Unit 2. Earth's atmosphere

Composition*

The average mixing ratio of the nine principal gases in the dry troposphere is given in Table 1. Because all these gases have lengthy atmospheric residence times, the values are relatively constant at all locations around the Earth.

Table 1. Average composition of the dry troposphere (VanLoon, Duffy, 2010)

Component	Mixing ratio
Nitrogen	78.08%
Oxygen	20.95%
Argon	0.93%
Carbon dioxide	387 ppmv
Neon	18 ppmv
Helium	5 ppmv
Methane	1.77 ppmv
Hydrogen	0.53 ppmv
Nitrous oxide	0.32 ppmv

The most highly variable major gaseous component in the troposphere is water. Its residence time is about 10 days – a period that is much smaller than the time required for complete mixing of the troposphere. It is for this reason that the mixing ratio of water vapour varies from day to day and place to place.

The greenhouse gases and aerosols*

The species that interact with thermal radiation emitted from the Earth's surface are now well known as "greenhouse gases". Their concentrations and contribution to warming are listed in Table 2.

Water

For the Earth, water vapour is actually the most important of all greenhouse gases. While the mixing ratio of water vapour is highly variable in time and space, the global average relative humidity is constant at about 1% and there are no anthropogenic activities that directly cause it to increase to a significant extent. Nevertheless, gaseous water is involved in feedback processes.

Positive feedback occurs in that increased global warming means increased evaporation from ocean and land surfaces leading to higher atmospheric mixing ratios for water – therefore enhanced warming.

Table 2. Past and present greenhouse-gas concentrations in the troposphere, and their contribution to radiative forcing (VanLoon, Duffy, 2010)

Gaseous compound	Tropospheric concentration		Contribution to radiative forcing /
	Before 1750	At present	

			W m^{-2}
Carbon dioxide	280 ppmv	387 ppmv	1.66
Methane	0.70 ppmv	1.774 ppmv	0.48
Nitrous oxide	0.27 ppmv	0.319 ppmv	0.16
Ozone	0.025 ppmv	0.034 ppmv	0.30 (net)
CFC-11	0 pptv	257 pptv	0.34 total for all halocarbons
CFC-12	0 pptv	544 pptv	
CFC-113	0 pptv	80 pptv	
Carbon tetrachloride	0 pptv	94 pptv	
Methyl chloroform	0 pptv	34 pptv	
HCFC-22	0 pptv	146 pptv	
HFC-23	0 pptv	14 pptv	
Perfluoroethane	0 pptv	3 pptv	
Sulphur hexafluoride	0 pptv	4.8 pptv	0.002
Aerosols			-1.2

Note. The contribution to greenhouse warming is usually referred to as increased radiative forcing; this describes the average additional energy in watts per square metre made available to the Earth associated with the increase in concentration of each gas.

Negative feedback results from the troposphere becoming more cloudy leading to increased reflection and absorption of the Sun’s radiation. Because of this, the solar flux reaching the solid / liquid surface of the Earth is reduced.

It is not clear, however, which of these two phenomena will be most important in the future. At present, greenhouse warming associated with water vapour is estimated to be about 110 W m^{-2}; this is also the historic value.

Carbon dioxide

Like water, carbon dioxide is a major contributor to greenhouse warming.

The many natural processes that are sources of carbon dioxide in the atmosphere include animal, plant, and microbial respiration and decay, and combustion of biomass ({ CH_2O}) through forest and grassland fires that are often started by lightning. Equation 1 in the left to right direction describes the overall reaction for all of these processes, recognizing of course that the biological reactions are very complex.

$$\{CH_2O\} + O_2 \leftrightarrow CO_2 + H_2O \quad (1)$$

Regions in the oceans too are important sources of carbon dioxide release to the atmosphere. In the mid latitudes of the Pacific, in particular, upwelling of carbon-dioxide-rich waters causes release of large quantities of the gas.

There are also Earth processes that act as natural sinks. Photosynthesis is one of these and takes place when plants and some microorganisms grow on land and within both oceans and fresh water. The overall reaction, again a summary of very complex steps, is also given by eqn. 1, this time reading from right to left.

Another uptake mechanism is dissolution in sea water where it then circulates in the great ocean currents. An “ultimate” sink for the oceanic dissolved carbonate is its precipitation as calcite (limestone, $CaCO_3$) to form part of the sedimentary material.

Added to the natural sources and sinks, human activities have a significant impact on the global carbon cycle. The anthropogenic contributions are what we hear so much about in news reports. These sources of atmospheric carbon dioxide include carbon release via combustion of fossil fuels and forest destruction and burning. Besides releasing carbon dioxide into the atmosphere, the burning of growing trees eliminates their future contribution to carbon dioxide removal by the photosynthesis reaction.

It is estimated that about 8.0 Gt (as C) of anthropogenic carbon dioxide are released to the atmosphere each year. Three-quarters is from fossil-fuel combustion and the rest from changing land use, primarily in the tropics. About 2.3 Gt (as C) of this are assimilated by dissolution in oceans and the same amount by increased plant growth rates. The remaining 3.4 Gt remain in the atmosphere. While the complex relations between sources and sinks are only partially understood, the net consequence of all the processes involving carbon dioxide is a steady annual increase of about 1.4 ppmv (about 0.5% of the 2009 concentration of 387 ppmv) in the atmosphere.

Methane

The present average tropospheric concentration of methane is 1.774 ppmv and its tropospheric lifetime is about 12 years.

Methane is produced where organic matter is found in an oxygen-depleted highly reducing aqueous or terrestrial environment. For example, it is released from wetlands, including both natural and constructed wetlands as well as cultivated paddy (rice) fields. The amount released is positively correlated with temperature, and is related to vegetation and soil type. Methane is also produced during extraction, transport, and inefficient combustion of fossil fuels. In particular, significant losses occur from leakages in natural-gas pipelines. A third major source is from the digestive tracts of ruminants (cattle, sheep, goats) and termites. Claims have sometimes been made that methane release occurs mostly in low-income countries in the tropics – where the ruminant and termite populations are high and rice production is common.

Recent estimates[1], however, show that these sources together produce only about 30‑40% of released methane. Other sources are not centred in the tropics and some, such as landfills and emissions associated with fossil fuels, are actually in greater abundance in highly industrialized societies. It is interesting that the rate of increase in atmospheric methane levels was about 20 ppbv per year up to 1998, but has since declined to about 8 ppbv per year. To a large degree this is attributed to improved maintenance on gas wells and pipelines in the countries of the Commonwealth of Independent States (CIS, States of the former Soviet Union).

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[1] CO_2 / Climate report / Canadian Climate Centre, Atmosphere Environment Service. Downsview, Ontario, 1998. Issue 98‑1.

The principal sink for methane decomposition is oxidation via hydroxyl radicals in the troposphere.

$$\mathrm{CH_4 + OH \rightarrow \underset{\substack{\downarrow \\ \text{other reactions}}}{CH_3} + H_2O} \quad (2)$$

Smaller amounts of methane are removed from tropospheric air when taken up by soils and by leakage into the stratosphere.

Ozone

Ozone acts as a highly efficient greenhouse gas. Greater production of NO_x by fossil-fuel burning and forest and grassland fires has resulted in net low-altitude ("bad") ozone concentrations increasing by about 1.6% per year in the Northern Hemisphere. The increased absorption of infra-red (IR) radiation contributes to warming, but this is partly offset by the decrease in concentration of ozone in the stratosphere. Ozone mixing ratios are highly variable in space and time, as would be expected from our discussion of urban air quality; its globally averaged mixing ratio is estimated to be 34 ppbv. The ozone radiative-forcing contribution in the troposphere is approximately 0.35 $W\ m^{-2}$; that due to stratospheric ozone is –0.05 $W\ m^{-2}$ resulting in net radiative forcing of 0.30 $W\ m^{-2}$.

Nitrous oxide

Some nitrous oxide is released from industrial processes such as the production of adipic acid and nitric acid. The major sources, however, are from microbial denitrification in soils, lakes, and oceans. Denitrification is a term describing a group of microbiological reactions that convert nitrate to nitrous oxide, along with other nitrogen species. While denitrification is usually termed a natural process, it can be enhanced by human activities. With increased application of nitrogenous fertilizer, including animal manure, the supply of the nitrate substrate required for denitrification is augmented, leading to the production of more nitrous oxide. The amount released from soils is also greater where temperature and soil-moisture levels are high and where oxygen has been depleted. Additional emissions of nitrous oxide are produced from urban waste-landfill sites, and where there is direct sewage disposal into large bodies of water. The influx of this and other types of organic matter leads to emissions from the oceans especially in coastal regions and estuaries. There are no important tropospheric sinks for this gas, so it is lost only by slow leakage into the stratosphere where it undergoes photolytic degradation; it therefore has a substantial tropospheric residence time estimated to be about 120 years. It has approximately the same effect on greenhouse warming as does ozone.

Chlorinated fluorocarbons (CFCs) and other halogenated gases

In addition to their role as agents for the catalytic decomposition of stratospheric ozone, CFCs are also important greenhouse gases. The recently developed hydrochlorofluorocarbons (HCFCs) also attenuate radiation within the same range, but their residence time in the troposphere is substantially shorter than the CFCs.

Three fully fluorinated gases of industrial origin have recently come to the fore as potentially important contributors to greenhouse warming. They are present in trace amounts, but have lifetimes of thousands or tens of thousands of years. Tetrafluoromethane (CF_4) and hexafluoroethane (C_2F_6) both arise during electrolysis of alumina (Al_2O_3) in cryolite (Na_3AlF_6) at carbon electrodes, and release of the gases is estimated to be about 0.77 and 0.1 kg, respectively, per tonne of aluminium produced. Together, their atmospheric concentration is approximately 0.08 ppbv. The other gas is sulphurhexafluoride (SF_6), which has no natural source and is formed during magnesium production. The atmospheric mixing ratio of sulphurhexafluoride is increasing at the rapid rate of about 5% per year. With such extraordinarily long atmospheric lifetimes, there is no practical means by which the amounts of these fluorinated compounds could be reduced within any reasonable time period.

Aerosols

Clouds are the most important atmospheric aerosol in terms of reflecting and absorbing incoming radiation and emitted radiation from the Earth. The cooling effects of clouds on warm days, and their warming effects on cool nights are phenomena we all have recognized. Other aerosols, too, add to the complexities of the global energy balance situation. In particular, ammonium sulphate and other sulphate-based solid aerosols are becoming increasingly important. The sulphate aerosol derives from natural oceanic sulphide, particularly dimethyl sulphide emissions, as well as from anthropogenic sources of sulphur dioxide. In the Northern Hemisphere, about 90% results from human activities, while in the South most has a natural origin. Besides its direct role in backscattering incoming shortwave solar radiation, the presence of sulphate in the aerosol also affects processes of cloud formation. The net result of the direct and indirect processes is complex and varies from region to region but, overall, sulphate aerosols contribute to a negative global radiative forcing and therefore a measure of atmospheric cooling. Sulphate particulates that are periodically injected by volcanoes into the stratosphere also contribute to cooling of the troposphere.

Some biomass aerosols derive from combustion, with the release of fine smoke and soot, often called black carbon, into the atmosphere. Their extent varies around the globe and from year to year. Recent years, especially 1997–98, have seen increased incidents of widespread biomass burning in countries like Malaysia and Indonesia, as well as in parts of North America. The higher average global temperature in those years may have contributed to drying of forested areas and greater opportunities for fires to ignite and spread. In recent years, there is also clear indication of reduced industrial emissions emanating from Europe and Russia, but this appears to be offset by the increased emissions from countries in the South.

In contrast to the sulphate-based aqueous aerosols, the dark particles add to the positive radiative forcing of greenhouse gases. In some parts of South-east Asia, the local warming reduces daytime cloud cover, further enhancing the heating effects. Aerosols of industrial origin are also largely combustion based, and are usually found in the lower (<2 km) parts of the troposphere. Because they are readily washed out with precipitation, they have small atmospheric residence times, of the order of a few days, so their contribution to greenhouse warming is local and short-lived.

The radiative forcing associated with atmospheric aerosols is estimated to be –1.2 W m^{-2}.

*Extracts from the book of VanLoon G.W. and Duffy S.J. "Environmental chemistry: a global perspective", 2010.

Task

1) *Enumerate green house gases and give the characteristic of one of them*.
2) D*escribe the picture, based on the information from the text*.

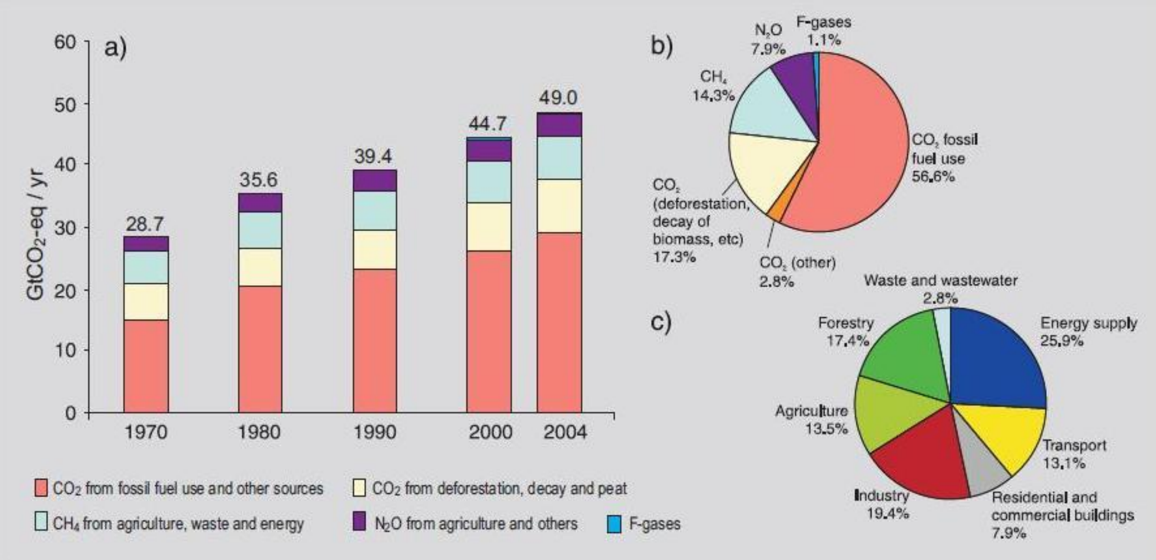

Figure 2. (a) Global annual emissions of anthropogenic GHGs from 1970 to 2004. (b) Share of different anthropogenic GHGs in total emissions in 2004 in terms of CO2-eq. (c) Share of different sectors in total anthropogenic GHG emissions in 2004 in terms of CO2-eq. (Forestry includes deforestation.) Redrawn from Climate change 2007: Synthesis report (Intergovernmental panel on climate change, WMO, UNEP).