

Lower Atmosphere

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Unit 4

Gases in our atmosphere

There are thousands of gases in the troposphere. In this unit we look in more detail at the most important components of the lower atmosphere.

Some of the gases are evenly spread all over the world, whereas the concentrations of others depends strongly on sources, local conditions and on the time of day. In this unit we give a short overview on how gases in our atmosphere can be characterised.

Part 1: Distribution & Concentration (1)

We have already learnt a lot about the gases which exist in our atmosphere. The greatest number of gases are found in the troposphere, the lowest layer of the atmosphere, but their concentrations vary greatly over both time and location.

How to describe a gas in the atmosphere?

Amount

A gas in the atmosphere can be:

- a) a major component of the air (oxygen, nitrogen, argon)
- b) a major trace gas (carbon dioxide, methane, ozone, nitrogen dioxide)
- c) a minor trace gas (organic gases such as butane, ethanol, CFCs)

Trace gases are gases which make up only a tiny fraction of the air.

Levels of these trace gases can be as low as one molecule in one billion or even one trillion air molecules.

Can you imagine one ppb?

ppb = parts per billion (American *)

**more correctly: nmol/mol
1 molecule in 1,000,000,000 molecules**

1 Indian in all India, 1 cent in 10 million EUROS, 1 second in 32 years.

And 1 ppt?

**ppt = parts per trillion
more correctly: pmol/mol
1 molecule among 1,000,000,000,000 molecules**

1 stamp in an area the size of Paris ...

These levels are so small, its really difficult to image them, but modern scientific techniques can detect them.

The misunderstanding of mixing ratio 'units' ppm and ppb

In numerous scientific publication the amount of a compound in the air is given in ppm (parts per million) or ppb (parts per billion). We also use this abbreviation here, because it is so common and you find it everywhere. But it can be very misleading.

Three typical mistakes:

1) You often see written: The concentration of CO₂ in the air is 370 ppm. This is wrong. 370 ppm is a mixing ratio and not a concentration. Mixing ratios give the number of molecules of a certain chemical in a fixed number of air molecules.

Concentrations are, for example, the number of moles of a compound in a fixed volume of air, for example 20 nmol m⁻³. They have a real unit.

2) Mixing ratios do not really have a unit, because you can cancel the units. If the mixing ratio is 370 ppm this means you have 370 molecules among 1,000,000 molecules. The more correct expression is 370 μmol/mol.

3) The terms billion and trillion are defined in different ways in different countries:

1 American billion = 1 British milliard (seldom used) = 1,000,000,000

1 American trillion = 1 British billion (seldom used) = 1,000,000,000,000

In many other languages, terms related to 1 British milliard (French: milliard, German: Milliarde) are more common than the American billion for 10⁹. So take care!

often used:	more correctly:	this means:
ppm (parts per million)	μmol / mol = 10 ⁻⁶ (micromol / mol)	1 in 1,000,000
ppb (parts per billion) <small>American</small>	nmol / mol = 10 ⁻⁹ (nanomol / mol)	1 in 1,000,000,000
ppt (parts per trillion) <small>American</small>	pmol / mol = 10 ⁻¹² (pikomol / mol)	1 in 1,000,000,000,000

Distribution

Depending on the local and temporary conditions in the atmosphere, a gas can be:



1. a) homogeneously distributed
(e.g. nitrogen, oxygen, carbon dioxide)

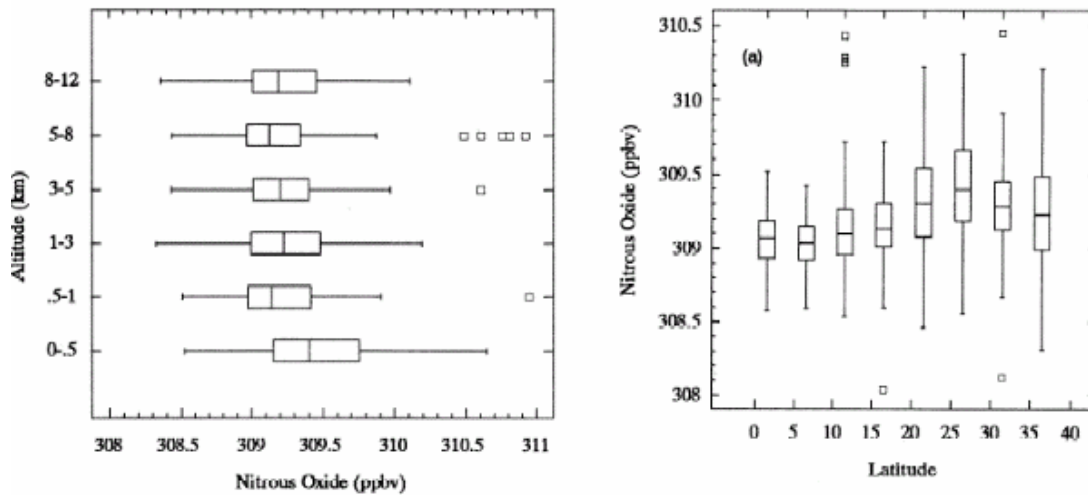
image: Elmar Uherek



b) inhomogeneously distributed
(e.g. water vapour, ozone, many minor trace gases)

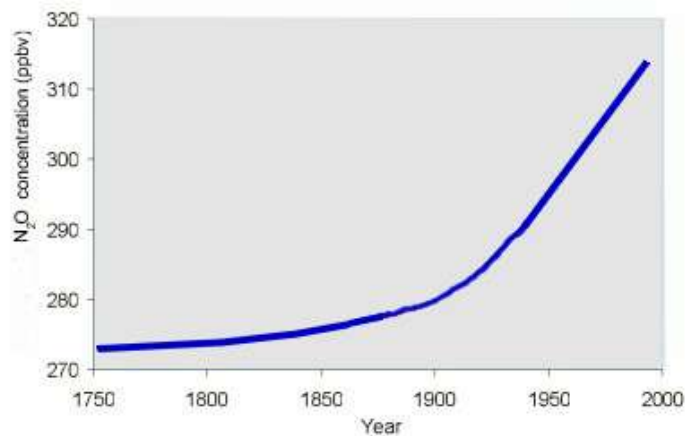
If a gas is homogeneously distributed this means that we find comparable mixing ratios of the gas everywhere around the globe and also at varying altitudes. This is the case for stable gases with a long life times. These gases are only slowly removed from the atmosphere and are either unreactive or react only very slowly.

Example: Nitrous oxide N₂O

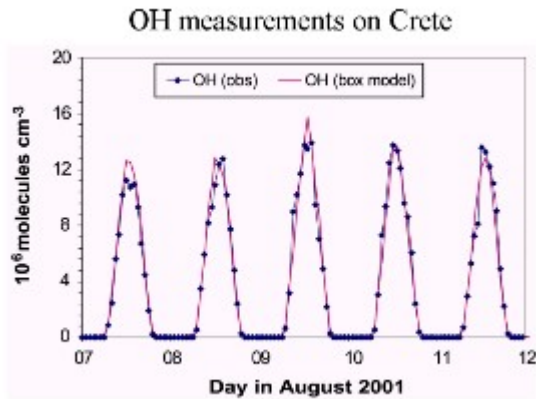


2. Distribution of nitrous oxide in the atmosphere. The graphs show mixing ratios over the Pacific Ocean at different altitudes and latitudes with associated error bars. J.E. Collins et al., Journal of Geophysical Research, 101, D1 (1996) p. 1975-84.

Nitrous oxide N₂O is a homogeneously distributed gas, similar amounts are seen all over the world and at different heights in the atmosphere. However, concentrations have increased over the past 200 years as a result, primarily, of human activity.



3. The change in N₂O levels over time. author Elmar Uherek.



4. Time profile of OH concentrations. Source: Presentation J. Lelieveld, MPI Mainz 2003.

Development over time

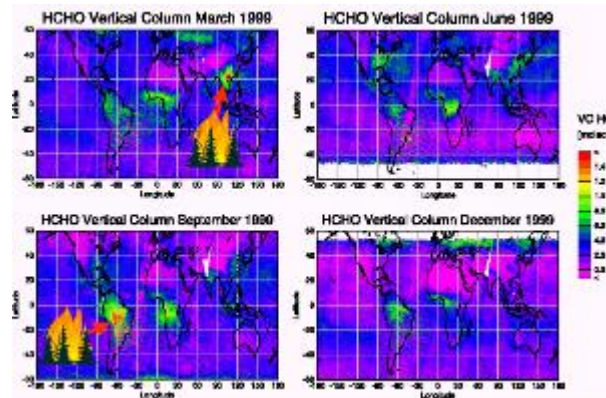
The amounts of some gases depend strongly on the strength of the Sun. The levels of these gases in the atmosphere shows a daily cycle and sometimes also a seasonal pattern

Daily variation: for example the hydroxyl radical OH

The hydroxyl radical is formed from the breakdown of ozone by sunshine. So atmospheric OH levels increase as the Sun rises, reaching a maximum after noon and then decrease through the afternoon and are negligible at night (see the unit on oxidation for more information).

Seasonal variation: for example formaldehyde

Vegetation fires are one source of the gas formaldehyde (HCHO). Concentrations of formaldehyde, as measured by the satellite based GOME instrument, are high during the fires seasons (March in Southeast-Asia, September in Brazil).

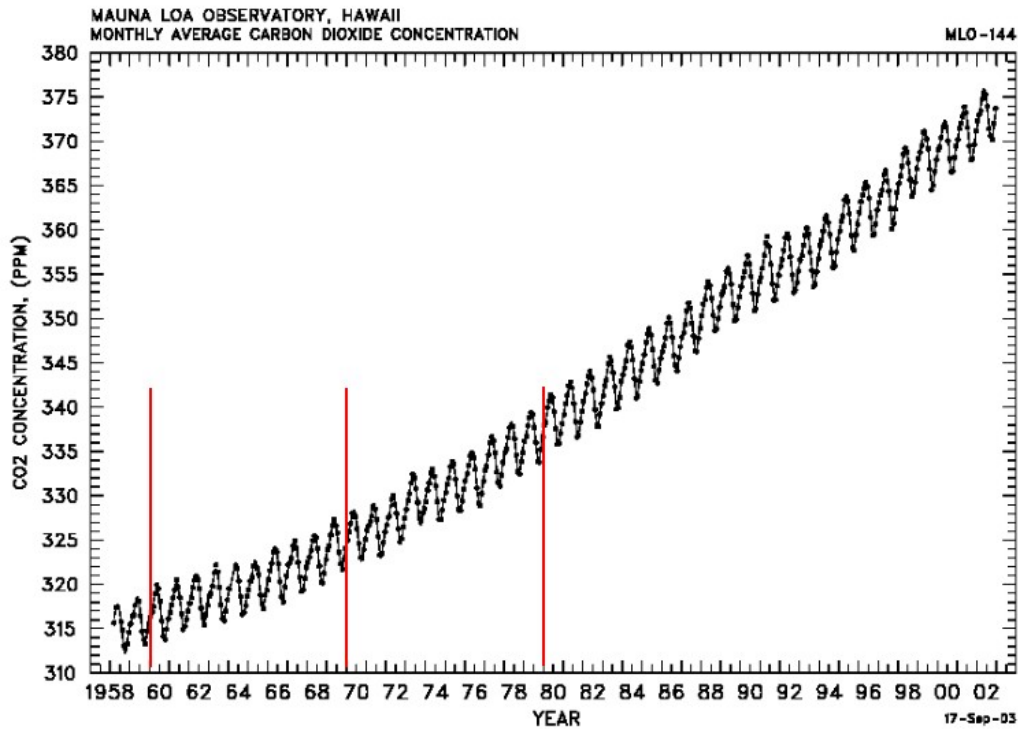


5. Formaldehyde - total columns observed by GOME from space. © IUP Bremen / ESA - GOME.

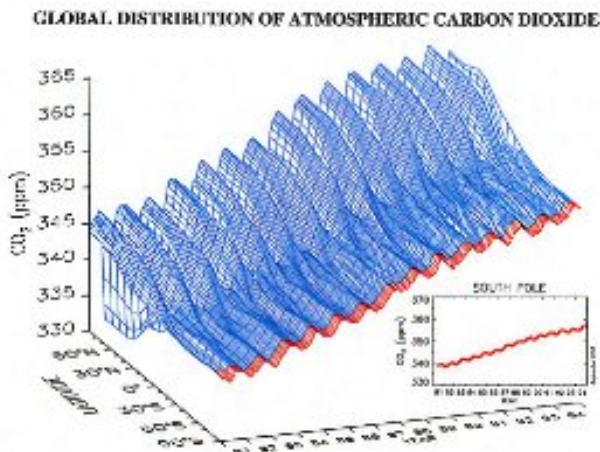
Some gases have increased or decreased in the long term over decades, hundreds, thousands or even millions of years. Since the industrial revolution, some 200 years ago, human activity has increased the average concentrations of many gases in the atmosphere.

The growing season and the impact of humans: for example carbon dioxide (CO2)

Carbon dioxide is an excellent example to study the global distribution of a gas. It is rather stable and therefore distributes itself over the whole globe. Atmospheric carbon dioxide levels are continuously increasing because of human activity. Most of the carbon dioxide is emitted from the Northern Hemisphere. The Northern Hemisphere contains much more land, a much higher human population (think about Europe, the U.S.A., China and India) and therefore has a much higher energy consumption than the Southern Hemisphere.



6. The CO₂ concentration trend recorded at the Mauna Loa Observatory, Hawaii. graph: © CDIAC US Department of Energy.



7. Global CO₂ distribution and annual and mid-term variations. © NOAA / CMDL.

Carbon dioxide levels, therefore, increase first of all in the Northern Hemisphere and then slowly rise in the south. Transport over the equator takes time since mixing within one hemisphere is much faster than mixing between the hemispheres. Along with this long time period change in CO₂ levels we also see that the annual pattern of CO₂ varies. In winter, the trees and other plants stop growing and, as a result, take up less CO₂. At the same time, we humans heat our houses and emit more CO₂. Consequently we see the highest CO₂ concentrations at the end of the heating period in May and about 5 ppm less CO₂ after the end of the growing period in October. The two graphs clearly show both patterns.

Part 2: Distribution & Concentration (2)

It's impossible to give average atmospheric concentrations for the less stable compounds in the air. Their concentrations depend strongly on the chemical conditions in the air at a particular time.

Vertical profiles

Sources, sinks and physical conditions (hours of sunshine, temperature, rainfall, wind strength and direction) affect both the horizontal and vertical distributions of a gas. Vertical profiles often show slightly decreasing mixing ratios with increasing altitude particularly in the free troposphere and the stratosphere. Ozone is an exception to this and has its highest mixing ratios and concentrations in the ozone layer in the stratosphere. Most of the chemistry in the atmosphere happens much lower in the atmosphere, in the planetary boundary layer. This is the layer of the atmosphere which is directly affected by the surface of the Earth and is where the chemical compounds are emitted. The graphs below show the vertical profiles for several organic and inorganic trace gases in the troposphere measured by a research aeroplane. Apart from carbon dioxide, ozone and methane, the typical values for mixing ratios are a few hundred parts per trillion (ppt) or a few parts per billion (ppb). The compounds shown are the more important trace gases, there are hundreds of other organic gases in the troposphere which have mixing ratios of just a few ppt.

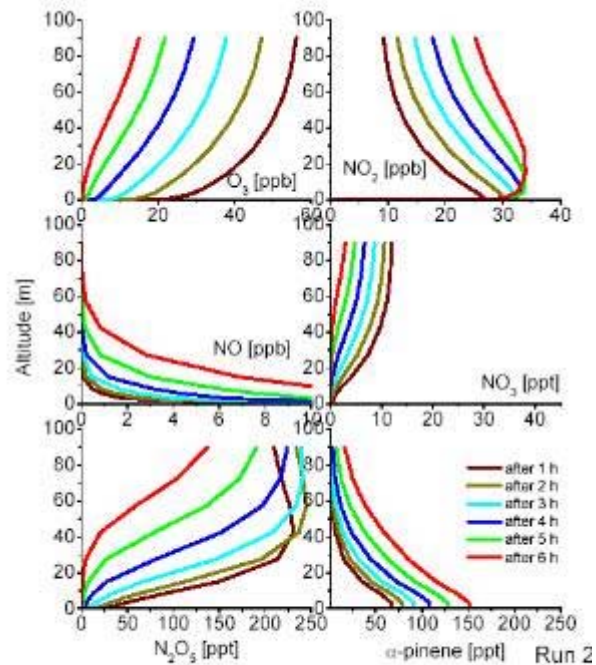
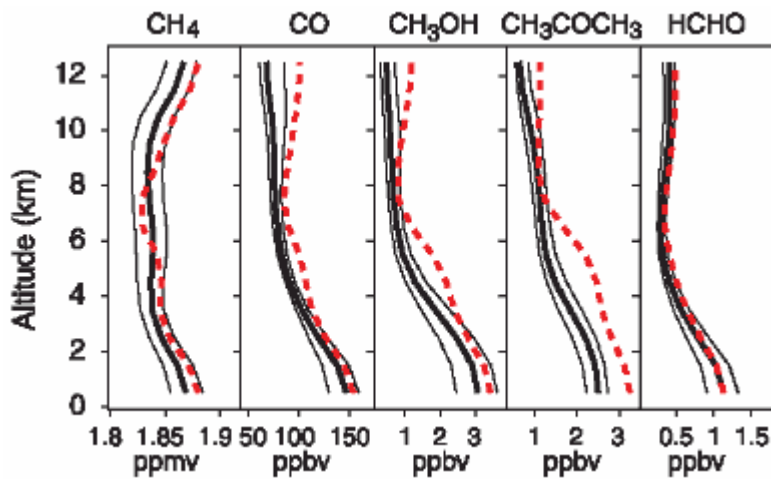


Figure 2. Vertical profiles of O₃, NO₂, NO, NO₃, N₂O₅, and α-pinene for urban scenario.

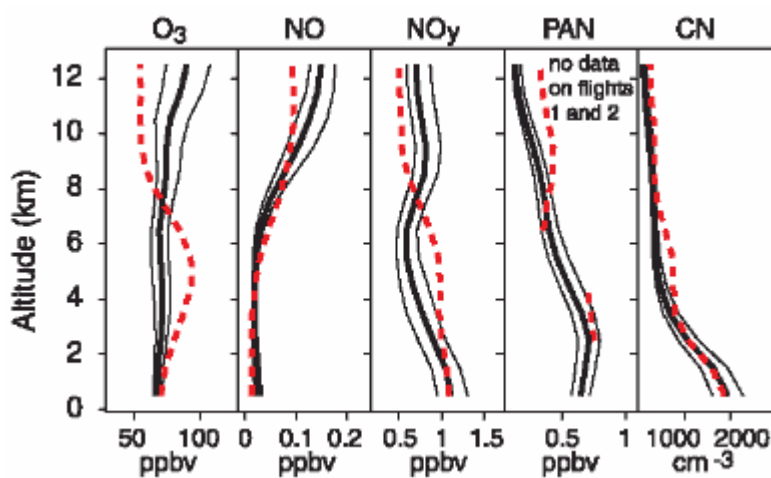
1. Mixing ratios of different compounds during the night close to the ground. The ratios are not measured but are the result of a chemical model which allows us to look at how the mixing ratios change over time.

Authors: Andreas Geyer, Shuihui Wang and Jochen Stutz.

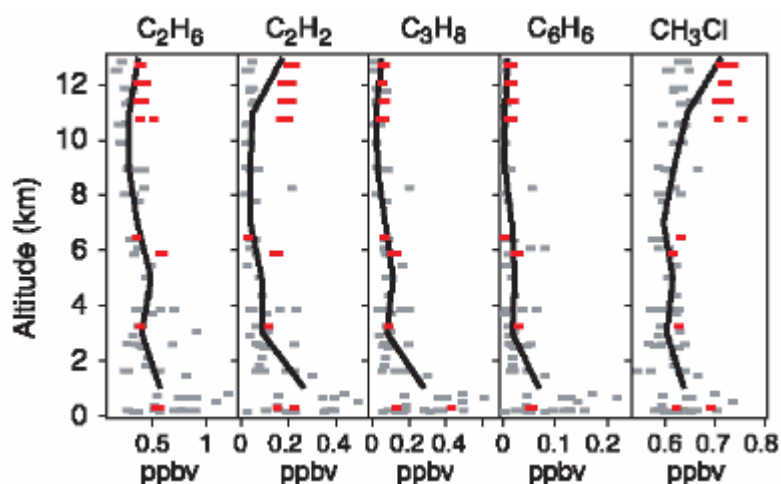


Measured compounds:

CH₄ = methane
CO = carbon monoxide
CH₃OH = methanol
CH₃COCH₃ = acetone
HCHO = formaldehyde



O₃ = ozone
NO = nitrogen oxide
NO_y = oxidised nitrogen compounds without NO, NO₂
PAN = peroxyacetylnitrate
CN = condensation nuclei (particles)



C₂H₆ = ethane
C₂H₂ = acetylene = ethyne
C₃H₈ = propane
C₆H₆ = benzene
CH₃Cl = chloromethane = methyl chloride

2. a-c) Vertical profiles of various organic gases and a few inorganic gases. The values were measured from a research aeroplane over the Mediterranean sea during the MINOS field campaign in August 2001. The strong black lines show the median vertical profiles, the thinner black lines give the standard deviation. Grey squares show values from canister samples. Red dashed lines and red squares are from another flight and give you an idea of how the values vary within a few days. Data and figures from: J. Lelieveld and co-authors.

Gases in the troposphere

Its very difficult to give an overview of the concentrations of trace gases in the troposphere. The same compound can be present at extremely low concentrations, for example, over the ocean and at very high concentrations in the urban environment. There are also many different gases which play an important role in the troposphere. So the following table just gives a few examples of the average mixing ratios near the ground for commonly measured compounds.

Overview of important gases in the free atmosphere:

name	formula	mixing ratio
nitrogen	N ₂	78.08 %
oxygen	O ₂	20.95 %
argon	Ar	0.93 %
water vapour	H ₂ O	0.1 - 4 % = 1,000 - 40,000 ppm
carbon dioxide	CO ₂	372 ppm*
carbon monoxide	CO	50 - 200 ppb
methane	CH ₄	1.7-1.8 ppm*
hydrogen	H ₂	0.5 ppm (480 - 540 ppb)
ozone	O ₃	10 -100 ppb troposph. average: 34* ppb
hydroxy radical	OH	< 0.01 - 1 ppt
nitrogen dioxide	NO ₂	1 - 10 ppb
nitrogen oxide	NO	0.1 - 2 ppb
nitrous oxide	N ₂ O	320 ppb*
nitrate radical	NO ₃	5 - 450 ppt
nitric acid	HNO ₃	0.1-50 ppb
ammonia	NH ₃	< 0.02 - 100 ppb
sulphur dioxide	SO ₂	1 ppb (background) 1 ppm (polluted air)
formaldehyde	HCHO	0.5 - 75 ppb
formic acid	HCOOH	< 20 ppb
acetone	CH ₃ COCH ₃	0.1 - 5 ppb
isoprene	C ₅ H ₈	< 1 - 50 ppb
monoterpenes	-	< 100 ppt
carbonyl sulfide	COS	500 +/- 50 ppt
CFC11	CCl ₃ F	258*
CFC12	CCl ₂ F ₂	546*

*These are gases whose concentrations have increased as a result of human activity and are relatively well mixed over the globe. Data from 2001-2003.

Mixing ratios, concentrations and different units:

Amounts of gases are often given in different units:

concentrations: molecules cm^{-2} or $\mu\text{mol m}^{-3}$

or mixing ratios: ppt (pmol mol^{-1}), ppb (nmol mol^{-1}), ppm ($\mu\text{mol mol}^{-1}$), % (10 mmol mol^{-1})

Mixing ratios are often more helpful for scientists. When air rises, it expands in volume and, as a result, the concentration of the gas changes. The mixing ratio (relative proportion of the gas to the total number of air molecules), however, remains the same.

Conversion from one unit to the other depends on the pressure (= the altitude) and the molecular weight of the compound. If we do the calculation for the surface of the Earth at a normal pressure of about 1 bar we can express the total molecules per volume of air in the following way:

$$1 \text{ mol} = 22.4 \text{ L} = 6 \times 10^{23} \text{ molecules} \Rightarrow$$

$$1 \text{ cm}^3 = 2.7 \times 10^{19} \text{ molecules}$$

$$1 \text{ dm}^3 = 1 \text{ L} = 2.7 \times 10^{22} \text{ molecules}$$

$$1 \text{ m}^3 = 2.7 \times 10^{25} \text{ molecules}$$

A rough estimate:

$2 \mu\text{g m}^{-3} = 2 \times 10^{-6} \text{ g m}^{-3} \text{ NO}_2$ is a typical value for nitrogen dioxide in a non-urban area.

the molecular weight of $\text{NO}_2 = 46 \text{ g mol}^{-1}$

This means: $2 \times 10^{-6} \text{ g m}^{-3} = 4.3 \times 10^{-8} \text{ mol m}^{-3} = 2.6 \times 10^{16} \text{ molecules m}^{-3}$

So the mixing ratio is about $2.6 \times 10^{16} / 2.7 \times 10^{25} = 10^{-9} = 1 \text{ ppb}$

Since ozone has a similar molecular weight, $M(\text{O}_3) = 48 \text{ g mol}^{-1}$, we can also say roughly that;

$2 \mu\text{g m}^{-3}$ of ozone = 1 ppb

This calculation is valid only for surface of the Earth where we live. So for ozone smog events in urban areas we can now calculate:

$120 \mu\text{g m}^{-3} = 60 \text{ ppb} \rightarrow$ high levels

$240 \mu\text{g m}^{-3} = 120 \text{ ppb} \rightarrow$ very high levels, no sports, risky for health

$360 \mu\text{g m}^{-3} = 180 \text{ ppb} \rightarrow$ extremely high levels, very unhealthy for the lungs, stay at home!