Lesson 1
INTRODUCTION TO AIR POLLUTION

2016

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1.1. CONCEPTS

AIR POLLUTION is "an atmospheric condition in which substances are present at concentrations higher than their normal ambient levels to produce measurable adverse effects on humans, animals, vegetation, or materials" *Seinfeld, 1986*

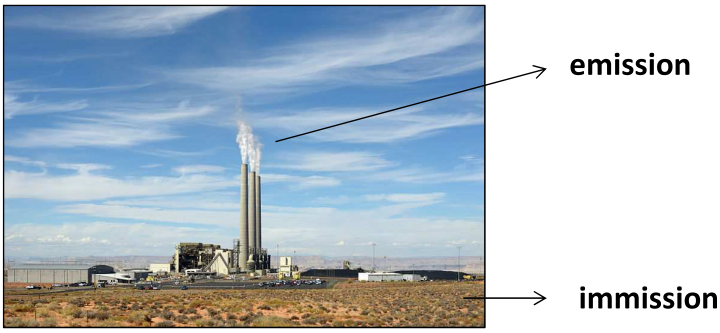
AIR POLLUTION is "the presence of materials, substances or energy-sources in the air that can harm public health, ecosystems, crops, materials or anything that society values" *Spanish Law 34/2007 on Air Quality and Protection of the Atmosphere*

"The Blue Marble 4463x4163" by NASA licensed under Public Domain

Pollutants are emitted into the **atmosphere.**

Because the atmosphere is a highly mobile fluid, it is unconfined and its motion is random, air pollution is a highly complex subject.

EMISSION is the continuous or discontinuous **release** of substances or energy from a source into the environment



"Navajo generating station" by W. Moroder licensed under CC BY-SA 3.0

IMMISSION relates to the effects of emissions on the environment. It expresses the **concentration** of the pollutants in ambient air for a given period of time.

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Harmful substances can be emitted to the atmosphere from either **natural** or **human sources**. Although industrialization and the use of motor vehicles are overwhelmingly the most significant contributors to air pollution, there are important natural sources of pollution as well.

Anthropogenic sources

"Factory in China" by High Contrast licensed under CC BY 2.0

Natural sources

"Mount Redoubt eruption" by R. Clucas licensed under Public Domain

NATURAL SOURCES mean "emissions of pollutants not caused directly or indirectly by human activities, including natural events such as volcanic eruptions, seismic activities, geothermal activities, wild-land fires, high-wind events, sea sprays or the atmospheric re-suspension or transport of natural particles from dry regions" *Directive 2008/50/EC of 21 May 2008 on ambient air quality and cleaner air for Europe*

Contributions from natural sources can be predicted and assessed but cannot be prevented or completely controlled.

Elements of Air Pollution

In air pollution problems the following 3 elements can always be found:

"SO_2 emissions from the Halemaumau" by Brocken Inaglory licensed under CC BY-SA 3.0

The places from which pollutants emanate are called **SOURCES**.

Pollutants are emitted to the atmosphere by a range of sources. They are classified as:

1. ORIGIN

- **Natural sources**: not caused directly or indirectly by human activities such as volcanoes, dust storms, oceans,…
- **Anthropogenic sources**: caused by human activities such as automobiles, heating systems, industrial processes,…

2. MOBILITY

- **Fixed or stationary sources:** sources that do not move such as factories, power plants, …
- **Mobile sources:** sources capable of moving under their own power such as automobiles, airplanes, trains, ships...

3. GEOMETRY

- **Area sources**: many small sources of air pollution located together such as residential wood burners.
- **Linear sources**: idealized geometric emitters, which can be represented by a simple line such as a roadway, railway or aircrafts.
- **Point sources:** single, identifiable sources which are located by the geographic coordinates such as power stations, oil refineries, paper mills,…

4. CONTROL/ MANAGEMENT

- **Controlled emissions**: identified and managed sources
- **Fugitive, uncontrolled** or **diffuse emissions**: emissions escaping from regulated processes.

The atmosphere serves as the **MEDIUM** through which air pollutants are transported and transformed, both by **physical and chemical reactions**.

Transport is the mechanism that moves the pollution from a source to a receptor. The **wind** is the means by which the pollution is transported from a source to a receptor. However, during this transit from a source to a receptor, due to **diffusion, mixing by turbulence** and **some other processes** (gravitational settling or wet removal), tend to make the concentration of the plume as it arrives at the receptor less than its concentration on release.

In addition to removal by physical processes, it can undergo **chemical transformations.** Oxidation is a prime chemical transformation from organic as well as inorganic gases.

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Sooner or later, the pollutants are removed from the atmosphere.

The places from which pollutants disappear from the air are called **SINKS**.

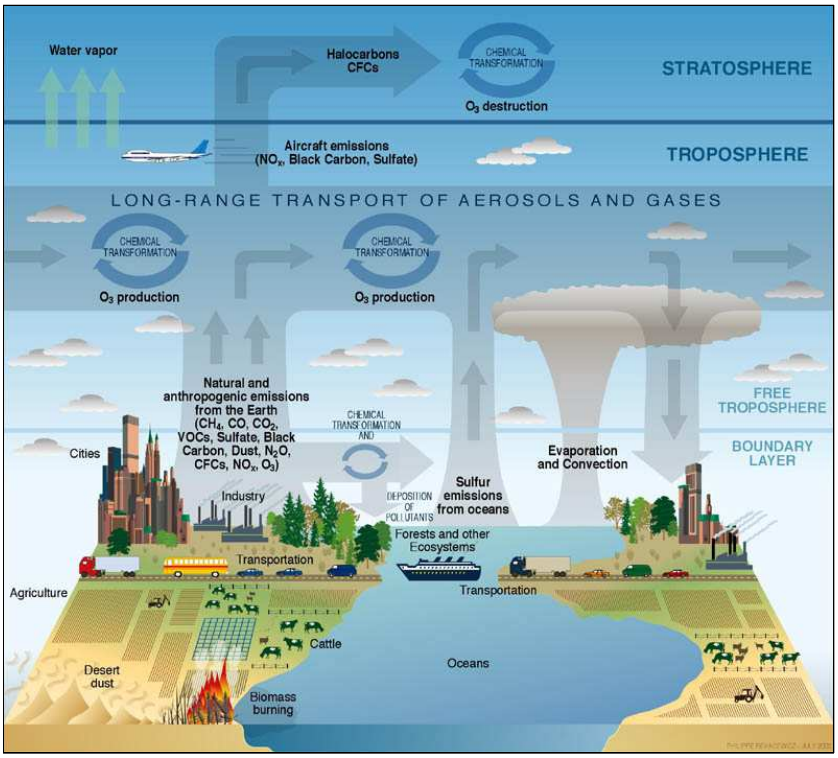
Sinks include soil, vegetation, structures, and water bodies.

A **RECEPTOR** is something which is adversely affected by polluted air.

A receptor may be a person or animal that breathes the air. It may be a tree or a plant that dies. It may also be some material such as leather, cloth, metal, stone or paint adversely affected.

The location of receptors relative to sources and atmospheric conditions affect the **dose** received; the sensitivity of receptors to these doses determines the **effects.**

It is quite usual to associate air pollution simply with urban and industrial areas; however, due to long-range transport and emissions from natural sources, air pollution is present everywhere.



“Atmosphere composition diagram" by US Climate Change Science Program Office licensed under Public Domain

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The measurements used for the aging of a pollutant are the half-life and lifetime.

HALF-LIFE ($t_{1/2}$) is the time it takes for one-half of the quantity of a pollutant emitted from a source to disappear into its various sinks.

LIFETIME (ζ) is defined as the time it takes for quantity of a pollutant emitted from a source to fall to 1/e of its initial value.

Both are related to the rate constant and to the concentration of any other reactants involved in the reactions. These relationships are given in a general form in the next table for 1st and 2nd order reactions:

Relationship between the rate constant, half-lives and lifetimes for first- and second-order reactions

Reaction order	Reaction	Half-life of A	Lifetime of A
First-order	$A \overset{k_1}{\rightarrow} Products$	$t^A_{(1/2)} = 0.693 / k_1$	$\zeta^A = 1 / k_1$
Second-order	$A + B \overset{k_2}{\rightarrow} Products$	$t^A_{(1/2)} = 0.693 / k_2 [B]$	$\zeta^A = 1 / k_2 [B]$

Imagine that we could follow all the individual molecules of a substance emitted into the air…. some might be removed close to their point of emission… others might get carried high into the atmosphere and be transported a great distance before they are ultimately removed. Averaging the life histories of all molecules of a substance yields an **average lifetime** or **average residence time** (t_R) for that substance.

If the rate of injection of all the sources of the substance is balanced by its sinks (*S*=*F*), the total mass of the substance (*M*) does not change with time.

Under these steady-state conditions, the average lifetime or average residence time is given by:

$$t_R = \frac{M}{F}$$

Where: *M*= substance concentration in the atmosphere [M]
F = rate of removal [M·T^{-1}]
S= rate of introduction from sources [M·T^{-1}]

Depending on their atmospheric lifetime, pollutants can exhibit an enormous range of spatial and temporal variability.

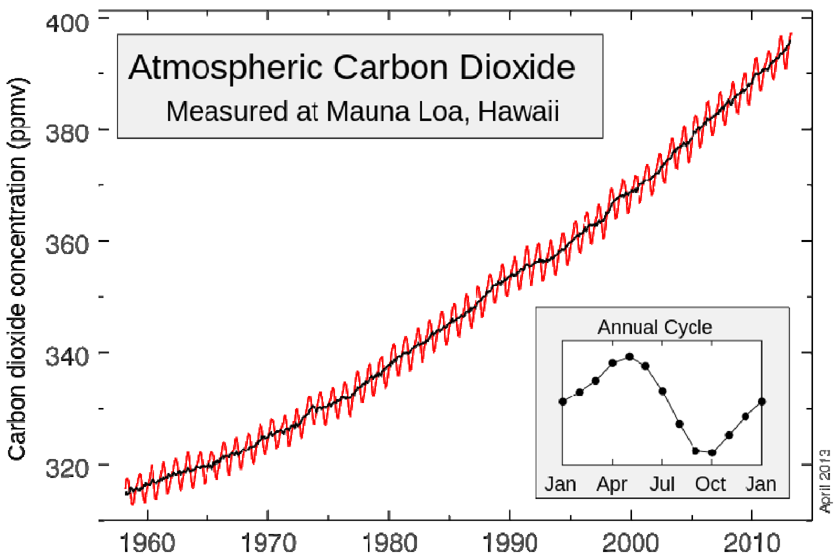
Long-lived species

Short lived species

Relatively long-lived species are uniformly distributed. As species' lifetimes become shorter, their spatial and temporal distributions become more variable.

Fortunately, most pollutants have a short enough residence time (**hours -10 days**) to prevent their accumulation in the air. However, several gases do appear to be accumulating in the air to the extent that measurements have documented an increase in their concentration from year to year. The best known example is CO_2.

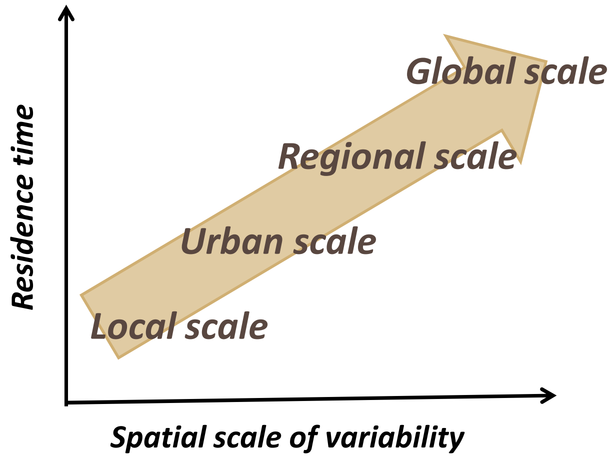
The data from Mauna Loa (Hawaii) show that even in the 1950s the CO_2 concentration had increased from the baseline of **280 ppm** to **315 ppm.** This has continued to climb over the last 50 years at a nearly constant rate of **1.6 ppm·year^{-1}**.



"Mauna Loa carbon dioxide" by Narayanese, Sémhur and NOAA licensed under CC BY-SA 3.0

1.2. SCALES OF AIR POLLUTION

Air pollution phenomena are decisively influenced by **atmospheric processes** which are commonly classified with regard to their spatial and temporal scale.



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1. LOCAL SCALE

The characteristic length is below **5 km.** Thus, the sources and receptors can be easily identified.

In general, air flow is very complex at this scale, as it depends strongly on the surface characteristics: topography, buildings,…

On this scale, the negative effects can be reduced or eliminated by controlling the sources of pollution.

For example, carbon monoxide (CO) emitted from motor vehicles, leads to high concentrations near roadways, with concentrations generally diminishing with distance. The reduction of traffic density or the substitution of conventional vehicles with electric vehicles would contribute to a reduction in the emissions.

“Bangkok traffic jam" by G. Longman licensed under CC BY 2.0

2. URBAN SCALE

This scale extends to the order of **50 km** horizontally and **1-2 km** vertically. In urban areas, pollution events and episodes can be registered when the meteorological conditions slow down ventilation.

Air pollution problems are generally of two types: 1) the release of primary pollutants such as carbon monoxide and nitrogen oxides (NO_x) and 2) the formation of secondary pollutants.

Tropospheric ozone (O_3) is the dominant urban problem resulting from the formation of secondary pollutants. Many metropolitan areas experience the formation of ozone from photochemical reactions of oxides of nitrogen and various species of hydrocarbons.

“Photochemical smog in Mexico city" by F. Gonzalez licensed under CC BY-SA 3.0

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3. REGIONAL SCALE or MESOSCALE

The characteristic lengths are between **50 km** and **1000-2000 km**.

At least two types of problems contribute to pollution at this scale. 1) The blend of urban oxidant problems and 2) the relative slow-reacting primary pollutants undergo reactions and transformations worsening the air quality of background and remote areas.

Sulfur dioxide (SO_2) and nitrogen oxides (NO_x) released through combustion of fossil fuels are oxidized during long-distance transport. These oxides react with water vapor to form sulfuric acid (H_2SO_4) and nitric acid (HNO_3) and, then to sulfate (SO_4^{2-}) and nitrate (NO_3^-) particles. These particles can precipitate and contribute to **acid rain.**

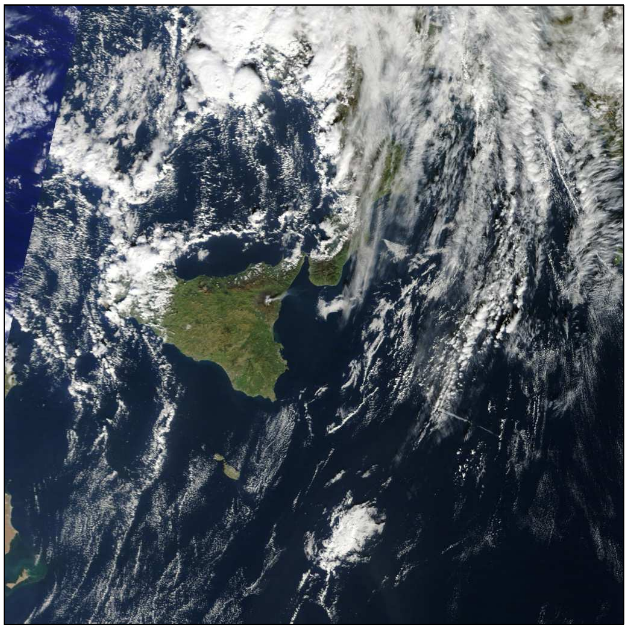
“Acid rain woods“ in Jizera Mountains (Czech Republic) by Nipik licensed under Public Domain

“Acid rain damaged gargoyle" by N. Barbieri licensed under CC BY 2.5

4. GLOBAL SCALE

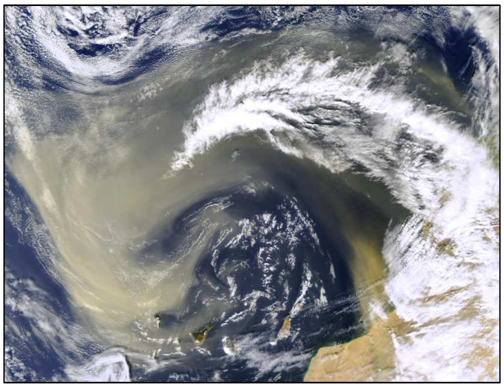
This scale extends **worldwide**. The atmospheric flow is associated with synoptic phenomena. Several observations demonstrate the effects of this long-range transport :

- Polychlorinated biphenyls (PCBs) observed in arctic mammals, thousands of miles from their sources.
- Chlorofluorocarbons (CFCs) used as propellants in spray cans and their effect in the ozone layer high in the atmosphere.
- Climate change generated by excessive amounts of greenhouse gases (GHG), especially methane (CH_4) and carbon dioxide.
- Distribution in the stratosphere of gases and aerosols from explosive volcanic eruptions

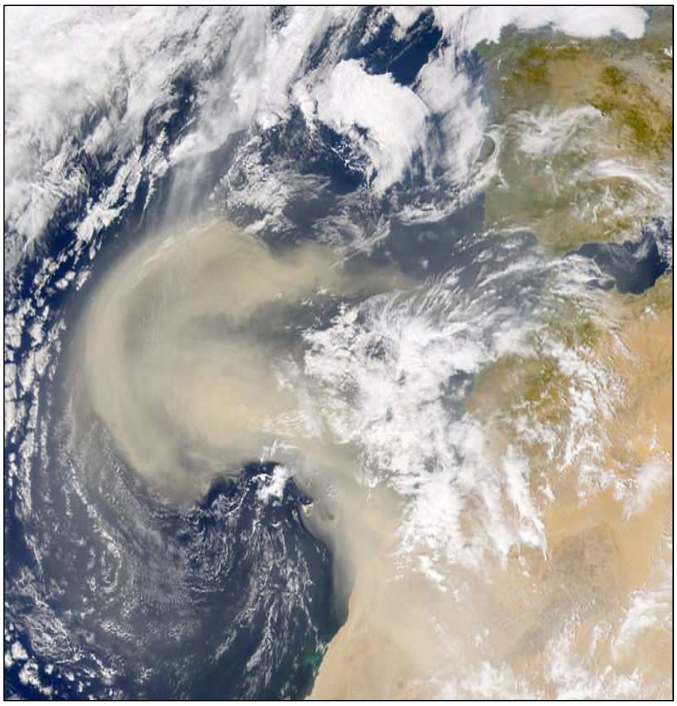


"January 2011 activity at Mt Etna" by MODIS Rapid response team under Public Domain

"Eruption of Eyjafjallajökull Volcano (Iceland) in 2010" by MODIS Rapid response team under Public Domain



"Saharan dust off Canary Islands" by NASA under Public Domain



"2000-Feb-26 NASA SeaWiFS African Dust Storm" by N. Kuring SeaWiFS under Public Domain

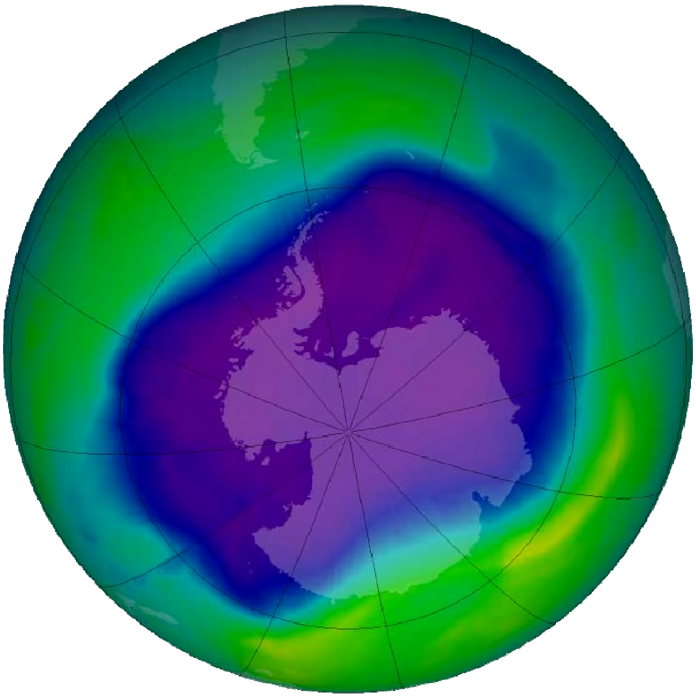


Image of the largest Antarctic ozone hole ever recorded (September 2006), over the Southern pole by NASA under Public Domain

1.3. PRIMARY AND SECONDARY POLLUTANTS

PRIMARY AIR POLLUTANTS are emitted directly into the atmosphere from sources.

A substantial portion of the gas and vapors emitted to the atmosphere tends to be relatively simple in chemical structure.

Examples
- Carbon dioxide (CO_2)
- Carbon monoxide (CO)
- Sulfur dioxide (SO_2)
- Nitrogen monoxide (NO)
- Hydrogen sulfide (H_2S)
- Ammonia (NH_3)
- Chlorhidric acid (HCl)

Chemical reactions may occur among the primary pollutants and the constituents of the unpolluted atmosphere.

The pollutants manufactured in the air are called **SECONDARY POLLUTANTS.**

They are not directly emitted but they form when primary pollutants react in the atmosphere.

Example Ozone (O_3)

It is the result of the reactions between the nitrogen oxides (NOx) and Volatile Organic Compounds (VOC) in the presence of solar radiation.

The primary pollutants that react are termed the **PRECURSORS** of secondary pollutants.

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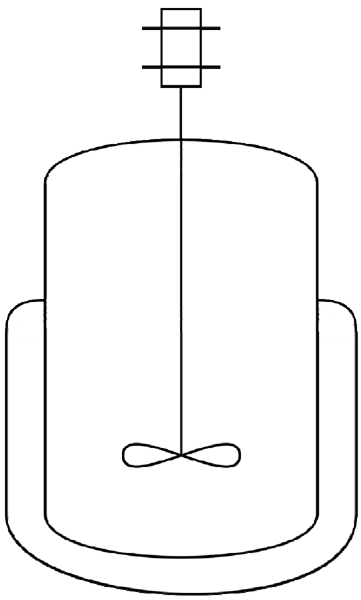
The atmosphere must be viewed as a **reaction vessel** into which reactable constituents are poured and in which a tremendous array of new chemical compounds, generated by gases and vapors reacting with each other and with the particles in the air, are produced.



Reactor by Laurent under Public Domain in openclipart

The concentration of the criteria pollutants in the ambient air is referred to as **ambient air quality**.

AMBIENT AIR QUALITY STANDARDS prescribe pollutant levels that cannot legally be exceeded during a specific time period in a specific geographic area.

The most recent report of the European Environmental Agency (EEA) about 'Air quality in Europe' affirm that *"Despite falling emission levels and reductions of some air pollutant concentrations in recent decades, air pollution problem is far from solved. Two specific pollutants, particulate matter and ground-level ozone, continue to be a source breathing problems, cardiovascular disease and shortened lives"*

European Environment Agency

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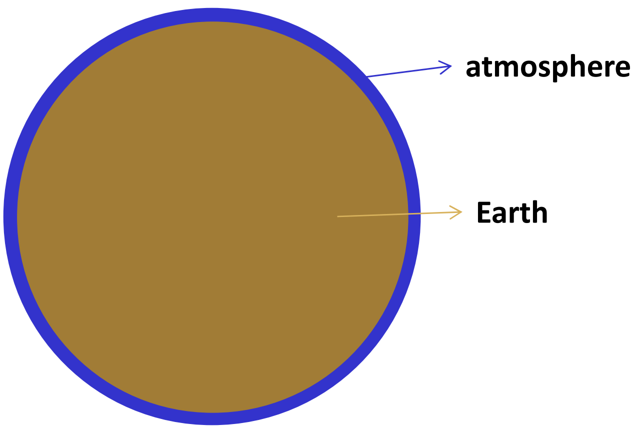
1.4. ATMOSPHERE

The **atmosphere** composes the layer of mixed gases covering the Earth's surface. Compared with the average radius of the Earth (6370 km), it is an incredibly thin layer.

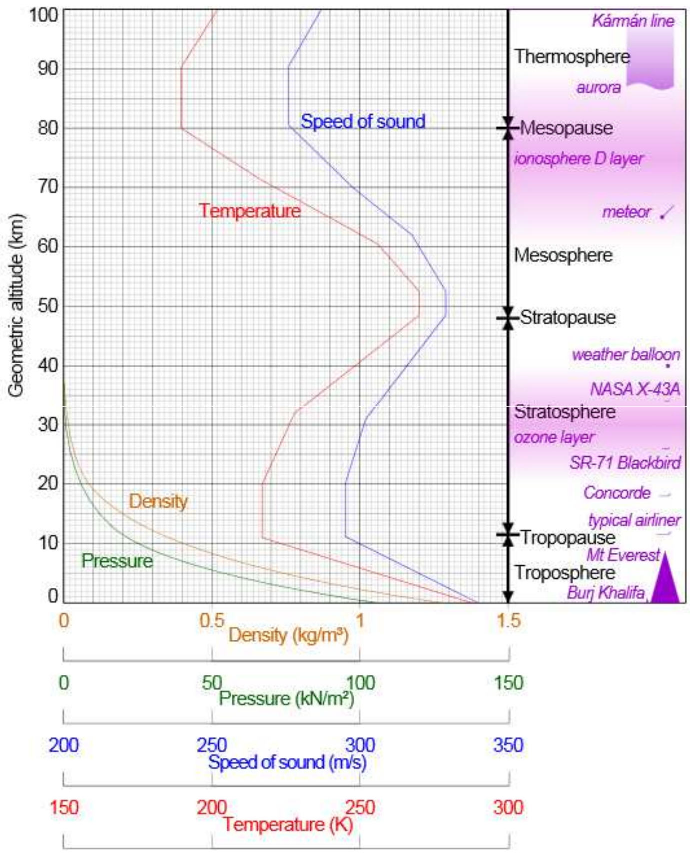


Structure of the atmosphere

The Earth's atmospheric **pressure** (density) varies with altitude, as does the **temperature**. Next figure shows the standard profiles of air pressure and temperature.

Pressure (density) decreases exponentially with increasing altitude; from an average of 1013 mb at the Earth's surface to 140 mb at 14 km. More than 99% of the total mass of the atmosphere is found within approximately 20 km of the Earth's surface.

Based on temperature, the atmosphere is divided into four layers: Thermosphere, Mesosphere, Stratosphere and Troposphere.



"Comparison standard atmosphere 1962" by Cmglee under CC BY-SA 3.0

1. Thermosphere > 85 km

Temperature increases with increasing altitude because O_2 and N_2 absorb very short ultraviolet wavelengths.

2. Mesosphere 50-85 km

Within this region temperature decreases with altitude.
Absorption and scattering of solar radiation.

The ionosphere and mesosphere are of interest to space scientists because they must be traversed by space vehicles en route to/from the moon/planets; they are also regions in which satellites travel in the Earth's orbit. In addition, these two regions are of interest to communications scientists because of their influence on radio communications. But these layers interest air pollution scientists primarily because of their absorption and scattering of solar energy.

3. Stratosphere 12-50 km

This layer features a large temperature inversion. It is caused by ozone, which absorbs harmful ultraviolet radiation. Ozone densities peak at at 25-32 km (**ozone layer**).
The stratosphere is of interest to aeronautical scientists because it is traversed by airplanes and to air pollution scientists because of global transport of air pollution, such as the debris of atomic bomb tests or volcanic eruptions.

4. Troposphere 10-12 km

The troposphere is the layer of the atmosphere closest to the Earth's Surface. It extends from the surface to the tropopause. It is characterized by a generally increasing temperature with increasing altitude. This layer is the **primary focus of air pollution**.

The lowest layer of the troposphere is called the atmospheric boundary layer.

Atmospheric Boundary Layer (ABL) is the part of the troposphere that is directly influenced by the presence of the Earth's surface, and responds to surface forcing with a time scale of about an hour or less

Characteristics

- It is ≈ 1000-1500 m deep, but can vary
- Its temperature varies diurnally, unlike the Free Atmosphere above
- It is influenced by surface friction and by heat fluxes
- It is characterized by turbulence

Composition of the atmosphere

The average gaseous composition of unpolluted tropospheric air is given in next table. Exclusively of water, atmospheric air is 78% nitrogen, 21% oxygen, 0.9% argon and 0.03% carbon dioxide.

Unpolluted air or **clean air** is a theoretical concept; what the composition of the air would be if humans and their influences were not on Earth. We will never know the precise composition of unpolluted air because by the time we had the means and the desire to determine its composition, humans had been polluting the air for thousands of years. Now, even at the most remote locations at sea, at the poles, and in the deserts and mountains, the air may be best described as **dilute polluted air**.

The gaseous composition of unpolluted or clean air (dry base)
(T=293.15 K, P=101325Pa)

	ppm (mL/m^3)	µg/m^3
N_2	780840	$9.085 \cdot 10^8$
O_2	209460	$2.78 \cdot 10^8$
H_2O	-	-
Ar	9340	$1.55 \cdot 10^7$
CO_2	379	$6.93 \cdot 10^5$
Ne	18.18	15245
He	5.24	872
CH_4	1.7	1130
Kr	1.0	3482
N_2O	0.3	549
H_2	0.5	42
Xe	0.08	436
Org. vapours	0.02	-

Energy balance

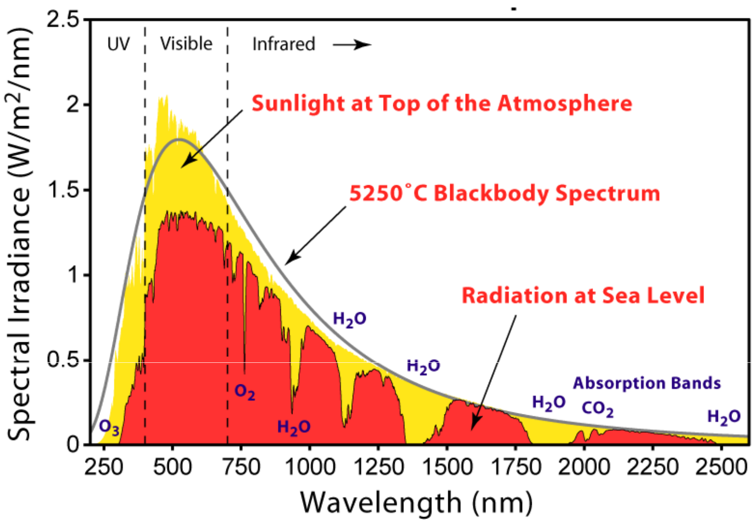
The Earth receives most of its energy from the sun.

The total solar flux is $3.9 \cdot 10^{26}$ W.

The sun radiates nearly as a blackbody with an effective temperature of 6000 K. Using **Wien's Law**, it has been found that the maximum intensity occurs at **0.5 µm** (**VIS**).

$$\lambda_{max}(\mu m) = \frac{2898}{T\ (K)}$$

Where λ =wavelength
T= temperature of the body



"Solar spectrum" by BetacommandBot under CC BY-SA 3.0

The intensity of this energy flux at the distance of the Earth is about 2 cal·cm^{-2}min^{-1} on an area normal to a beam of solar radiation, approximately, ≈ 1370 W·m^{-2}. This value is called the **solar constant**.

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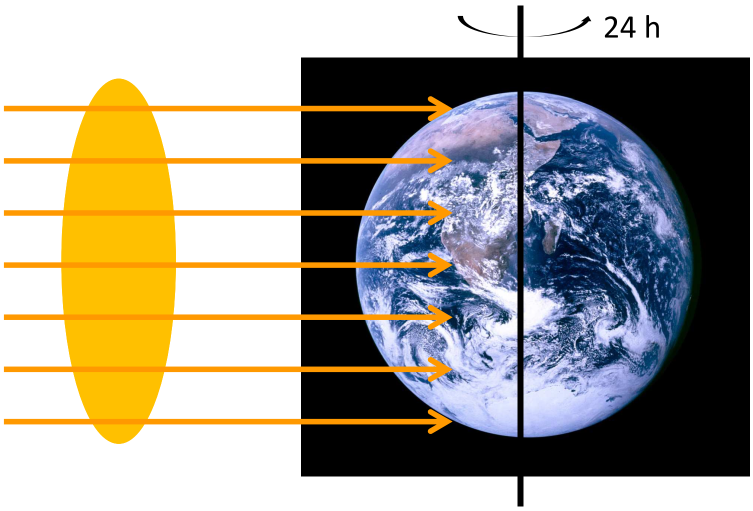
Since the area of a solar beam intercepted by the Earth is ΠR^2, where R is the radius of the Earth, and the energy falling within this circle is spread over an area of the Earth's sphere ($4\Pi R^2$), the average energy reaching the top of the atmosphere is ≈ **342 W·m^{-2}d^{-1}**



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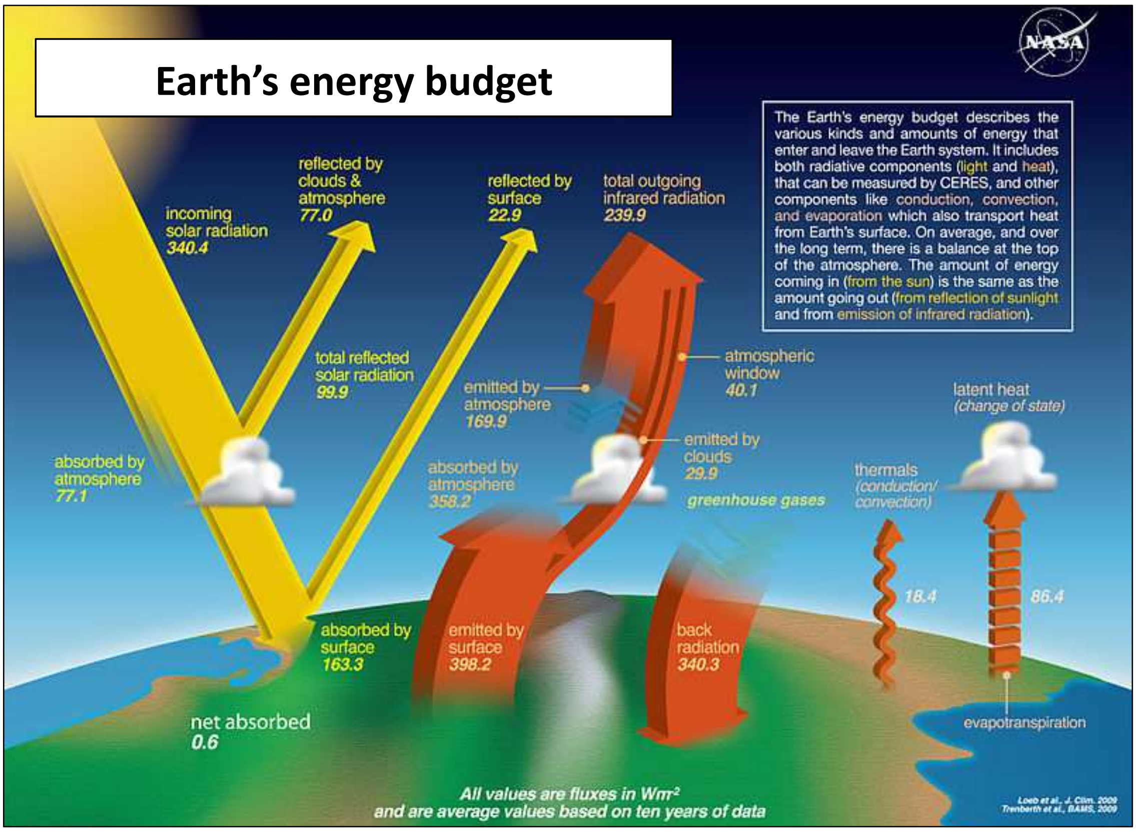
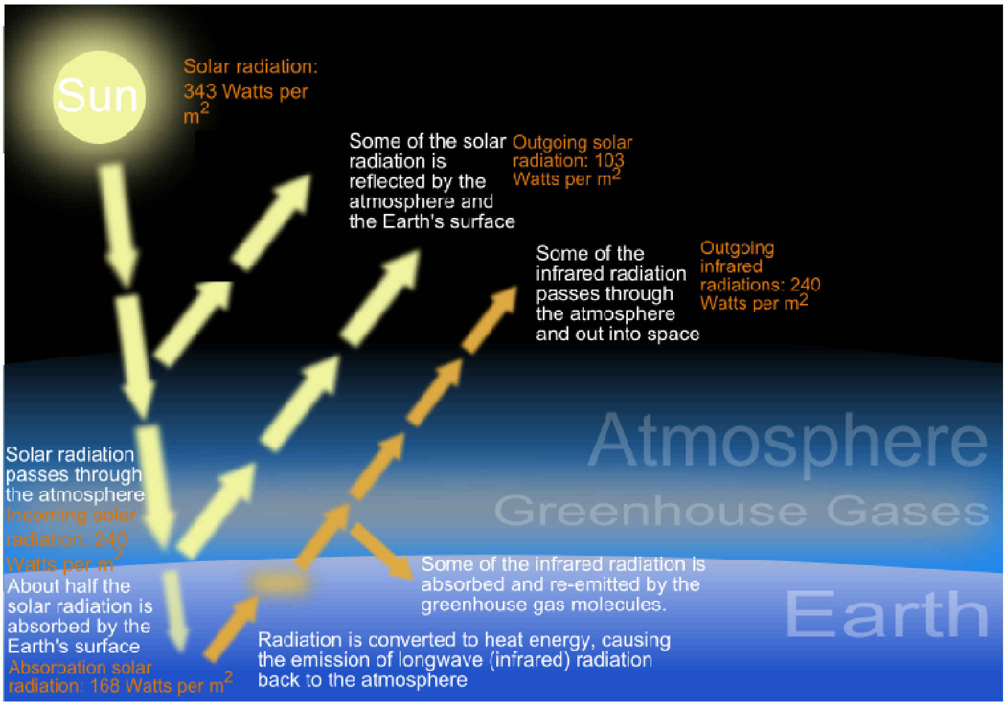


The Earth's energy budget by NASA licensed under Public Domain

This average radiant energy reaching the outer limits of the atmosphere is depleted as it attempts to reach the Earth's surface, by absorption by molecular oxygen, ozone and water vapor, scattering and reflection to space by clouds. With average cloudiness, about the 50% of the incoming radiation (≈ **168 W·m^{-2}**) reaches the Earth's surface. Because most ultraviolet radiation is absorbed, the peak of solar radiation which reaches the Earth's surface is in the **visible** part of the spectrum.

The Earth re-radiates as a blackbody at a mean temperature of 290 K. The resulting **infrared** radiation extends over wavelengths of 3-8 µm, with a peak around **10-11 µm**. As this radiation tries to reach outer space, water vapor and several gases in the atmosphere absorb and reemit it.

This natural effect is referred as the **greenhouse effect.**

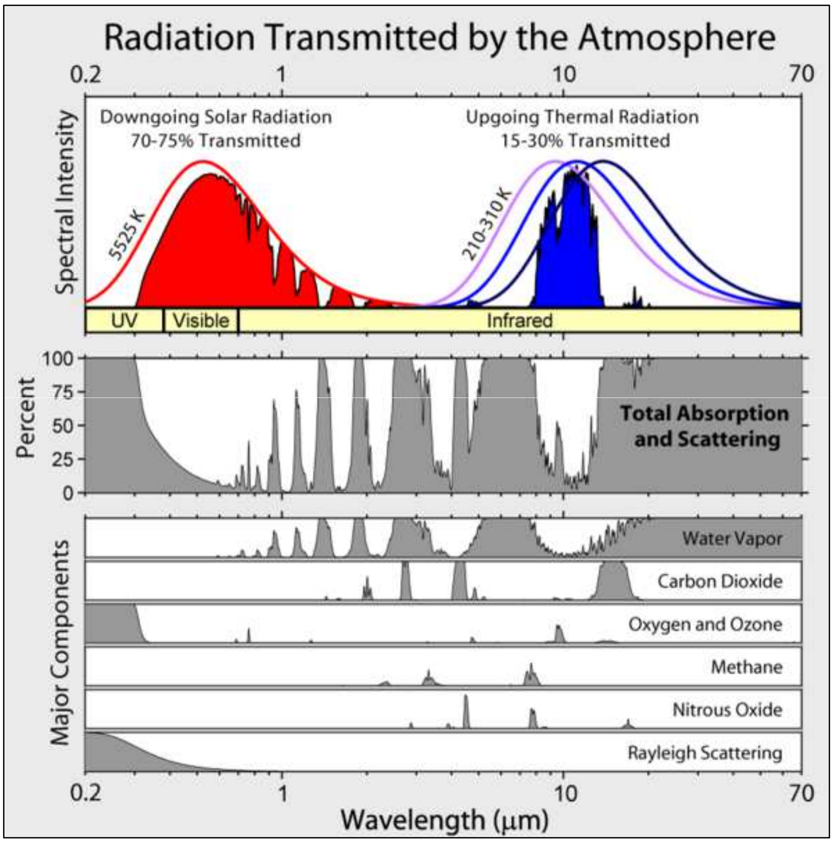


The greenhouse effect by ZooFari licensed under CC BY-SA 3.0.

The gases with absorptive wavelengths in the spectrum of the **terrestrial** radiation, but transparent to most of the **solar** radiation, are called **GREENHOUSE GASES (GHG)**

Without this natural greenhouse effect, the Earth's temperature would be much cooler (≈ -18ºC) than it is in the present time and it would not support most life on Earth.

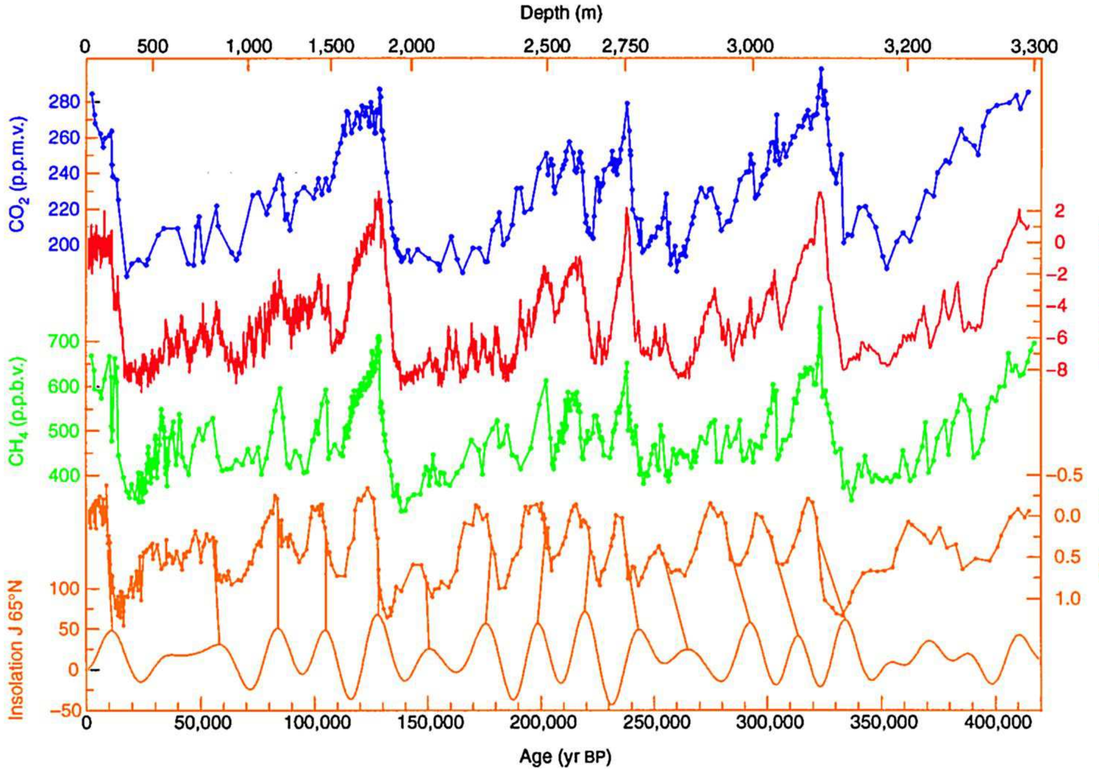
Curiously, the molecules which both solar radiation (O_3 and water vapor) and terrestrial radiation (water vapor, CO_2 and O_3) more intensely, are the less abundant ones. Quite obviously, a slight increase in the concentration of any of these GHG greatly limits the amount of heat transmitting into space, thus promoting the **warming** of the atmosphere and **climate change**.



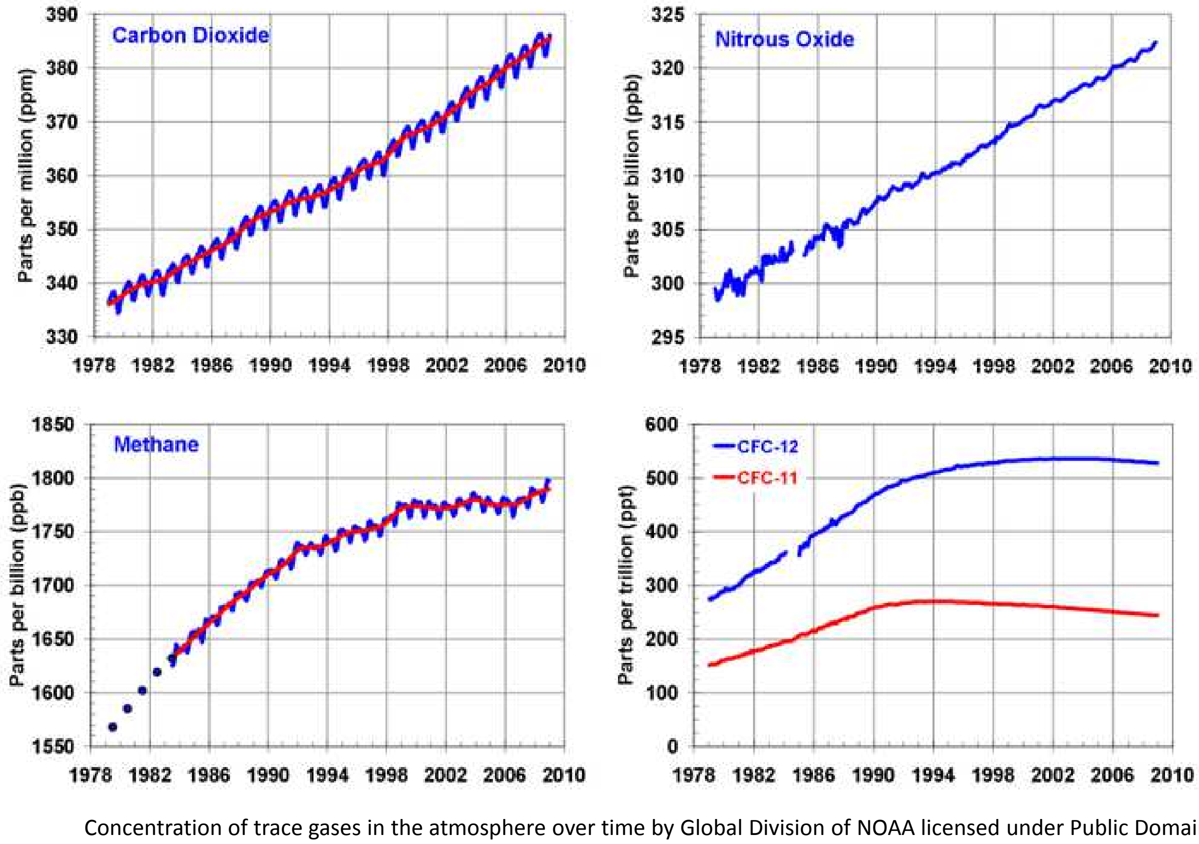
“Atmospheric transmission" by BetacommandBot licensed under CC BY-SA 3.0

The warmer temperatures that we experience on Earth surface are due to an increasing concentration of the GHG.

Ice cores have been drilled to examine the variation of the composition of the air trapped in bubbles in the ice representing global atmospheric conditions as much as 1000 years ago. Atmospheric concentrations of CO_2 and CH_4 in the microscopic bubbles of air trapped in the ice cores correlate well with the Antarctic air temperature throughout the record. This correlation indicates that these two gases may have contributed significantly to the glacial-interglacial changes over this period.



51 Concentrations of CO_2 and CH_4, insolation and air temperature at Vostok station (Antartica) during the last four glacial-interglacial cycles by P. Kuiper under Public Domain



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Concentration of trace gases in the atmosphere over time by Global Division of NOAA licensed under Public Domain

According to **Intergovernmental Pannel on Climate Change** (IPCC) “Global atmospheric concentrations of CO_2, CH_4 and N_2O have increased markedly as a result of human activities since 1750 and now far exceed pre-industrial values”.

“Most of the observed increase in global average temperatures since the mid-20th century is very likely due to the observed increase in anthropogenic GHG concentrations; mainly, CO_2, CH_4, N_2O and fluorinated gases”.

The panel stated that “warming of the climate system is unequivocal, as is now the evident from observations of increases in **global average air and ocean temperatures**, widespread **melting of snow and ice** and **rising global average sea level**.”

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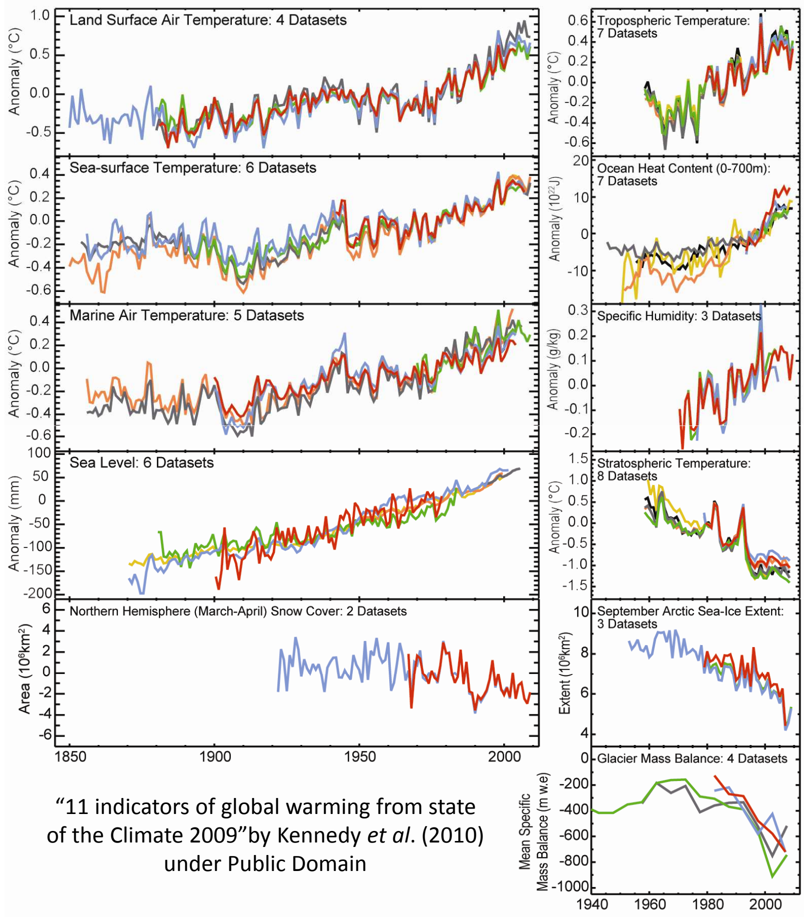

“11 indicators of global warming from state of the Climate 2009”by Kennedy *et al*. (2010) under Public Domain