AND ANALYSIS

Grab sampling

All of these techniques need very careful assessment and management to be successful.

The bags and bottles need to be made of **inert material** and scrupulously clean and leak-free. For some applications, preconditioning of the sample holder with high concentrations of the pollutant gas may be necessary to reduce uptake of the gas from subsequent samples.

The samples **must be returned to the laboratory as rapidly as possible for analysis**, before they **degrade**. By their nature, grab samples tend to be used at remote sites to which a sampling expedition is a major undertaking. If any of these quality assurance aspects is insecure, it may only be discovered that the samples are worthless after returning home.

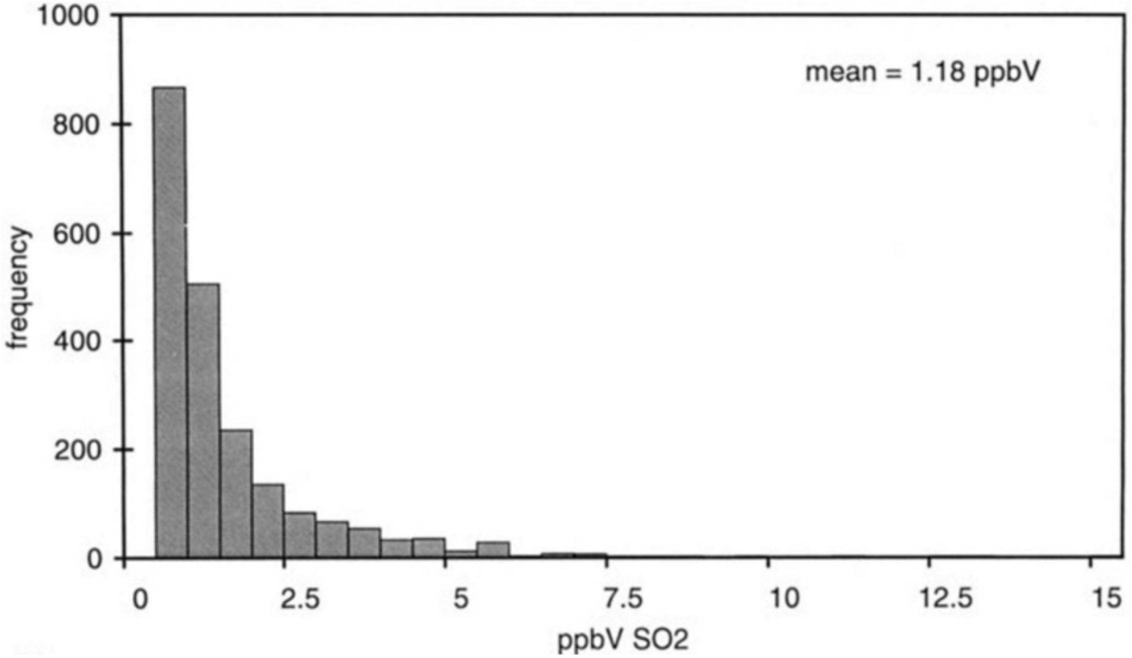
The risks can be minimized by a careful **validation program**, i.e., a comparison of concurrent real-time and grab samples, and sequential analysis of stored samples over a period of time.

2.2 SAMPLING PROCEDURES AND ANALYSIS

The importance of sampling and averaging

The average concentration of a pollutant gas can be described in terms of the **arithmetic mean, measured over days, months or years**. Tue arithmetic mean alone, however, tells very little about the variation that is observed about the mean value, which may have implications for potential harmful effects.

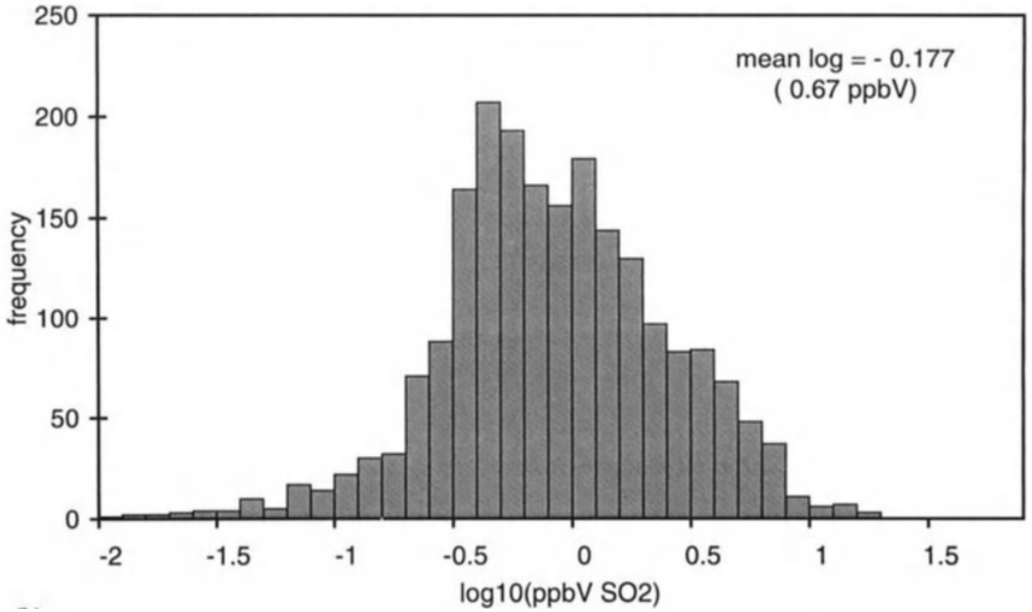
A few hours during a year at very high concentrations may not show in an annual mean value but may cause acute damage to vegetation. For many primary pollutants, the statistical distribution of gas concentrations is characterized by fairly low concentrations for most of the time, with occasional large values.
This kind of measurements typically point out a **skewed distribution**.



2.2 SAMPLING PROCEDURES AND ANALYSIS

The importance of sampling and averaging

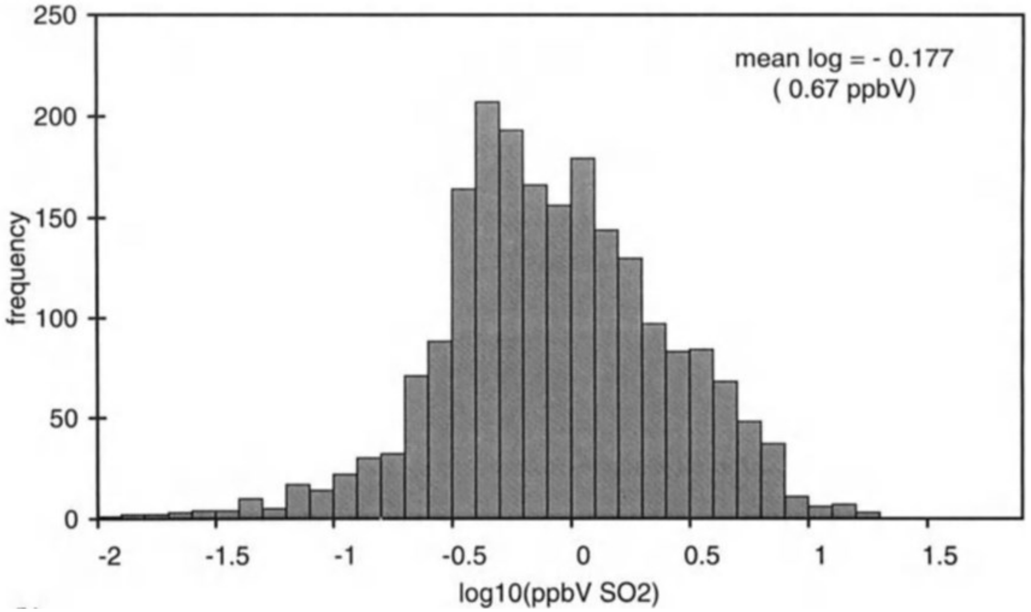
This pattern is usually well described by a **log-normal distribution**, i.e. the distribution of the logarithm of the pollutant concentrations has a symmetrical normal distribution. The skewed distribution becomes symmetrical after log-transformation. The **mean and standard deviation** of the log-transformed data can be used to predict the proportion of time that a particular threshold concentration is exceeded.

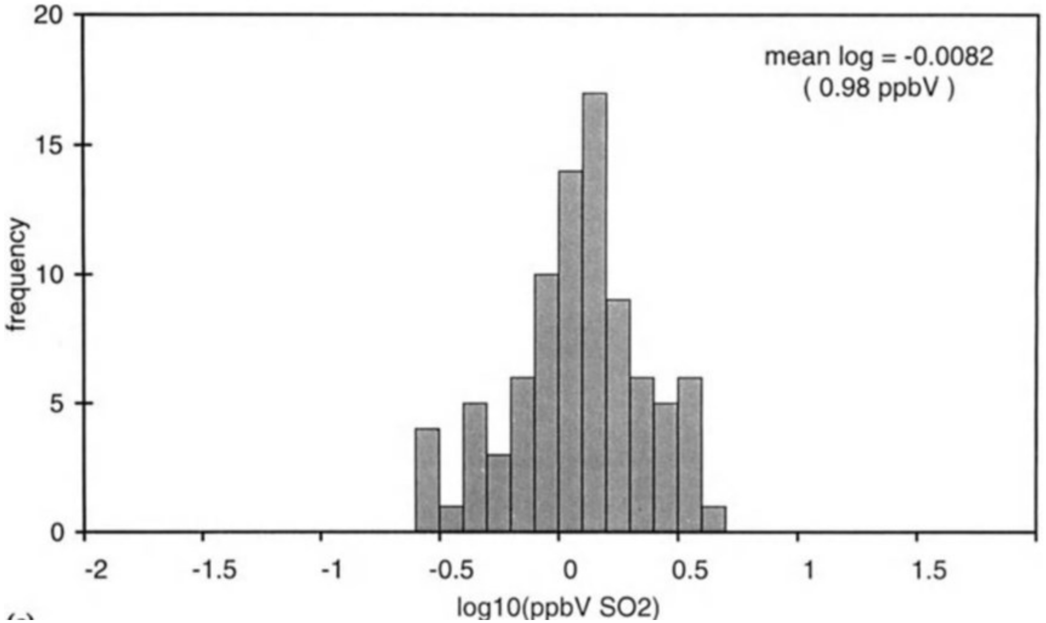


2.2 SAMPLING PROCEDURES AND ANALYSIS

The importance of sampling and averaging

Because concentration data have a **skewed distribution, time averaging loses information on the scale** of the variation. The daily mean concentrations, formed by simple arithmetic integration of the hourly data in the example above, also have a skewed distribution, but one which is less skewed, and with a larger geometric mean than hourly data.





2.3 GREENHOUSE EFFECT AND GLOBAL WARMING

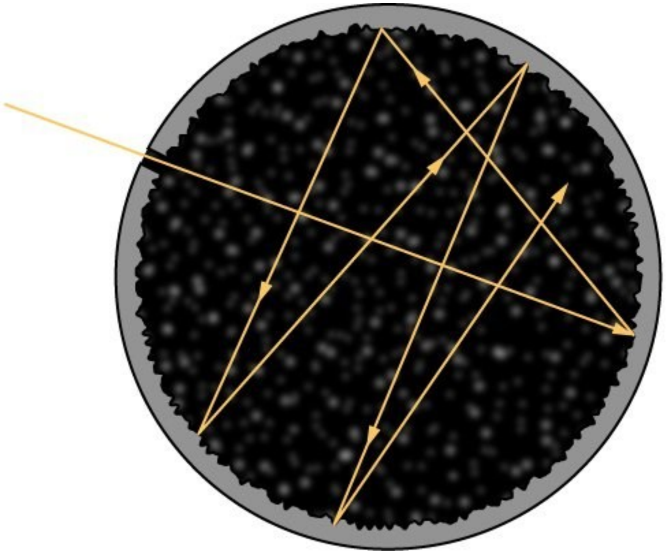
Blackbody radiation

A **blackbody** is an ideal body, which absorbs all incoming radiation, acquires a certain **temperature T** and re-emits its radiation.

Blackbody emission spectrum can be calculated starting from **Planck's law**:

$$I_\lambda d\lambda = \frac{2\pi hc^2}{\lambda^5}\frac{1}{e^{hc/\lambda kT}-1}\,d\lambda \qquad (2.20)$$

Where $I_\lambda d\lambda$ is the radiation energy with wavelengths between λ and $\lambda+d\lambda$ passing a square meter per second [Wm^{-2}]. Therefore, the intensity I_λ has the dimension of [$Wm^{-2}\ \mu m^{-1}$] or [$Wm^{-2}\ nm^{-1}$]



2.3 GREENHOUSE EFFECT AND GLOBAL WARMING

Blackbody radiation

The **peak wavelength** of blackbody radiation spectrum can be correlated to its temperature by means of **Wien's displacement law**:

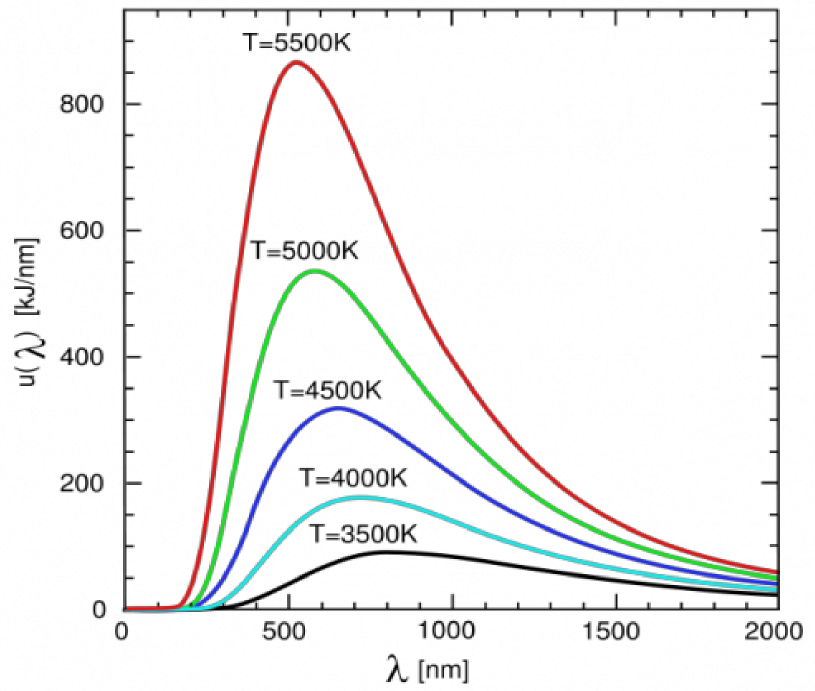
$$\lambda_{peak} T = b \tag{2.21}$$

Where ***b*** is the Wien's displacement constant, equal to 2.898×10^{-3} m·K

The maximum of the emitted radiation distribution depends on the temperature of the blackbody. The intensity emitted in the whole spectrum at a fixed temperature T can be obtained by integrating Eq. (2.20), resulting in:

$$I(T) = \sigma T^4 \; [W m^{-2}] \tag{2.22}$$

Which is known as the **Stefan–Boltzmann's law**, and σ is the Stefan–Boltzmann constant, independent of the blackbody material.



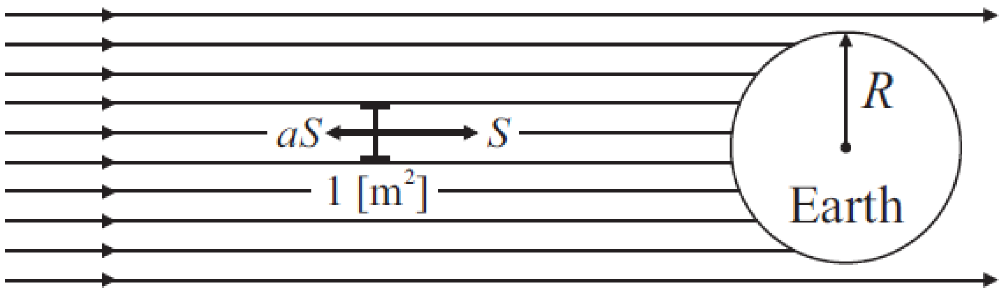
2.3 GREENHOUSE EFFECT AND GLOBAL WARMING

The Greenhouse Effect

Blackbody radiation can be used to calculate Earth temperature and the influence of **greenhouse effect** on it. In the simplest calculation the temperature of the earth is determined by the solar radiation coming in and the infrared (IR) radiation leaving the earth, or **energy in = energy out**.

The amount of radiation entering the atmosphere per [m^2] perpendicular to the radiation is called ***S***, the total **solar irradiance** or solar constant in units [Wm^{-2}].

Looking at the earth from outer space it appears that a fraction ***a***, called the **albedo**, is reflected back. Therefore, an amount $(1 - a)S$ penetrates down to the surface. With earth radius R, the incident energy on Earth is $(1 - a)S\pi R^2$.



2.3 GREENHOUSE EFFECT AND GLOBAL WARMING

The Greenhouse Effect

It is possible to approximate the Earth as a **blackbody with temperature T**. According to Stefan–Boltzmann's law, it will emit an intensity $I = \sigma T^4 \, [Wm^{-2}]$, thus the total outgoing radiation from the earth then becomes $\sigma T^4 \times 4\pi R^2$. Balancing the input and output energy, we have:

$$(1-a)S \times \pi R^2 = \sigma T^4 \times 4\pi R^2 \tag{2.23}$$

Thus resulting in:

$$(1-a)\frac{S}{4} = \sigma T^4 \tag{2.24}$$

Experimental estimated value of the albedo is about *a* = 0.30. Substituting this value in Eq. 2.24, results **T = 255 K**, which is way below the true average **earth surface temperature of 15°C = 288 K**.

The difference of 33°C is due to the **greenhouse effect**, for which the Earth's atmosphere is responsible.

2.3 GREENHOUSE EFFECT AND GLOBAL WARMING

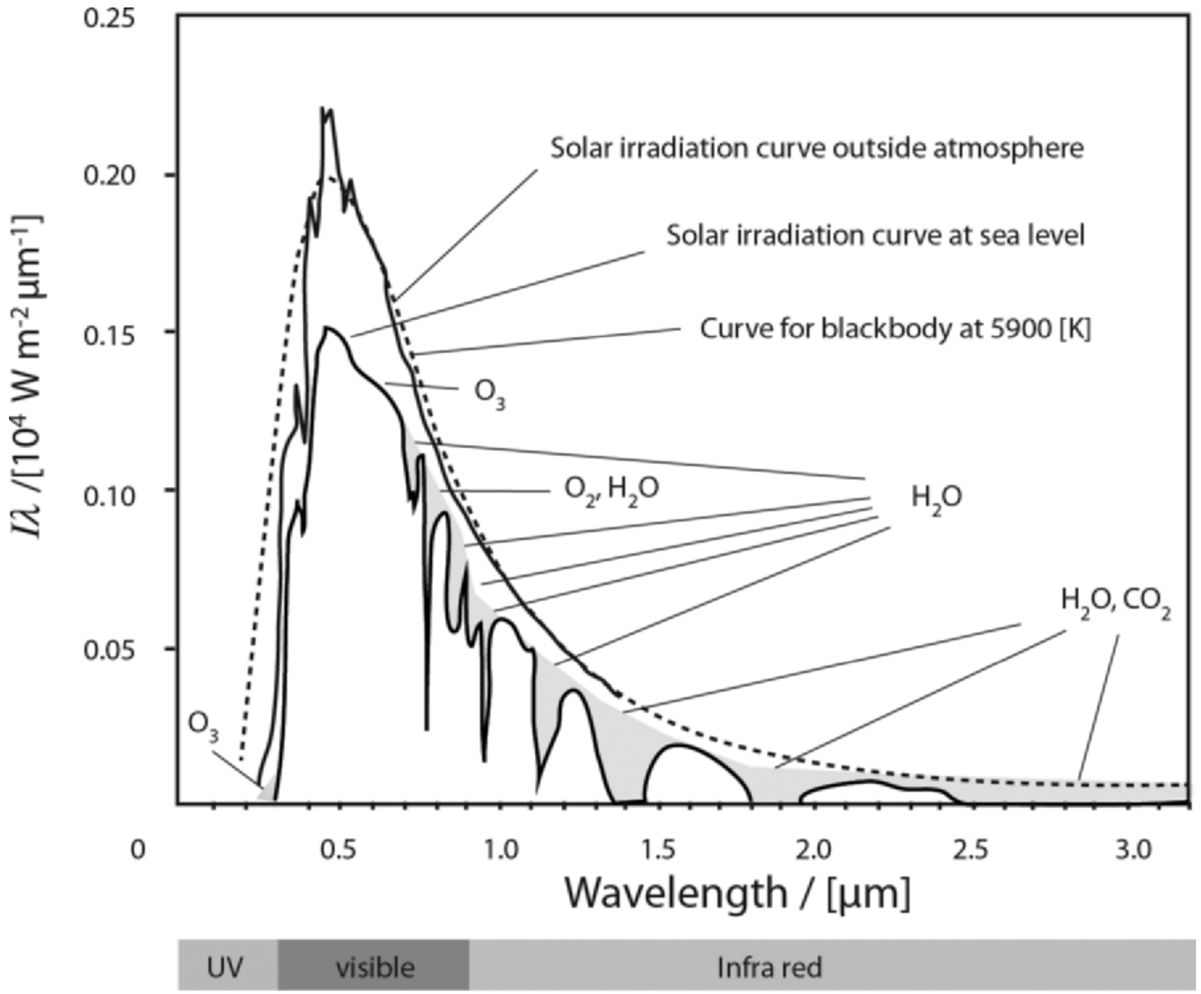
Emission spectrum of the Sun

The Sun can be also approximated to a blackbody.

In figure, both the emission spectrum of the sun is shown as it enters the top of the atmosphere, and as it is observed at sea level.

The difference is due to the **absorption of the solar light in the earth's atmosphere**.

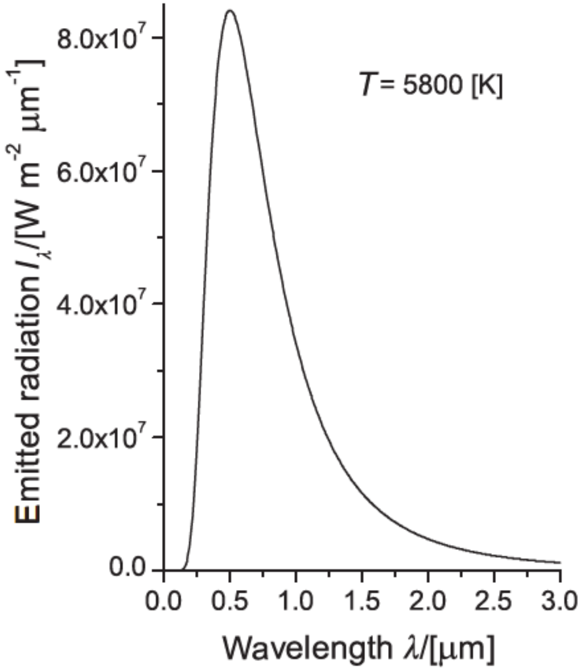
The gases mainly responsible for this absorption are indicated: CO_2, H_2O, O_2 and O_3.

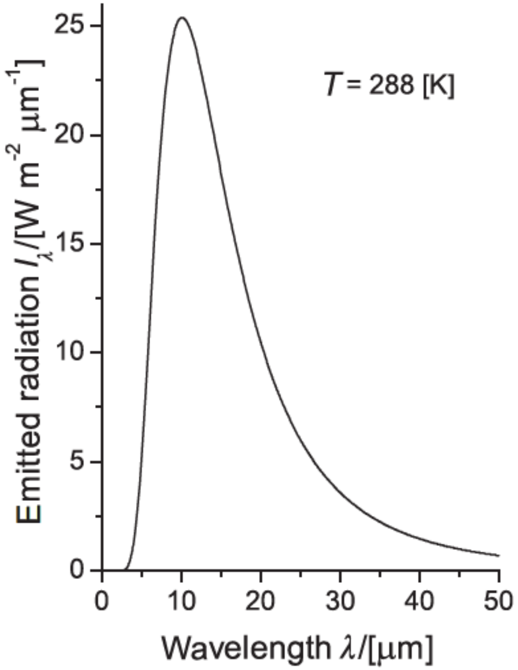


2.3 GREENHOUSE EFFECT AND GLOBAL WARMING

Thermal wavelengths

The emission **temperature of sun is around 5800 K and 5900 K**, and it’s peaked around **0.5 µm (visible spectrum)**. At temperatures such as we experience on Earth, the black-body radiation has peak intensity in the far infrared, way out of the visible region. At **T = 288 K, the peak wavelength is ~10 µm**. Bodies at temperatures of 373 K (100 °C) still do not emit appreciably in the visible part of the spectrum. We cannot see, but ‘feel’ the IR radiation when we put our hands near a hot-water bottle.





2.3 GREENHOUSE EFFECT AND GLOBAL WARMING

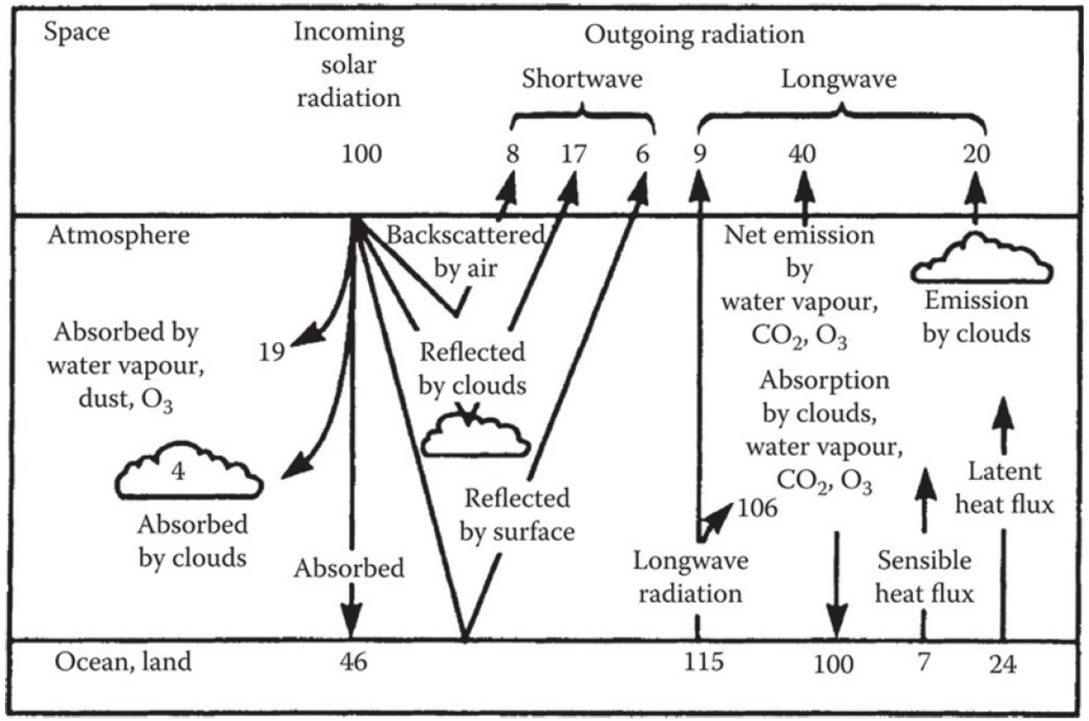
The Radiation Balance and the Greenhouse Effect

Earth receives all its initial energy supply as shortwave radiation from the Sun.

The Earth **reflects** some of this energy, **absorbs** the rest, and then **reradiates** it into space in the longwave form. As the Earth moves through the almost perfect vacuum of space, there can be no energy transfer by conduction or convection, and **the sum of shortwave and longwave energy leaving the planet must balance the shortwave input** in order to maintain **thermal equilibrium**.

For the planet as a whole, the equilibrium radiative temperature (i.e. the temperature required to reradiate all the energy received from the sun) at the outside of the atmosphere is 255 K (–18°C).

If the atmosphere was perfectly transparent to all wavelengths of radiation, then it could neither absorb nor emit radiation, and **the average temperature at the surface would also be close to 255 K.**



2.3 GREENHOUSE EFFECT AND GLOBAL WARMING

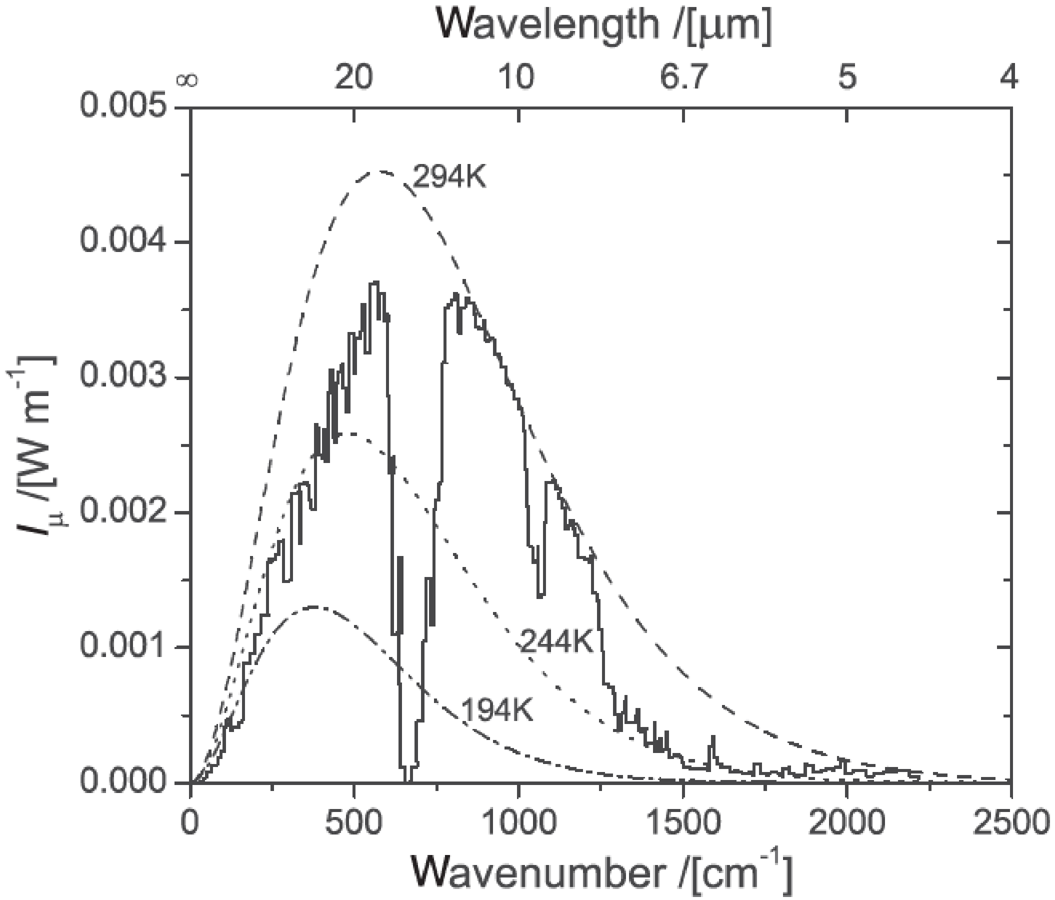
The Radiation Balance and the Greenhouse Effect

The **absorption of IR radiation** by the atmosphere is **strongly dependent on its wavelength**.

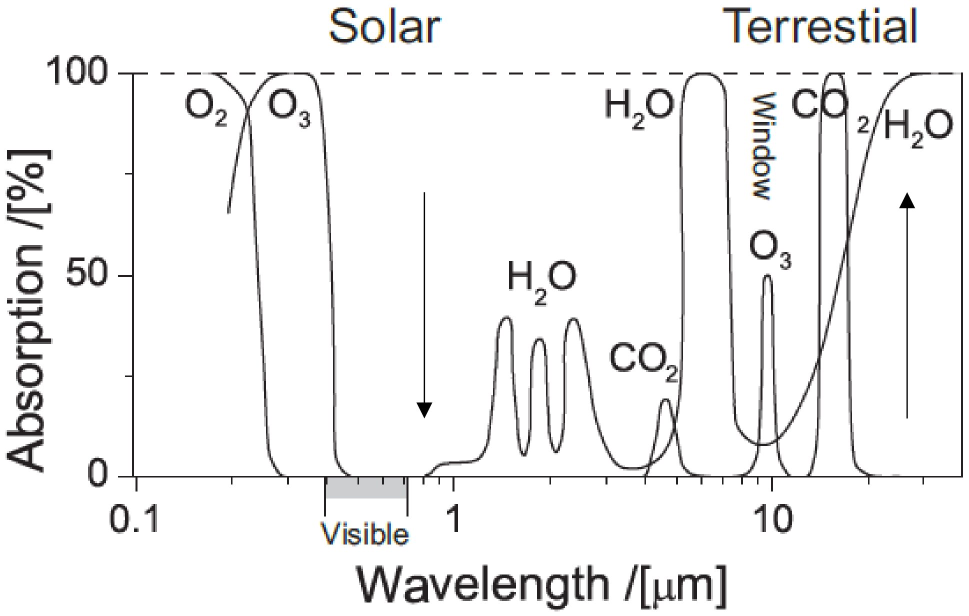
A measure of the upward IR flux at the tropopause shows that the atmosphere is:

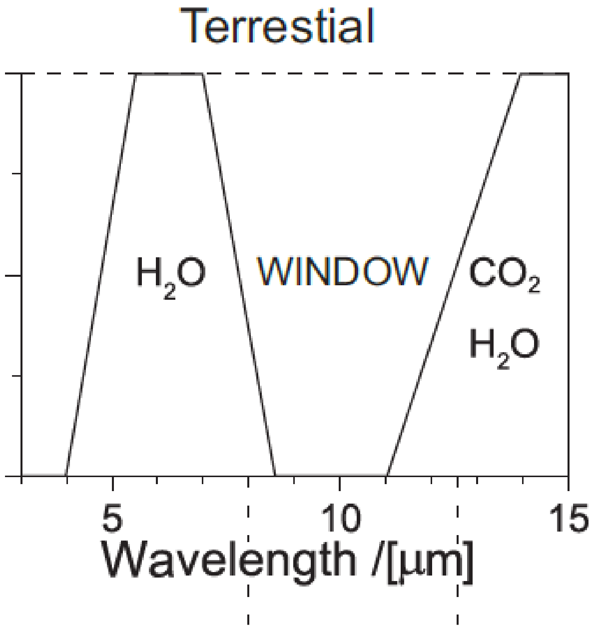
- **transparent** for wavelengths in the spectral window **between 8 µm and 12.5 µm**
- **opaque** at wavelengths **around 15 µm.**

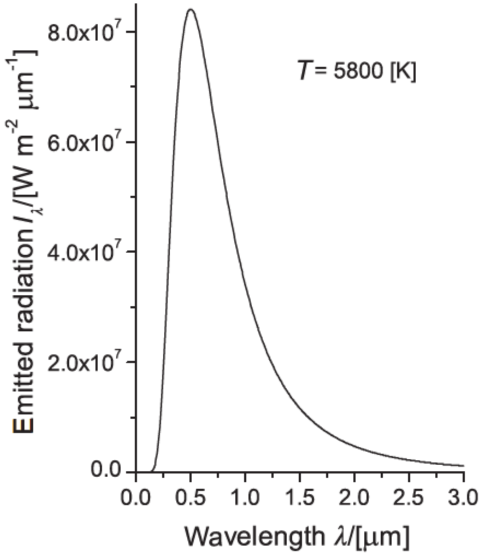
These are the results of **greenhouse gases absorption** in the atmosphere.

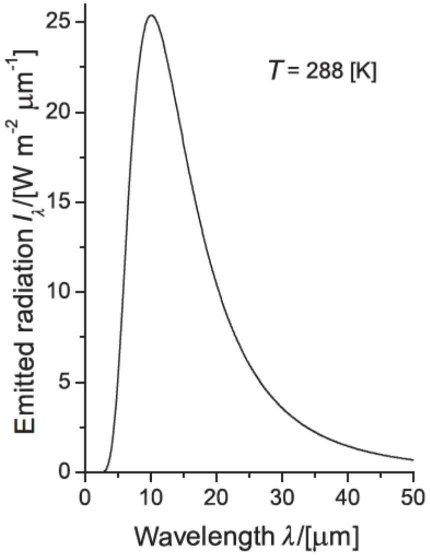


2.3 GREENHOUSE EFFECT AND GLOBAL WARMING









- **Solar radiation** is absorbed from top to surface, in the spectral range from 0.1 µm to 3 µm.
- **Terrestrial radiation** is absorbed from surface to top, in the spectral range from 4 µm to 50 µm.

2.3 GREENHOUSE EFFECT AND GLOBAL WARMING

Radiative forcing and global warming

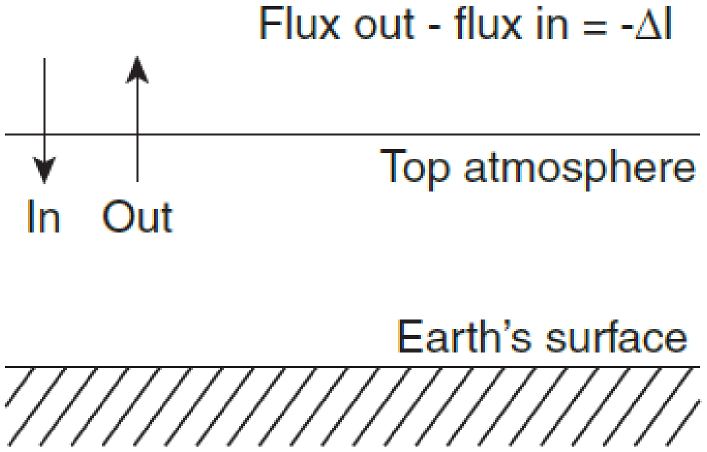
What is the effect of the increase of greenhouse gases concentration?

The net radiation flux at the top of the atmosphere vanishes under equilibrium conditions, determining the Earth temperature. **An increase in the concentration of greenhouse gases would lead to a net reduction in the outgoing long-wavelength radiation at the top of the atmosphere by ΔI**. The incoming energy from the sun remains the same. The energy balance at the top of the atmosphere should be restored by an increase ΔT of the earth's surface temperature.

Modifying Eq. 2.24 to account for both the **Earth surface and the atmosphere as two separate blackbodies**, we have:

$$(1-a)\frac{S}{4} = \sigma T_a^4 + t \cdot \sigma T_s^4 \qquad (2.25)$$

where T_a and T_s are the temperature of atmosphere and Earth's surface, respectively, and t is the atmosphere IR transmission (~6%).



2.3 GREENHOUSE EFFECT AND GLOBAL WARMING

Radiative forcing and global warming

The incoming energy from the sun remains the same. **The energy balance at the top of the atmosphere should be restored by an increase ΔT of the earth's surface temperature**. This effect is called **radiative forcing**: the radiation imbalance at the top of the troposphere enforces a rise in temperature.

The required flux increase ΔI to compensate for the decrease by greenhouse gas absorption will be connected with the increase of the surface temperature ΔT_s by the relation:

$$\Delta T_s = G\Delta I \tag{2.26}$$

where is called the **gain factor**, which operates on the cause ΔI to produce the effect ΔT_s.

However, modelling the radiative forcing is nontrivial as multiple effects concur to mitigate or enhance the effects of global warming.

2.3 GREENHOUSE EFFECT AND GLOBAL WARMING

Radiative forcing and global warming

Effects **reinforcing** the global warming as it increases, are:

- Melting of ice and snow will lower the albedo.
- More water vapor in the air will lead to smaller transmission *t*.
- The increase in the cloud cover from higher evaporation will have the same effect.
- Several processes will cause (further) increase in CO_2 concentration: a higher sea water temperature gives less CO_2 absorption in sea water; higher polar temperatures will cause a smaller ocean circulation and decreasing absorption; a faster decay of organic materials will give more CO_2 and CH_4 (from rotting).
- Thawing of permafrost, covering some 20% of the earth’s land surface, may liberate large quantities of CH_4 and CO_2 trapped in the frozen soil

2.3 GREENHOUSE EFFECT AND GLOBAL WARMING

Radiative forcing and global warming

Effects **mitigating** global warming as it increases, are:

- An increase in sea water temperature would lead to an increase in the growth of algae. They would use CO_2 for photosynthesis and reduce the CO_2 concentration in the water, absorb more from the atmosphere and reduce the atmospheric CO_2 concentration. Most CO_2 is due to burning of fossil fuels, which liberates aerosols, small particles that will increase the earth's albedo a by backscattering incoming solar radiation.

- With a higher surface temperature more sea water will evaporate. At higher altitudes it will condense, heating the upper layers more and cooling the surface.

- More CO_2 leads to an increased growth of plants which will bind CO_2.

2.3 GREENHOUSE EFFECT AND GLOBAL WARMING

Greenhouse gases (GHGs)

The main gaseous species contributing to global warming and greenhouse effects are reported here:

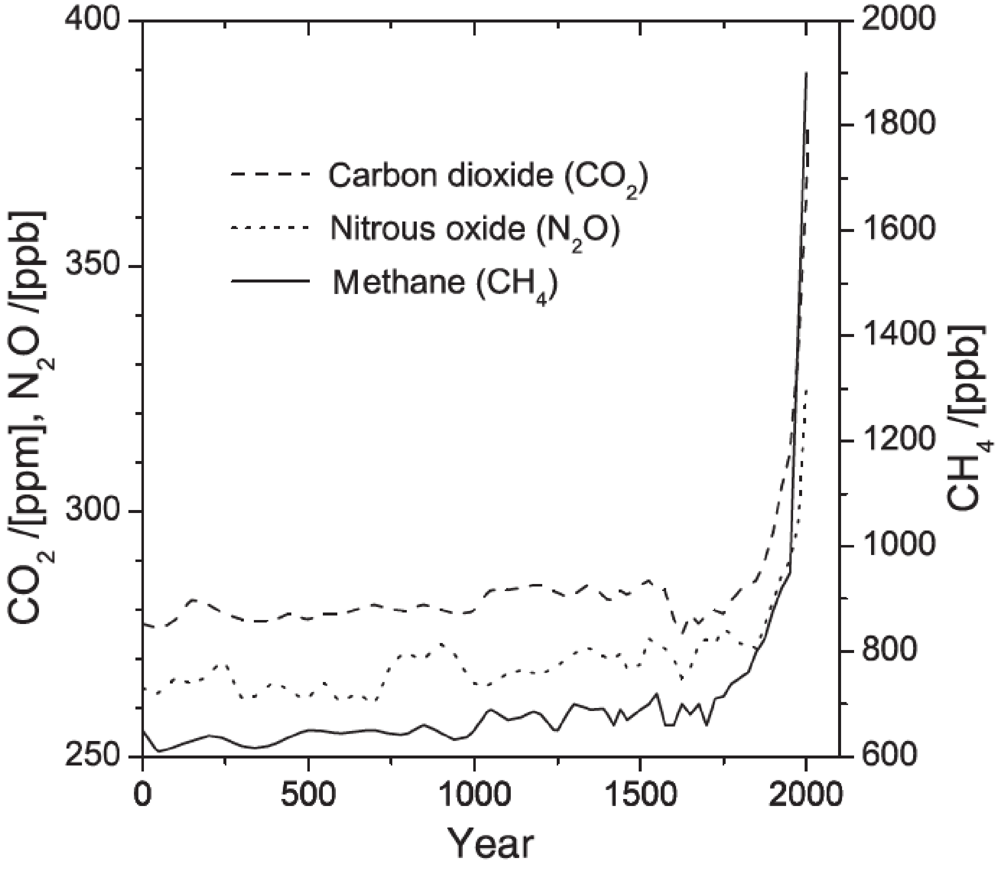
Gas	Concentration (ppm)	Lifetime (years)	GWP (20 yr)	GWP (100 yr)
CO_2	415	50 - 200	1	1
N_2O	0.33	114	289	298
CH_4	1.92	12	72	25
SF_6	$11*10^{-6}$	3200	16300	22800

https://gml.noaa.gov/ccgg/

The CO_2 concentration is most widely discussed and it is taken as the standard. The **global warming potential (GWP)** of a certain gas then compares the warming effect of adding 1 kg of the gas to the warming effect of the addition of 1 kg of CO_2. Because of the different lifetimes the GWP will depend on the time horizon one considers.

2.3 GREENHOUSE EFFECT AND GLOBAL WARMING

Greenhouse gases sources



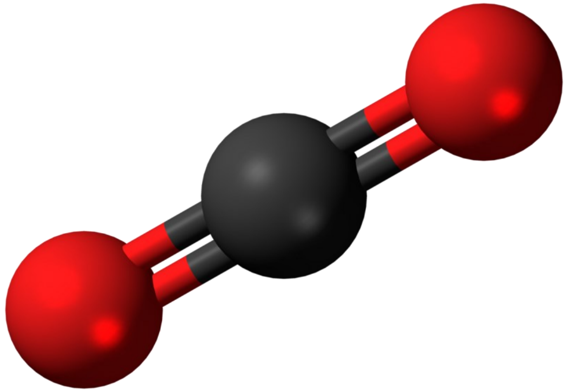
The main sources of greenhouse gases are:

- **CO_2**: Combustion of fossil fuels, gas flaring, cement production, biomass burning
- **CH_4**: Wetlands (rotting), rice agriculture, biomass burning, ruminant animals
- **N_2O**: Microbes in fertilized agricultural lands
- **SF_6**: Electrical insulation fluid, inert tracer for studying transport processes

The most relevant increase in their concentrations started around 1750 with the beginning of the industrial revolution. Therefore, this year is used as reference point in calculating human influences.

2.3 GREENHOUSE EFFECT AND GLOBAL WARMING

Carbon dioxide



Carbon dioxide (CO_2) is a colorless gas having a faint sharp odor and a sour taste. It represents the most important greenhouse gas.

CO_2 concentrations and its relationship with **Earth temperature** have been widely investigated by analyzing **ice cores**. When snow falls, air is trapped amongst the ice crystals. Subsequent snowfalls build up in layers, each of which is a record of the air and water quality prevailing at the time. Eventually, the snow layers become compressed into ice, and the air is trapped in bubbles within the ice.

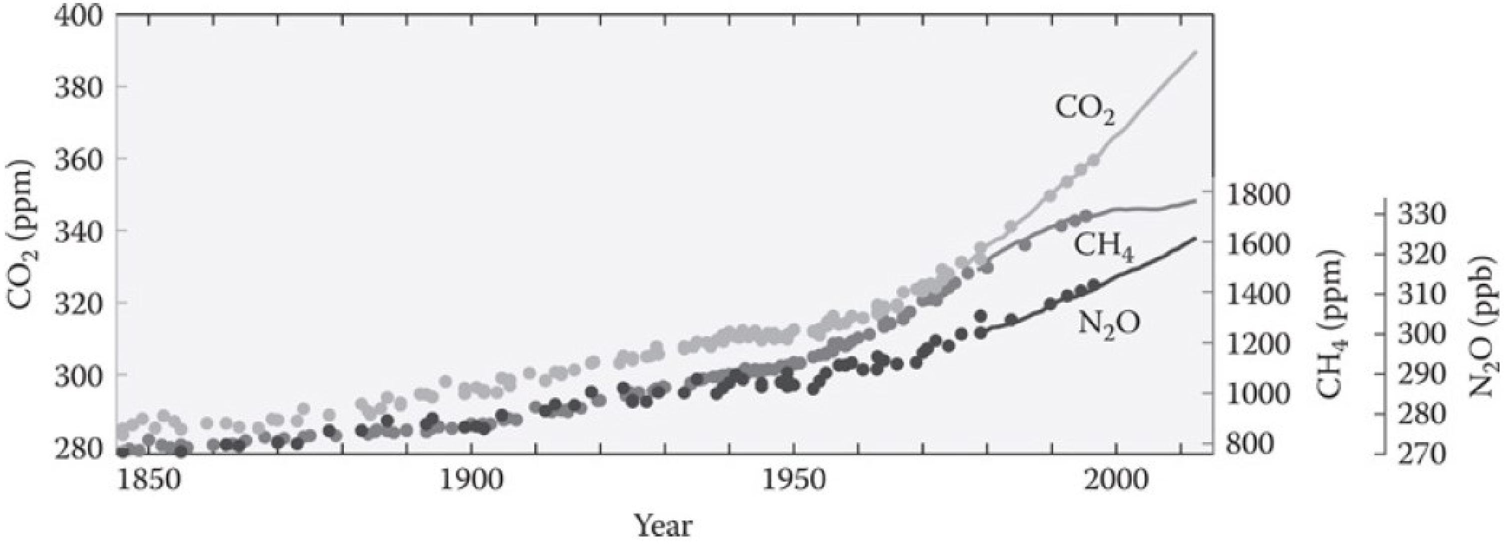
These measurements allowed us to trace the CO_2 concentration and the Earth temperature variations (derived from the $^{18}O/^{16}O$ ratio) back to **400,000 years ago**. At the start of this record, carbon dioxide was close to its **preindustrial concentration of 280 ppm**.

2.3 GREENHOUSE EFFECT AND GLOBAL WARMING

Carbon dioxide

Although there were major variations in CO_2 throughout the period, the concentration was never greater than 320 ppm. During the past 1000 years, the concentration has shot up at an unprecedented rate, **from the previous typical peak level of 280 ppm to the current value of 415 ppm.**

This recent sharp rise in CO_2 concentration is due to the **anthropogenic addition of CO_2** to the Earth's atmosphere by biomass burning and combustion of fossil fuels, strongly associated with population growth and industrialization. **The whole picture is still evolving.**



2.3 GREENHOUSE EFFECT AND GLOBAL WARMING

Carbon dioxide

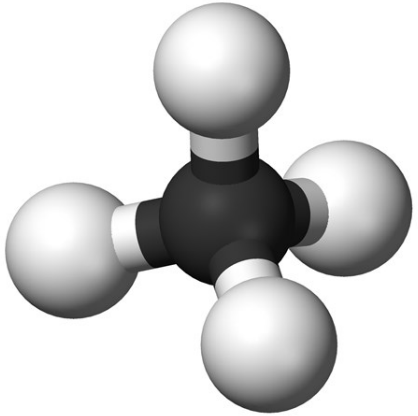
Carbon is also involved in natural cycles of living organisms.

On the **plant side**, the Earth's terrestrial and aquatic plants take up CO_2 from the atmosphere by **photosynthesis** and lock up the carbon as plant parts. The carbon is eventually returned to the atmosphere: slowly by respiration and rotting, or rapidly by forest fires. Animals burn food and release CO_2 as a by-product. There is a large continuing exchange between the atmosphere and the oceans, in which the surface layers are saturated with CO_2 and alternately take up new CO_2 from the atmosphere and release it back again. **Human being release carbon dioxide during breathing**, in a concentration which can reach the 5% of the sample composition.

In addition to a global rise, CO_2 undergoes **diurnal variations locally** and **annual variations globally** due to assimilation and respiration by plants and the release from decaying biomass.

2.3 GREENHOUSE EFFECT AND GLOBAL WARMING

Methane



Methane (CH_4) is a colorless, odorless gas that occurs abundantly in nature and as a product of human activities. It is the second most important greenhouse gas, but it is more dangerous than CO_2 because of its GWP.

Methane is produced by a wide variety of anaerobic processes. The main **natural source is bacterial decay** in wetlands, while **anthropogenic sources are paddy fields, the digestive tracts of ruminant animals such as cattle, and natural gas emissions from fossil fuel supplies**.

Methane is eventually oxidized to CO_2 in the atmosphere. As this is achieved via reaction with the OH radical, **CH_4 is also involved in ozone photochemistry**. If the oxidation occurs in the presence of high NOx concentrations, then O_3 is produced; if NOx is low, then O_3 is consumed.

The long-term ice core record shows a very similar pattern of fluctuations to that of CO_2, ending up with a **pre-industrial concentration of 700–800 ppb**.

2.3 GREENHOUSE EFFECT AND GLOBAL WARMING

Methane

In general, farm animals produce a lot of methane. One cow emits about 70 kg methane per year, one sheep about 8 kg, and one pig about 1.5 kg. Cattle and sheep emit about 70% and 20% respectively of the total animal emission.

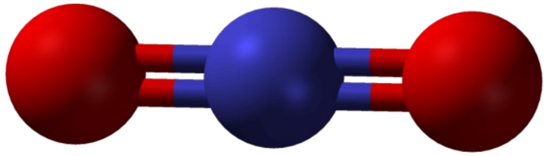
Coal and methane are always associated, and methane is released during mining and ventilated to atmosphere.

Petrochemical activities are also associated to methane emission from natural gas sources, as natural gas consists of CH_4 in mixing ratio from 70% up to 90%.

In recent years, **waste, livestock, and agriculture** have been the most dominant sources. Compared to the previous decades, the corresponding emissions from landfill and energy related fugitive emissions have fallen by over 70%, while the aggregated emissions from agriculture sector have remained largely unchanged.

2.3 GREENHOUSE EFFECT AND GLOBAL WARMING

Nitrous oxide



Nitrous oxide (N_2O) a colorless gas with pleasant, sweetish odor and taste, which when inhaled produces insensibility to pain preceded by mild hysteria, sometimes laughter. It is also known as laughing gas.

Nitrous oxide (N_2O) is produced by a variety of biological nitrification and denitrification processes in water and in soil. Although **not toxic at normal atmospheric concentrations, it is a radiatively active gas that contributes to the greenhouse effect and climate change**.

The soil component of the emission results from anaerobic microbial denitrification and nitrification. This is **more intensive in agricultural areas where N is added to the soil**, but wet and dry N deposition to other areas could be increasing N_2O emissions. Land-use changes such as forest clearance, drainage and cultivation stimulate emission.

2.3 GREENHOUSE EFFECT AND GLOBAL WARMING

Nitrous oxide

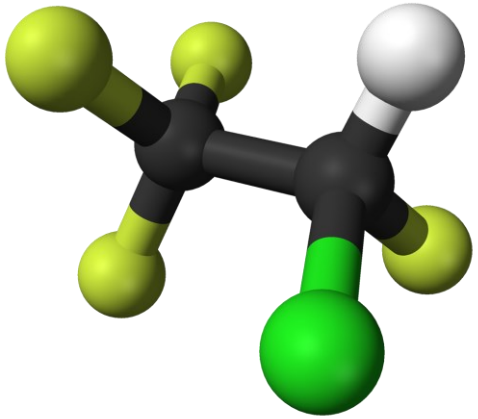
The major removal mechanism of N_2O is photolysis in the stratosphere. **Pre-industrial concentrations of N_2O were about 285 ppb, have since increased to about 330 ppb**, and are currently rising at the rate of 0.8 ppb yr^{-1}.

Natural emissions make up about 80% of the total. The component from cultivated soils is potentially the largest of the man-made sectors, although there is a lot of uncertainty attached to it. **Agricultural activities form the most dominant source** (both soil and manure management), whereas **industrial processes and combustion processes in power generation** and road transport contribute to additional N_2O.

The gas is also used as a propellant and has a variety of applications from rocketry to food aerosols (E number: E942). In automobile racing, nitrous oxide is injected into an engine's air intake; the extra oxygen allows the engine to burn more fuel per stroke. N_2O has been used in dentistry and surgery, as weak anesthetic and analgesic.

2.3 GREENHOUSE EFFECT AND GLOBAL WARMING

Halocarbons



Halocarbons are a class of chemical compound consisting of carbon and one or more halogens (bromine, chlorine, fluorine, iodine). Unlike carbon dioxide, methane and nitrous oxide, **halocarbons have no natural source or background**. There are at least 12 principal halocarbons that are a cause of concern for the Earth’s radiation balance.

In the past, they have been used for three main purposes: i) as the heat transfer medium in refrigerators and air conditioning systems; ii) as the propellant in aerosol spray cans; iii) and as the foaming agent in expanded polystyrene packaging and insulation.

Two of the desirable properties that make them so suitable for these purposes are their **chemical inertness and thermal stability**, the very properties that also result in their having **very long lifetimes in the atmosphere.**

2.3 GREENHOUSE EFFECT AND GLOBAL WARMING

Halocarbons

Halocarbons are particularly dangerous for the atmosphere due to their chemical reactions with stratospheric ozone, which led to the ozone depletion in the so-called “**ozone hole**”.

However, halocarbons has also an additional physical effect. **The halocarbon molecules absorb infrared radiation effectively in the waveband of the atmospheric window**. They are hence strongly radiatively active on a per-molecule basis and contribute a significant radiative forcing despite their low concentrations.

The most dangerous halocarbons are the **chlorofluorocarbon (CFC)** molecules. These compounds are characterized by a **GWP of 5–10,000**. As a result, the tiny CFC concentrations account for about 20% of the radiative forcing in the tropics. The two most important halocarbons are the chlorofluorocarbons CFC-11 and CFC-12, which have average concentrations of a few hundred ppt.

Although their destructive effect on the ozone layer led to an international agreement (the **Montreal Protocol**) to phase out production, their **long lifetimes** mean that their effects will persist for a considerable portion of the twenty-first century.

2.4 INDOOR MONITORING

Indoor monitoring: why?

The **contamination of indoor air** by a variety of toxic and/or hazardous pollutants has in the last decade become increasingly recognized as a serious (or potentially serious) public health problem.

Indoor air pollution is an age-old problem, dating back to prehistoric times when humans came to live in enclosed shelters. It began when the utility of fire was discovered and brought indoors for cooking and heating.

What is new about the problem of indoor air pollution is our emerging awareness of it and the increasing attention given to its various dimensions by research scientists and regulatory authorities.

In terms of documentable health effects, it appears to be enormously more significant than ambient (outdoor) air pollution, a problem for which the implementation of control measures has cost the United States over $200 billion in the past decade.

2.4 INDOOR MONITORING

Indoor monitoring: why?

Indoor air quality monitoring has risen as a powerful tool in different scenarios, such as those related to COVID-19 spread.

Viruses, such as COVID-19 can be transmitted through airborne contaminants. Released into the air through acts such as breathing, talking, or coughing, virus particles generally attach to larger particles such as dust or saliva and can typically travel one to two meters, however this is not always the case with smaller droplets travelling much further.

Ventilation can play a large part in mitigating the risk of airborne transmission indoors, with aerosols and virus particles accumulating within enclosed spaces. Options such as natural or mechanical ventilation systems (HVAC) can provide a solution by cycling fresh air through the space and diluting the airborne contaminants.

How do we know when it is time to refresh the air in a room?

2.4 INDOOR MONITORING

Indoor monitoring: why?

Indoor CO_2 monitoring is an established means to assess whether ventilation is adequate for the number of people occupying the space.

CO_2 levels range from 350 to 450 ppm in the outdoor environment, but **people gathering and breathing inside a closed environment will cause CO_2 to accumulate to much higher levels unless removed through ventilation.** The more people that occupy a space and the more intense their physical activity, the more ventilation is required to maintain occupant comfort. CO_2 levels are also a proxy for other difficult-to-detect pollutants (e.g., VOCs) that may accumulate in the space. Typically, indoor air quality guidelines have adopted **a value of 1000 ppm CO_2 as reference for acceptable indoor air quality**, although this value is not a formal standard.

Because CO_2 levels increase with the number of occupants in a space, and one or more of those occupants could potentially be infected, it seems logical that respiratory disease risk should scale upwards with indoor CO_2 levels, as investigated by multiple studies.

[1]https://pubs.acs.org/doi/10.1021/acs.estlett.1c00183
[2]https://assets.publishing.service.gov.uk/government/uploads/system/uploads/attachment_data/file/928720/S0789_EMG_Role_of_Ventilation_in_Controlling_SARS-CoV-2_Transmission.pdf

2.4 INDOOR MONITORING

Indoor/outdoor relationships

Indoor and outdoor monitoring can’t be separated, as there is a continuous exchange of air from the environment and vice versa.

During alert, warning, and emergency stages of episodes (periods of high ambient air pollution), episode control plans call for air pollution and public health authorities to advise citizens in the affected area to remain indoors. **This advice is based on the premise that pollutant concentrations will be lower indoors.**

For two of the pollutants of major concern under episode conditions, such advice is in fact appropriate. **For SO_2 and O_3**, both reactive gases, **indoor concentrations are only a fraction** of ambient (outdoor) levels.

2.4 INDOOR MONITORING

Indoor/outdoor relationships

Indoor concentrations of **combustion-generated contaminants** such as **nitrogen oxides (NO_X), carbon monoxide (CO), and particulate** have widely variable indoor/outdoor ratios. This variation is due in good measure to the fact that both indoor and outdoor environments can contribute (under varied circumstances) to indoor levels.

For NO_2, a relatively reactive gas, indoor/outdoor ratios of less than or near unity are typical of residences that have no indoor sources. In residences with gas cooking stoves and/or unvented gas or kerosene heaters, indoor NO_2 levels often exceed those in the ambient environment. Because of its low reactivity, indoor/outdoor ratios of CO in the absence of indoor sources typically approach unity.

In general, however, particulate levels are considerably higher indoors than they are in the ambient environment. The primary reason for this is tobacco smoking, which is the single most significant contributor to indoor particulate levels.

2.4 INDOOR MONITORING

Indoor/outdoor relationships

Organic compounds, as **formaldehyde, VOCs, and pesticides**, often occur **indoors at concentrations that exceed ambient levels** by several fold or, in the case of formaldehyde, one to two orders of magnitude.

Because of the widespread use of organic solvents in building materials, paints, adhesives, and furnishings, indoor nonmethane hydrocarbon levels have been seen to exceed ambient levels by 1.5-1.9 times. Concentrations of **specific VOCs may exceed ambient levels by a factor of 2 or more and by as much as a factor of 10**.

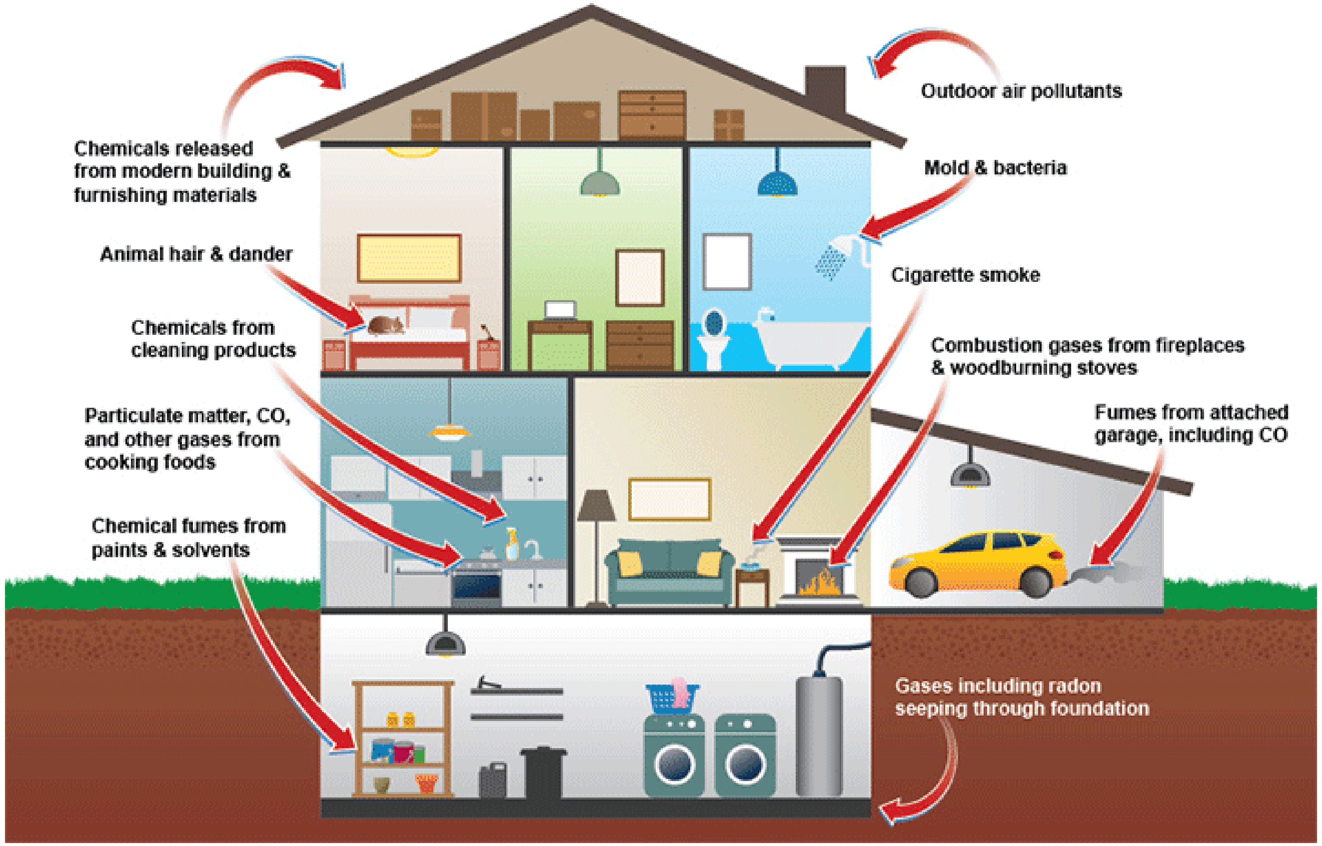
Differences in indoor/outdoor ratios have special relevance to controlling indoor contamination. If the indoor/outdoor ratio is below 1, the effect of applying general ventilation for contaminant control is increased indoor concentrations of those particular contaminants, notably SO_2 and O_3 and, in summer months, mold spores. On the other hand, when indoor/outdoor ratios are high, considerably exceeding 1, the use of general ventilation for contaminant control would be particularly appropriate.

2.4 INDOOR MONITORING

Sources of indoor pollution

The main risks for indoor air quality come from different gas species and compounds:

- Combustion-generated pollutants
- VOCs and particulate
- Formaldehyde
- Asbestos



2.4 INDOOR MONITORING

Combustion-generated pollutants

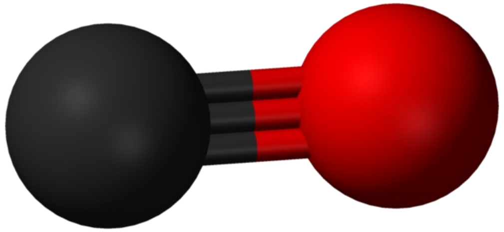
Indoor air pollution associated with combustion has a long history, one that goes back to the first human dwellings and use of fire. Twentieth-century advancements in technology have provided advanced societies with vented gas and oil space heating and electric heating and cooking. Modern technology has provided us the opportunity to live in "smoke-free" homes and buildings.

Sources of pollutants include **wood stoves, furnaces, and fireplaces** whose emissions are vented to the ambient environment through flues and chimneys, **unvented gas and kerosene space heaters**, and **gas cooking stoves and ovens**. Significant contamination of indoor spaces by combustion by-products may also occur from **tobacco smoking**.

Main combustion-generated pollutants are: CO, CO_2, NO_X, SO_2

2.4 GREENHOUSE EFFECT AND GLOBAL WARMING

Carbon monoxide



Carbon monoxide (CO) is an odorless, colorless and toxic gas. It is known as "**the silent killer**". CO production is mainly related to incomplete combustion, therefore its concentration in outdoor environment is typically negligible and associated with CO_2 emissions. Conversely, it poses a serious threat for indoor environments.

Acute effects on health are due to the formation of carboxyhemoglobin in the blood, which inhibits oxygen intake. **The TWA-REL suggested by NIOSH is 35 ppm, while the IDLH level is 1200 ppm.**

At low concentrations, it causes fatigue in healthy people and chest pain in people with heart disease. At higher concentrations, the exposition results in impaired vision and coordination, headaches, dizziness, confusion, and nausea. Can cause flu-like symptoms that clear up after leaving home.

Average levels in homes **without gas stoves vary from 0.5 to 5 ppm.** Levels near **properly adjusted gas stoves are often 5 to 15 ppm** and those near **poorly adjusted stoves may be 30 ppm** or higher.

2.4 INDOOR MONITORING

VOCs in indoor monitoring

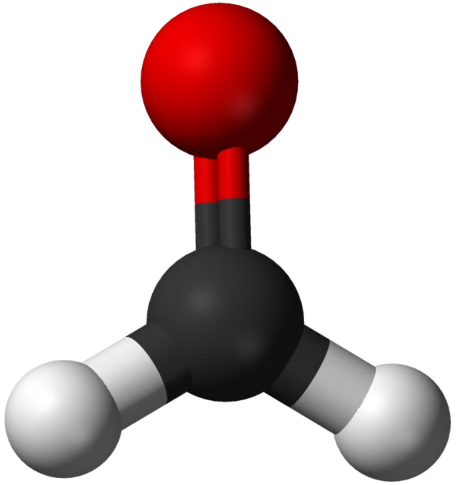
A significant variety of organic compounds are known to contaminate indoor air. **Organic contaminants may also be present as major constituents of indoor aerosols.**

The large number of chemical species present in indoor air, and the inherent difficulty and cost associated with the identification and quantification of organic chemicals in mixtures, is a major obstacle to VOCs monitoring in indoor environment.

The studies that have been conducted indicate that indoor air is contaminated to various degrees by a wide variety of **hydrocarbons and hydrocarbon derivatives** including aliphatics, aromatics, alkylbenzenes, ketones, polycyclic aromatics, and chlorinated hydrocarbons. **Multiple and different VOCs sources can be identified**, including: combustion by-products, cooking, construction materials, furnishings, paints, varnishes and solvents, adhesives and caulks, gasoline and motor vehicle emissions, office equipment, home and personal care products, and pesticides.

2.4 INDOOR MONITORING

Formaldehyde



Formaldehyde (CH_2O) is a colorless, flammable gas at room temperature and has a strong odor. Because of the extensive use of building materials and furnishings which release it, **formaldehyde is a ubiquitous contaminant of indoor air.**

Elevated levels in indoor environments, have resulted in numerous odor and health complaints associated with formaldehyde contamination of indoor spaces, most notably in the late '70s and the early '80s. The formaldehyde indoor air quality problem has received considerable public and research attention. In the past decade it has been the major indoor air quality issue and public health concern.

Though many products have the potential for releasing formaldehyde into indoor air, relatively few are responsible for causing significant levels of contamination, such as: fiberboard, plywood paneling, particleboard and foam insulation. **Major CH_2O sources are formulated, in whole or in part, from urea-formaldehyde (U-F) resins. Excess or residual formaldehyde trapped in the resin is later released, but significant formaldehyde release also occurs when the resin polymer undergoes hydrolytic decomposition.**

2.4 INDOOR MONITORING

Asbestos

Asbestos is a collective term for a variety of asbestiform minerals that satisfy particular industrial-commercial needs. The term is used in reference to well-developed and thin, long-fibered varieties of certain minerals. These include chrysotile, anthophyllite, riebeckite, cummingtonite-grunerite, and actinolite-tremolite.

Asbestos fibers are characterized by their small diameter, high length-to width ratio, and smooth and parallel longitudinal faces. They have great strength and flexibility, with high tensile strength.

Asbestos as a potentially serious indoor contamination problem came to public attention in the 70's when health authorities recognized that **friable asbestos-containing material** used as a fire/heat retardant and acoustical plaster in buildings had the potential for **releasing a significant quantity of asbestos fibers into indoor air.**

Four main diseases have been clearly associated with exposures to asbestos: lung cancer, mesothelioma, asbestosis, and nonmalignant pleural disease.