The Chemistry of Global Climate

Environmental Chemistry, vanLoon & Duffy – Chapter 8

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Introduction

Global Warming !!!!!

science fiction?
a serious threat?
green activists fake?
the inevitable end of civilization?

Greenhouse – not only for tomatoes

•Greenhouse gases are an important issue in the current discussion about global climate change

•Is there any evidence for climate change?

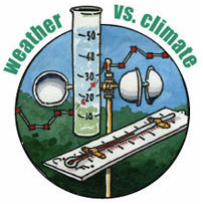
•What are the consequences?

•What are Greenhouse gases, what is their origin and how do they act?

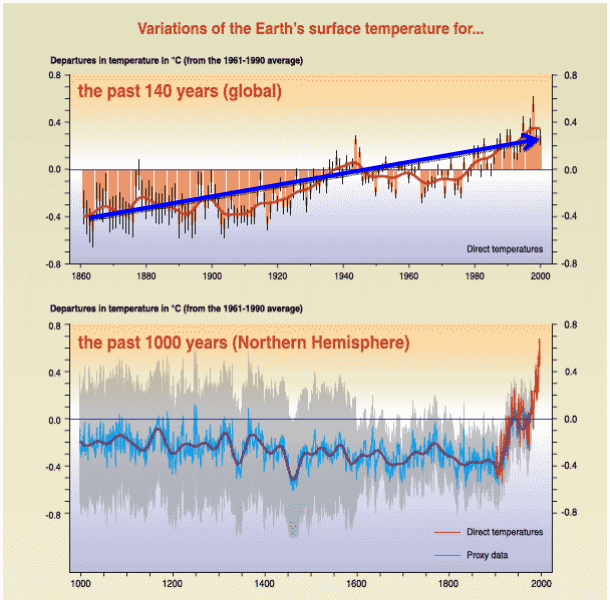
•Can we control the concentration of Greenhouse gases?

Weather and Climate

- Weather is the condition of the atmosphere in terms of temperature, humidity, winds and precipitation.
  - *Weather is considered at the short term.*
- Climate is defined as the average weather over various time periods ranging from a few weeks to decades to geological timescales.
  - *Climate is a good approximation to describe the average conditions in a climate zone .*
- Weather and climate are ultimately determined by location, topography, and the exchange of radiant energy between the Sun, Earth, and Space.

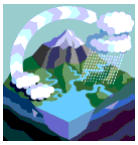


Temperature Variation Over the Years



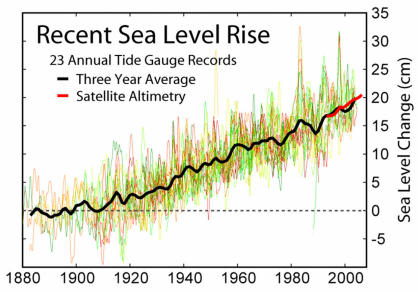
Consequences of Global Warming

- Sea level rise:
  - Beach erosion.
  - Coastal wetland loss.
  - Loss of low-lying territories (*Bangladesh*).
- Change in the pattern of ocean current.

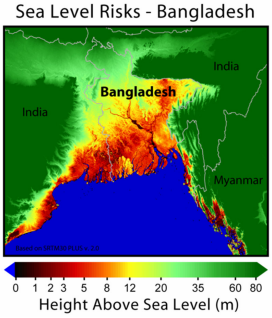


- Water resources change:
  - Precipitation pattern shift.
  - Increases instances of heavy precipitation (p_{vapor}).
  - New burdens on water capture, storage and distribution system to be expected.
- Effects on agriculture:
  - Changes in the length of growing season.
  - Growth of undesirable plant species.

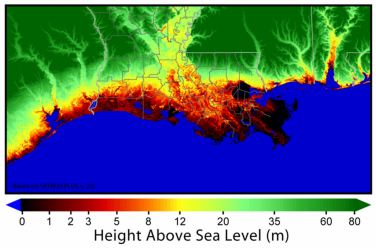
Consequences of Global Warming



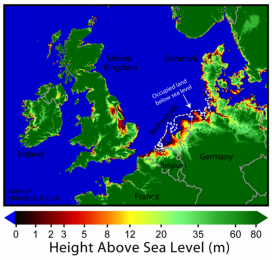
Sea Level Risks - Bangladesh



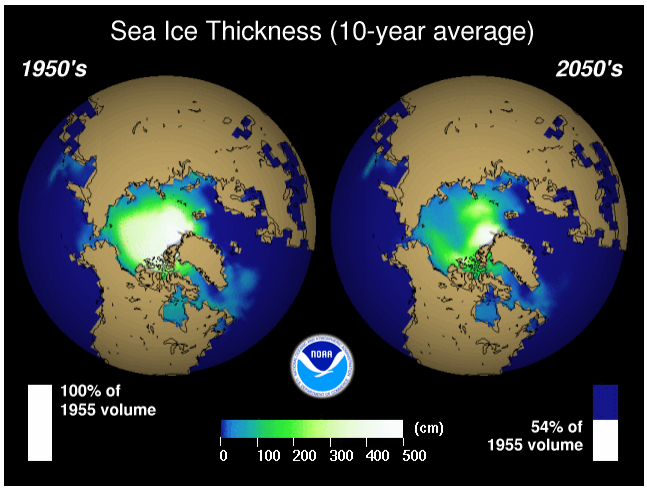
Sea Level Risks - Louisiana



Sea Level Risks - North Sea



Consequences of Global Warming



AUB

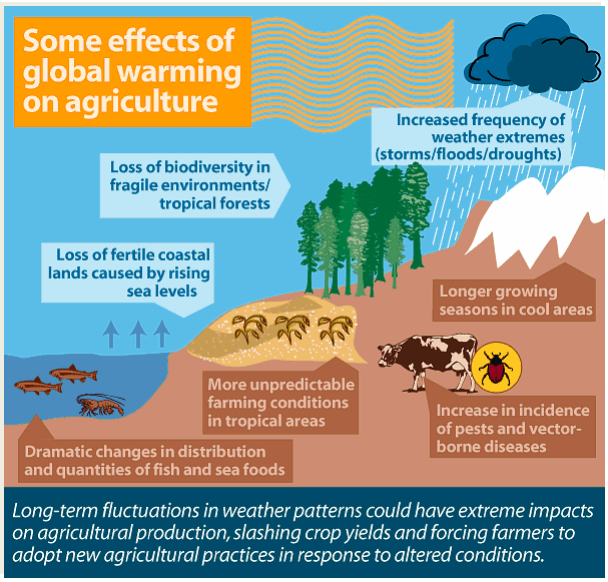
Consequences of Global Warming

- Effects on air quality:
  - Increase in reaction rates and concentrations of certain atmospheric species→ increase in O_3 in urban areas.
  - More droughts→ widespread forest fire→ worsen air quality.
  - Change in how pollutants are dispersed.

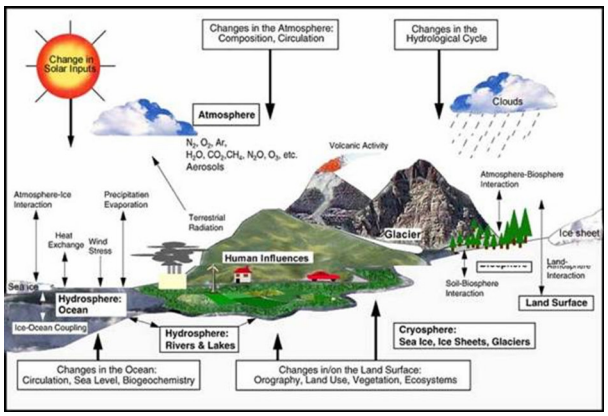
- Impacts on human health:
  - Changes in patterns of sickness and death.
  - Respiratory problems affected by air quality change.

- Biodiversity:
  - Some species may grow too quick and overshoot their reproductive period (e.g. reef corals).
  - Forest could be devastated if the rate of climate change outpaced the rate at which forest species could migrate.

Consequences of Global Warming

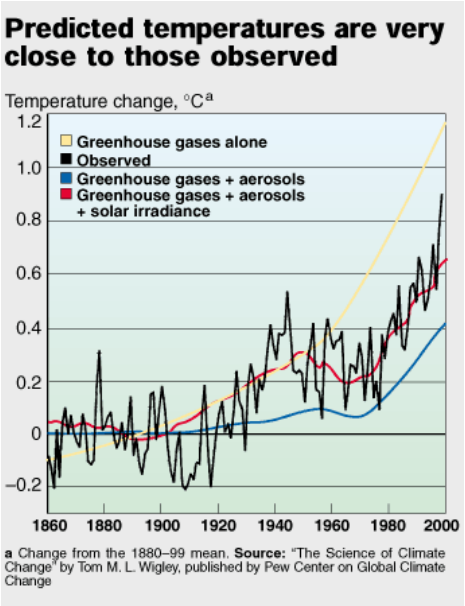


Components of the Global Climate



Components of the global climate system-atmosphere, oceans, sea ice, land surface, surface hydrology, and the biosphere.

Temperature Change

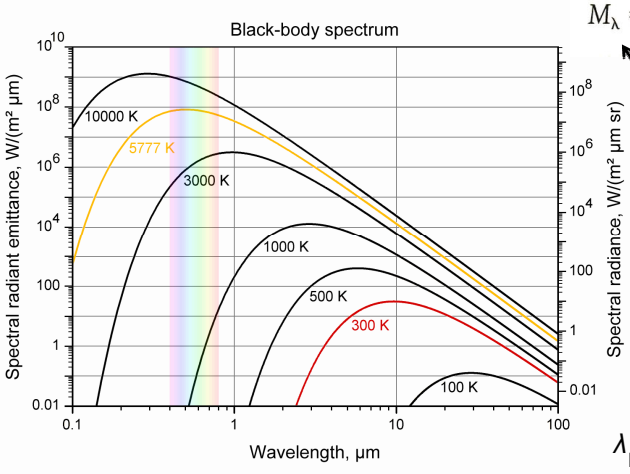


- When greenhouse gases are the only input, predicted temperature are higher than those observed.

- When greenhouse gases, aerosols, and changes in solar irradiance are used as inputs into general circulation models, predicted temperatures are very close to those observed.

Energy Balance – Energy from the SUN

The ultimate source of most energy available on Earth is the Sun.

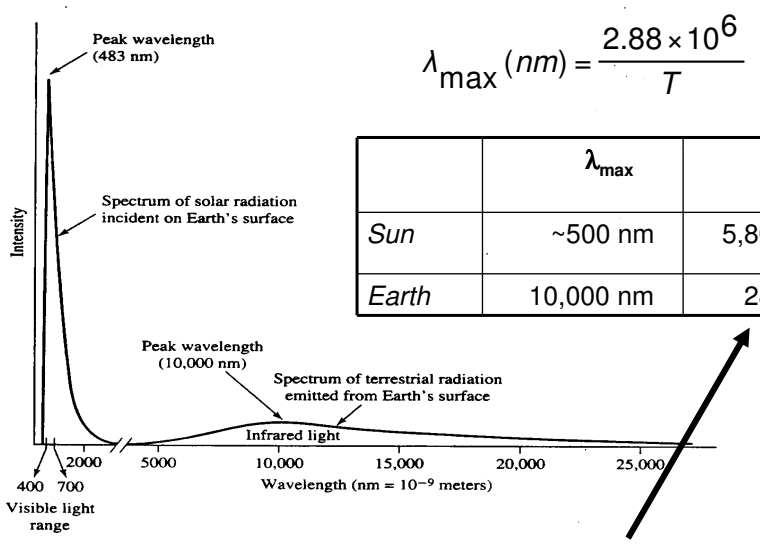


$$M_\lambda = \frac{2\pi hc^2}{\lambda^5}\left(\frac{1}{e^{(hc/kT\lambda)}-1}\right)$$

Emissive Energy (W m^{-2})

$$\lambda_{max}\,(nm) = \frac{2.88\times10^6}{T}$$

Energy Balance – Energy from the SUN



$$\lambda_{max}\,(nm) = \frac{2.88 \times 10^{6}}{T}$$

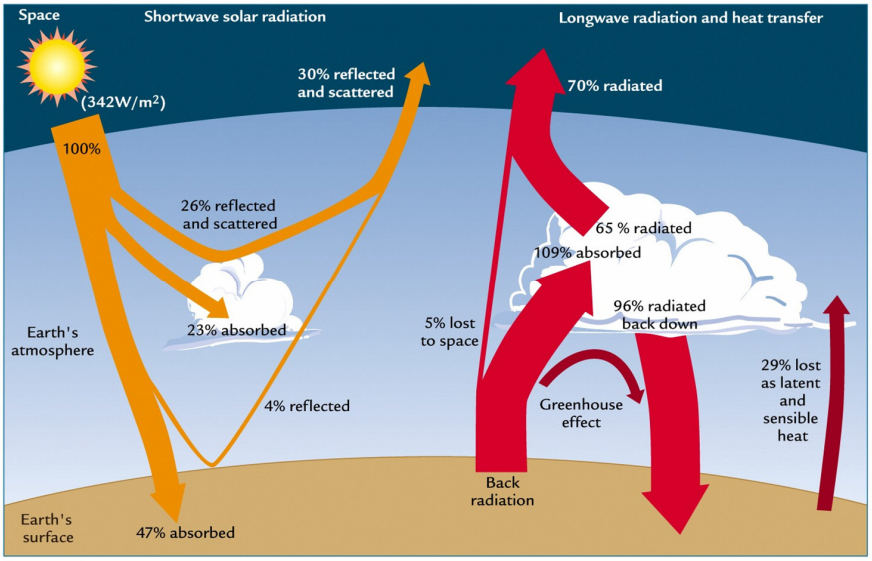
	λ_{max}	T_e (K)
Sun	~500 nm	5,800 K
Earth	10,000 nm	288 K

Approximate the earth surface temperature

Energy Balance – Solar Energy & the Earth

- The Earth's climate system constantly tends to maintain a *balance* between the energy from the Sun that is absorbed by the Earth, and the energy that goes from Earth back out to space. We refer to this process as Earth's "radiation budget."
- This radiation budget allows the Earth to maintain the moderate temperature range essential for life as we know it.
- The components of the Earth system that are important to the radiation budget are the planet's surface, atmosphere, and clouds.

Energy Balance – Solar Energy & the Earth



Energy Balance – Solar Energy & the Earth

- The fraction of solar energy that is reflected back to space is called the ***albedo (A)***.
- Different parts of the Earth (surface and cloud cover) have different albedo.
- Over the whole Earth, about 30 percent of incoming solar energy is reflected back to space.
- Clouds account for two-thirds (67%) of the global albedo.
- Backscattering from gaseous molecules and particles in air: 20%
- Earth's surface: 13%

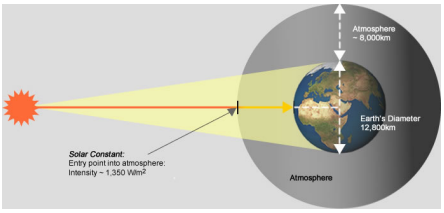
Albedo Table

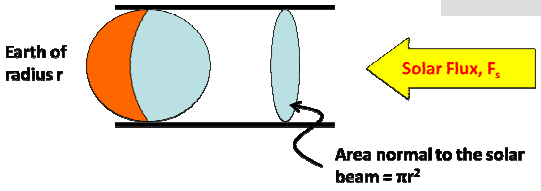
Type of Surface	Albedo
sand	0.2 - 0.3
grass	0.2 - 0.25
forest	0.05 - 0.10
water	0.03 - 0.05
water (sun near horizon)	0.5 - 0.8
fresh snow	0.8 - 0.85
thick cloud	0.7 - 0.8

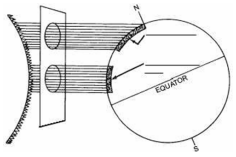
Solar Irradiation – Solar Constant

Solar constant: The amount of solar energy received per unit of area outside the Earth's atmosphere, normal to the direction of propagation of the light.

$$F_s = 1368 \text{ J s}^{-1} \text{ m}^{-2} = 1368 \text{ W m}^{-2}$$







Solar Irradiation – Energy Budget

Therefore, the total energy reaching the earth is:

$$E_s = F_s(\pi r^2)$$

The Total energy absorbed by the earth is:

$$E_s = F_s(1\text{-}A)\ \pi r^2$$ *Where a is the albedo.*

The radiative emission from the earth is:

$$F_e = \sigma T_e^4$$

F: radiated energy per unit time per unit area

T_e: Blackbody temperature

The Total energy emitted by the earth is:

$$E_e = 4\pi r^2\, \sigma T_e^4$$

σ = the Stefan-Boltzmann constant $\sigma = \frac{2\pi^5 k^4}{15h^3c^2} = 5.67 \times 10^{-8} \text{W m}^{-2}\text{K}^{-4}$

In the steady state, total energy absorbed from the sun E_s is equal to the total energy emitted by the earth E_e:

$$\mathbf{F_s(1\text{-}A)\,\pi r^2 = 4\pi r^2\,\sigma T_e^4}$$

$$F_s(1\text{-}a)\,\pi r^2 = 4\pi r^2\,\sigma T_e^4 \Rightarrow$$

$$T_e = [F_s(1\text{-}a) / 4\sigma]^{1/4} \Rightarrow$$

$$T_e = \left(\frac{1368\, Wm^{-2}(1-0.31)}{4 \cdot 5.67 \cdot 10^{-8}\, Wm^{-2}K^{-4}} \right)^{1/4}$$

T_e = 254 K = -19°C

AUB Solar Irradiation – Energy Budget

Why the blackbody temperature of the earth-atmosphere system seen from the space is 34 K colder than the average temperature at the earth surface?

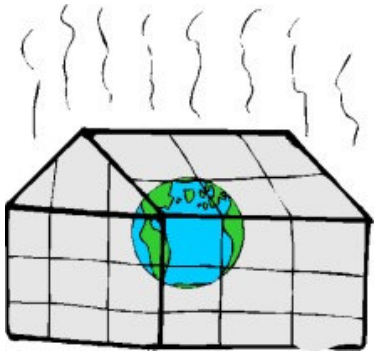
Earth-Atmosphere system: 254 K

Earth surface average temperature: 288 K

Answer: ***Greenhouse effect*.**

The atmosphere traps much of the heat emanating from Earth's surface and radiates it back, raising the surface temperature.

Greenhouse Effect of the Atmosphere



The gases in the atmosphere that act like glass in a greenhouse are called greenhouse gases.

- Light from the sun includes the entire visible region and smaller portions of the adjacent UV and infrared regions.
- Sunlight penetrates the atmosphere and warms the earth's surface.
- Longer wavelength infrared radiation is radiated from the earth's surface.
- A considerable amount of the outgoing IR radiation is absorbed by gases in the atmosphere and reradiated back to earth.

What Makes a Gas Greenhouse Gas?

Able to absorb infrared light:

Must have molecular vibration(s)

- This excludes monoatomic gases as greenhouse gases. (That is why argon, the third most abundant atmospheric constituents is transparent to infrared irradiation)

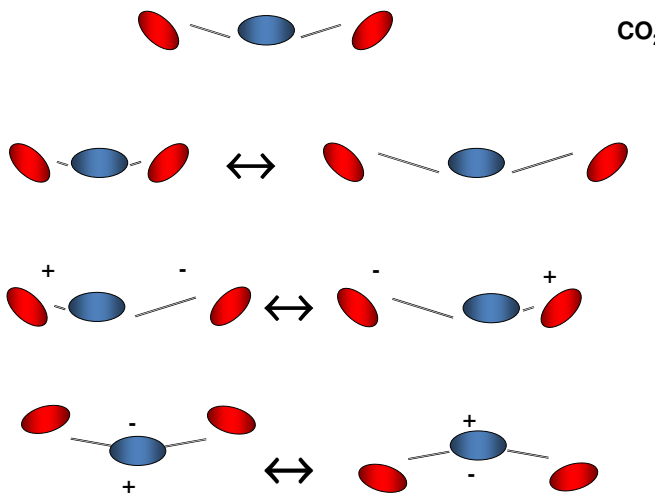
The molecular vibrations must be non-symmetric, i.e. infrared active

- Homonuclear diatomic molecules only have symmetric vibrations. That's why N_2, O_2 are not greenhouse gases.

H_2O CO_2 CH_4
N_2O O_3 CFCs SF_6

what's on with
O_2 N_2 Ar

Bond Vibrations in Carbon Dioxide



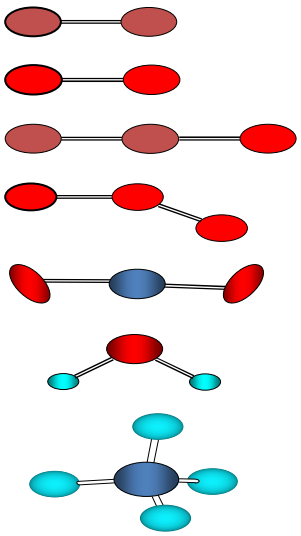
CO_2 Non-polar

Sym. stretch (non-polar)

Asym. stretch (dipolar)

Bend (dipolar)

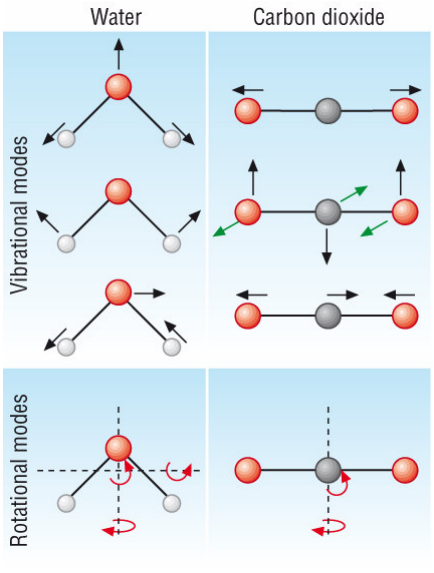
Infrared Activity of Atmospheric Gases



N_2	Non-IR
O_2	Non-IR
N_2O	IR active
O_3	IR active
CO_2	IR active
H_2O	IR active
CH_4	IR active

Table 8.3 Past and present greenhouse gas concentrations in the troposphere, and their increased contribution to radiative forcing[a].

Gaseous compound	Tropospheric concentration		Contribution to warming / W m^{-2}
	Before 1750	At present	
Carbon dioxide	280 ppmv	378 ppmv	1.46
Methane	0.70 ppmv	1.78 ppmv	0.48
Nitrous oxide	0.27 ppmv	0.32 ppmv	0.18
Ozone	0.025 ppmv	0.034 ppmv	0.35
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	
Sulfur hexafluoride	0 pptv	4.8 pptv	0.002



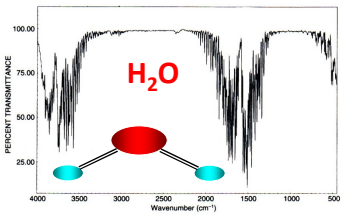


Fig. 8.6 Infrared absorption spectrum of water. The relation between wave number and wavelength is: wave number (cm^{-1}) = 10 000/wavelength (μm)

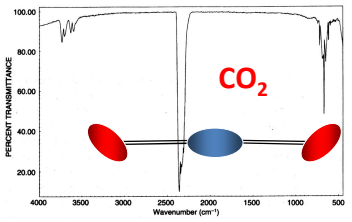


Fig. 8.7 Infrared absorption spectrum of carbon dioxide. The relation between wave number and wavelength is: wave number (cm^{-1}) = 10 000/wavelength (μm)

What determines the contribution of a greenhouse gas to global warming?

Concentrations

- H_2O and CO_2 are the two biggest contributors to the atmospheric warming because of their higher concentrations.

Lifetime

- The longer-live a gas is, the higher the contribution.
  e.g. N_2O contribution > CH_4

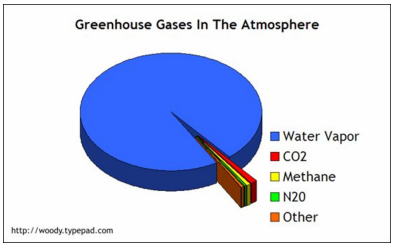
Effectiveness as an infrared absorber

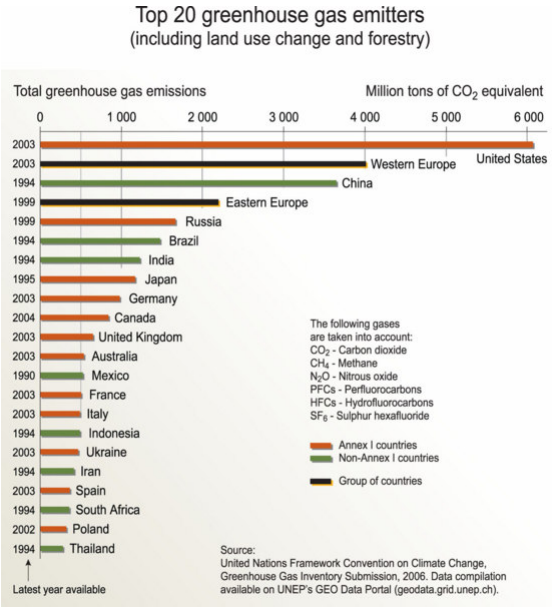
- For example, CFC-11 and CFC-12.

What determines the contribution of a greenhouse gas to global warming?

	CO_2	CH_4	CFC-11	CFC-12	N_2O
Concentration	**ppm**	**ppm**	**ppt**	**ppt**	**ppb**
Preindustrial (<1800)	280	0.7	0	0	270
Current (2007)	387	1.77	257	544	319
Atmospheric lifetime (yr)	50-100	10	65	130	150
Per molecule of radiative forcing relative to CO_2	1	21	12,400	15,800	206

What determines the contribution of a greenhouse gas to global warming?

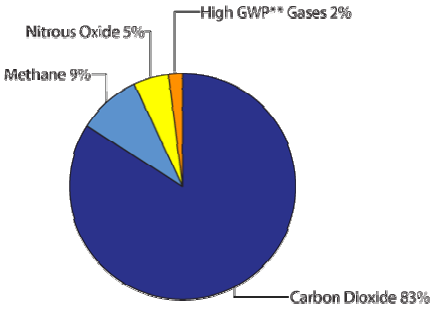




What determines the contribution of a greenhouse gas to global warming?

Greenhouse Gas Emissions

United States, 2004

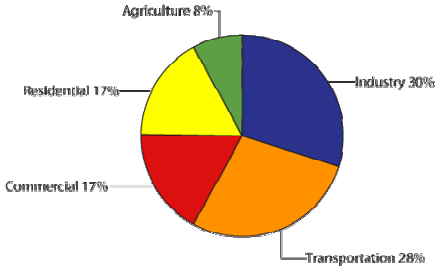


Total Emissions* = 7,074 MMT CO_2E

* Net Emissions (Sources + Sinks) = 6,204 MMT CO_2E
** High GWP Gases include: HFCs, PFCs, and SF_6
Data expressed in Million Metric Tons of Carbon Dioxide Equivalents (MMT CO_2 E)
Source: US EPA Inventory of Greenhouse Gas Emissions and Sinks, 2006.

Greenhouse Gas Emissions by Sector

United States, 2004



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Data expressed in Million Metric Tons of Carbon Dioxide Equivalents (MMT CO_2 E)
Source: US EPA Inventory of Greenhouse Gas Emissions and Sinks, 2006.

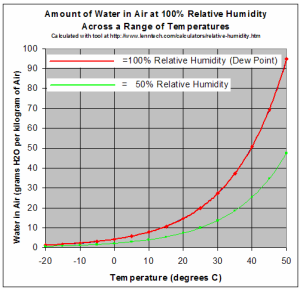
Water H_2O

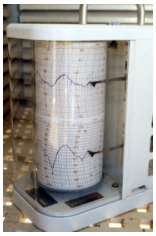
For the Earth, water vapor is actually the most important of all greenhouse gases.

The global average relative humidity is constant at about 1%. There is no significant anthropogenic activities that directly cause its increase.

❖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 enhancing warming.

❖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.





A hygrometer is a device used for measuring the humidity of the air

Carbon Dioxide CO_2

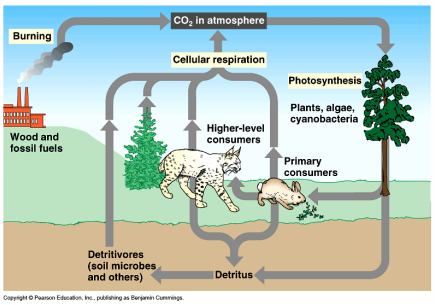
Sources

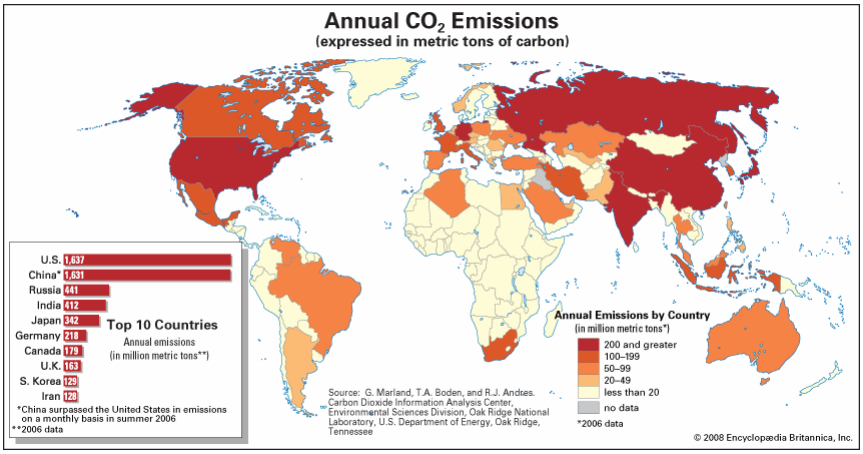
- Natural: respiration of animals and vegetation, and soil detritus, release from oceans (CO_2-rich regions).
- Man-made: Fossil fuel combustion, deforestation, biomass burning.

Sinks

- Photosynthesis
- Slow exchange of carbon between surface waters and deep layers of ocean.

  (Seawater is alkaline while CO_2 is acidic → The oceans are a vast reservoir of CO_2).




Annual CO_2 Emissions
(expressed in metric tons of carbon)
U.S. 1,637
China* 1,631
Russia 441
India 412
Japan 342
Germany 218
Canada 178
U.K. 163
S. Korea 129
Iran 128
Top 10 Countries
Annual emissions
(in million metric tons**)
*China surpassed the United States in emissions on a monthly basis in summer 2006
**2006 data
Annual Emissions by Country
(in million metric tons*)
200 and greater
100–199
50–99
20–49
less than 20
no data
*2006 data
Source: G. Marland, T.A. Boden, and R.J. Andres. Carbon Dioxide Information Analysis Center, Environmental Sciences Division, Oak Ridge National Laboratory, U.S. Department of Energy, Oak Ridge, Tennessee
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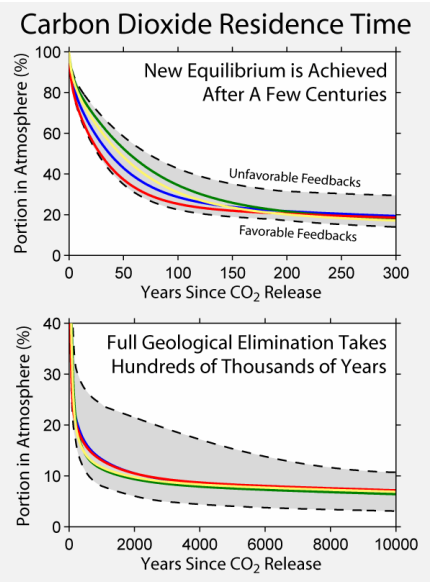
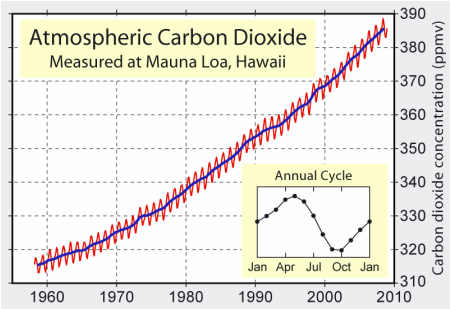
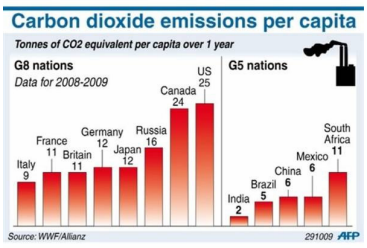

Carbon Dioxide Residence Time
New Equilibrium is Achieved
After A Few Centuries
Unfavorable Feedbacks
Favorable Feedbacks
Portion in Atmosphere (%)
Years Since CO_2 Release
Full Geological Elimination Takes
Hundreds of Thousands of Years
Portion in Atmosphere (%)
Years Since CO_2 Release


Atmospheric Carbon Dioxide
Measured at Mauna Loa, Hawaii
Annual Cycle
Jan Apr Jul Oct Jan
Carbon dioxide concentration (ppmv)


Carbon dioxide emissions per capita
Tonnes of CO2 equivalent per capita over 1 year
G8 nations
Data for 2008-2009
G5 nations
Italy 9
France 11
Britain 11
Germany 12
Japan 12
Russia 16
Canada 24
US 25
India 2
Brazil 5
China 6
Mexico 6
South Africa 11
Source: WWF/Allianz
291009 AFP

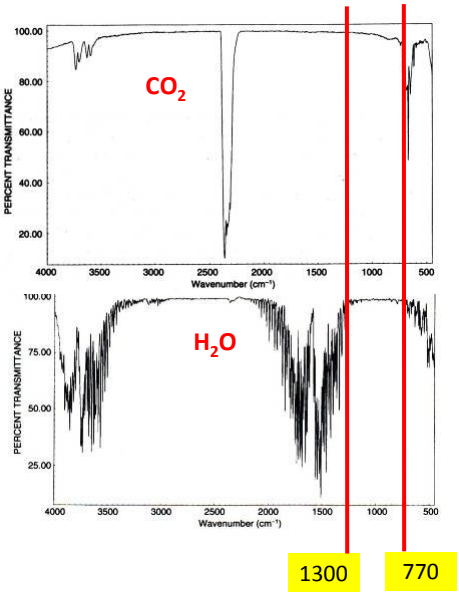
Water and Carbon Dioxide

H_2O and CO_2 absorb much of the radiation in the thermal IR region above 1300 cm^{-1} and below 770 cm^{-1}.

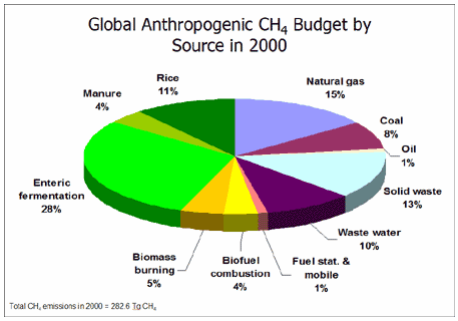
This leaves the region between 770 and 1300 cm^{-1} as a "window" through which thermal energy escapes into space.

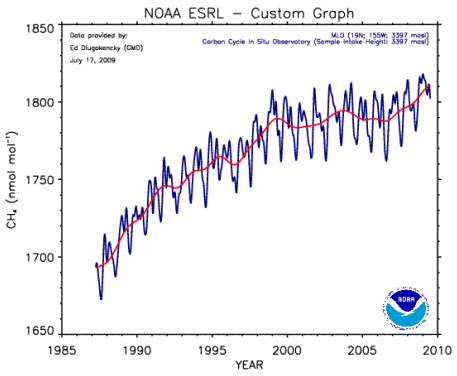
Other gases absorb in this region partially closing the window.

These greenhouse gases can have a major effect on heat retention in the atmosphere of the Earth.



Methane CH_4





Atmospheric methane has increased steadily to present day levels; this increase is highly correlated with human population growth and with related activities, including agricultural practices.

Methane CH_4

Methane absorbs radiation in the ranges from 3300 to 2800 cm^{-1} and 1400 to 1200 cm^{-1}.

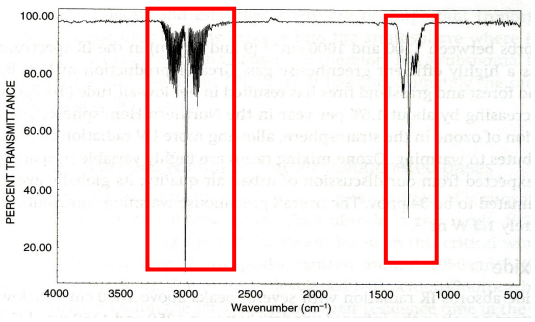
It is produced where organic matter is found in an oxygen-depleted highly reducing aqueous or terrestrial environment.

It is released from wetlands, including both natural and constructed wetlands as well as cultivated rice fields.

The amount released is positively correlated with temperature, and is related to vegetation and soil type.

CH_4 is also produced during extraction, transport, and inefficient combustion of fossil fuels.

A third major source is from digestive tracks of ruminants an termites.



Methane CH_4

Sources

- Natural: end-product of the metabolism from an anaerobic bacteria: methanogenesis Natural wetlands, enteric fermentation (wild animals), termites, biomass burning, ocean/fresh water
- Man-made: rice paddies, gas drilling and transmission, landfills, coal mining, biomass burning, enteric fermentation (domestic animals)

Sinks:

- $\bullet OH + CH_4 \rightarrow CH_3\bullet + H_2O$
- Biodegradation $CH_4 + 2O_2 \rightarrow CO_2 + 2\ H_2O$

Ozone O_3

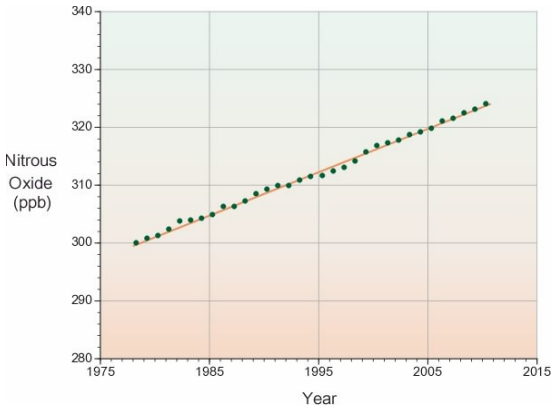
Ozone absorbs between 1100 and 1000 cm^{-1} in the IR spectrum and therefore acts as highly efficient greenhouse gas.

Greater production of NO_x by fossil fuel burning and forest and grassland fires has resulted in the net low-altitude (bad) ozone concentration increasing by about 1.6% per year in the Northern Hemisphere.

The decrease in the concentration of ozone in the stratosphere allowing more UV radiation to reach the Earth, also contributes to warming.

Ozone mixing ratios are highly variable in space and time. Its globally averaged mixing ratio is estimated to be 34 ppbv.

Nitrous Oxide N_2O



Rate of increase 0.25%/year

Use of fertilizer increases both nitrification and denitrification → increase N_2O production

Nitrous Oxide N_2O

Sources

- denitrification process for energy production by anaerobic bacteria.
- Nitrification process ($NH_4^+ \rightarrow NO_3^-$)

} **natural**

- Fertilizer use
- Biomass burning
- Combustion
- Unknown sources

} **Man-made**

Sink

- Photolysis in the stratosphere
- biological processes (not in the atmosphere)

CFCs

Sources

- No natural sources
- Synthetic chemicals

Sink

- Photolysis in the stratosphere.