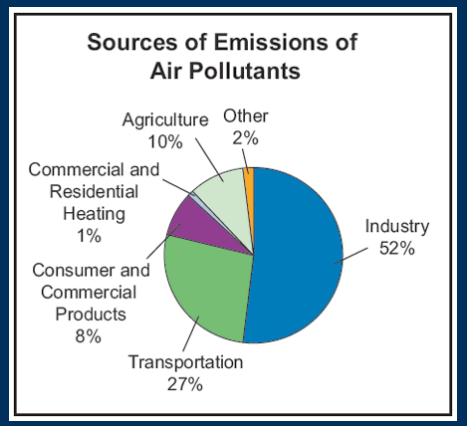
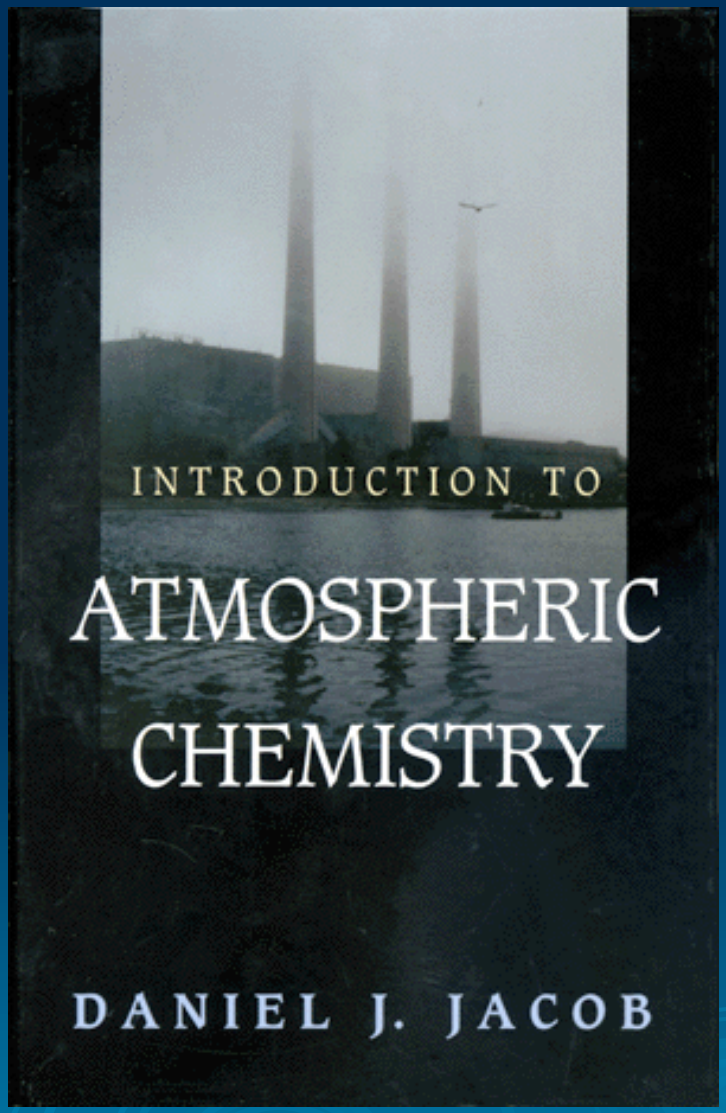
GGS 319
Part 1: Air Pollution Fundamentals

- ✓ The atmosphere and its components
- ✓ ***How air pollutants are categorized***
- ✓ ***The source/cycle of air pollutants***
- ✓ How pollution affects health and welfare
- ✓ Clean air acts
- ✓ Air quality management & standards



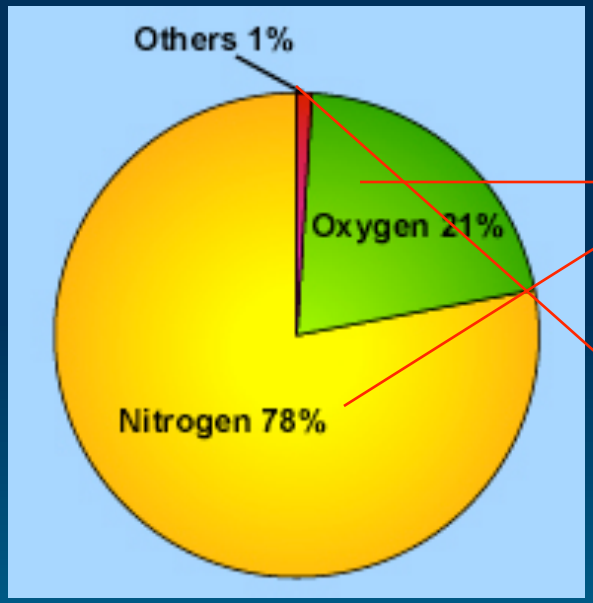





INTRODUCTION TO
ATMOSPHERIC
CHEMISTRY
DANIEL J. JACOB

The Greenhouse Gases

- ✓ We have examine the geochemical cycle of N_2, O_2 and CO_2
- ✓ We will now examine atmospheric gases in controlling the temperature of the Earth indicated by bold-faced type below

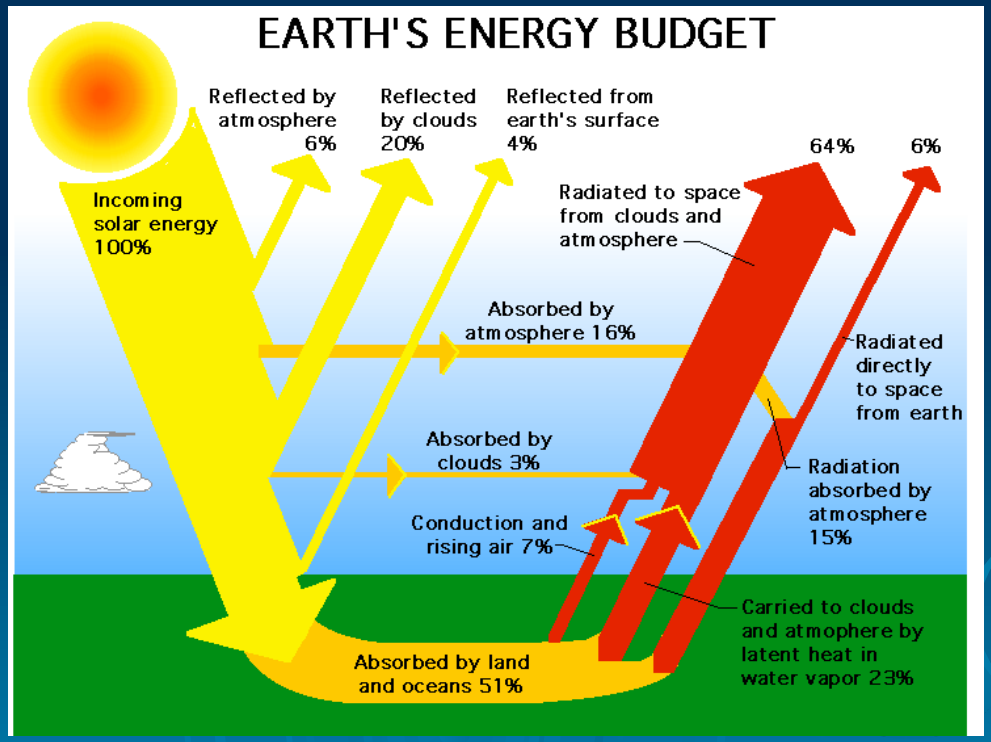


Constituent[a]	Molecular weight	Fractional concentration by volume
Nitrogen (N_2)	28.013	78.08%
Oxygen (O_2)	32.000	20.95%
Argon (Ar)	39.95	0.93%
Water vapor (H_2O)	18.02	0–5%
Carbon dioxide (CO_2)	44.01	380 ppm
Neon (Ne)	20.18	18 ppm
Helium (He)	4.00	5 ppm
Methane (CH_4)	16.04	1.75 ppm
Krypton (Kr)	83.80	1 ppm
Hydrogen (H_2)	2.02	0.5 ppm
Nitrous oxide (N_2O)	56.03	0.3 ppm
Ozone (O_3)	48.00	0–0.1 ppm
CFCs		

CFCs have also accumulated in the atmosphere over the past decades

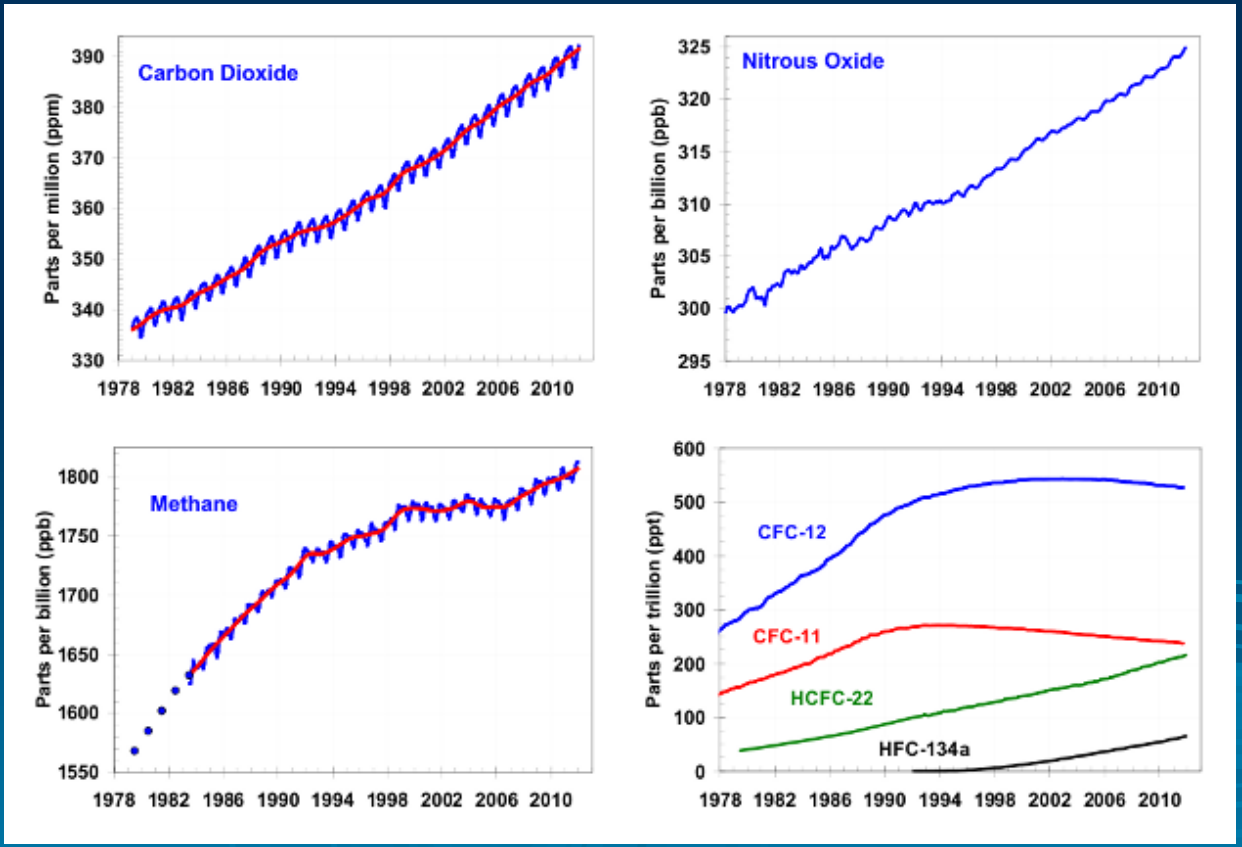
The Greenhouse Gases (Earth's Energy Balance)

- The best estimate solar constant is 1368 Wm^{-2}
- The solar flux density received at the surface of the earth is smaller than their values at the top of atmosphere, because of the depletion of solar radiation in passing through the atmosphere



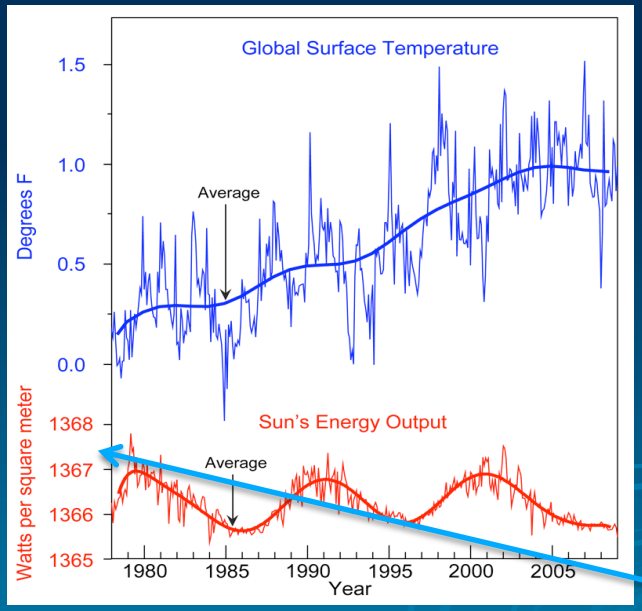
The Greenhouse Gases (Deviation from the Balance)

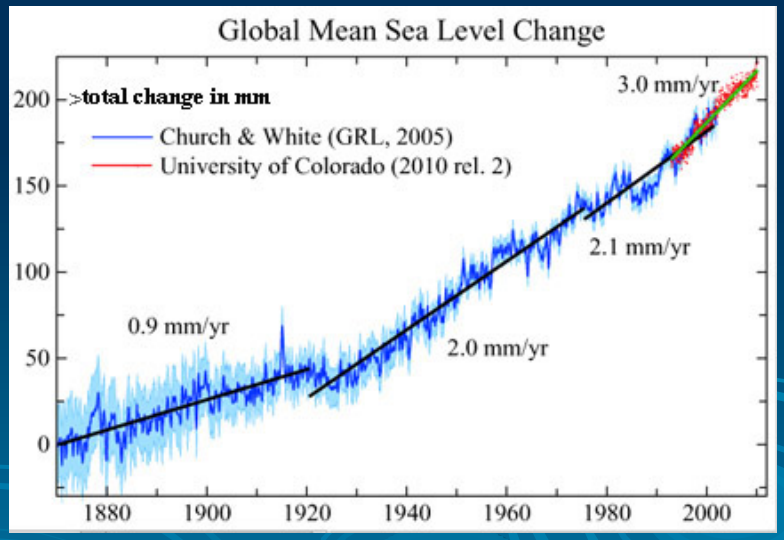
- ✓ Naturally occurring greenhouse gases CO_2, CH_4, and N_2O show large increases over the past century due to human activity
- ✓ Additional greenhouse gases produced by the chemical industry, such as CFCs



The Greenhouse Gases

- ✓ Global mean surface temperature has increased by about 0.6 K
- ✓ Sun's energy has not changed
- ✓ Energy from the Sun has not changed
- ✓ Global mean sea level has been rising at an average rate of about 1.7 mm/year over the past 100 years
- ✓ Current rate is 3mm per year, equal to about 12 inches a century

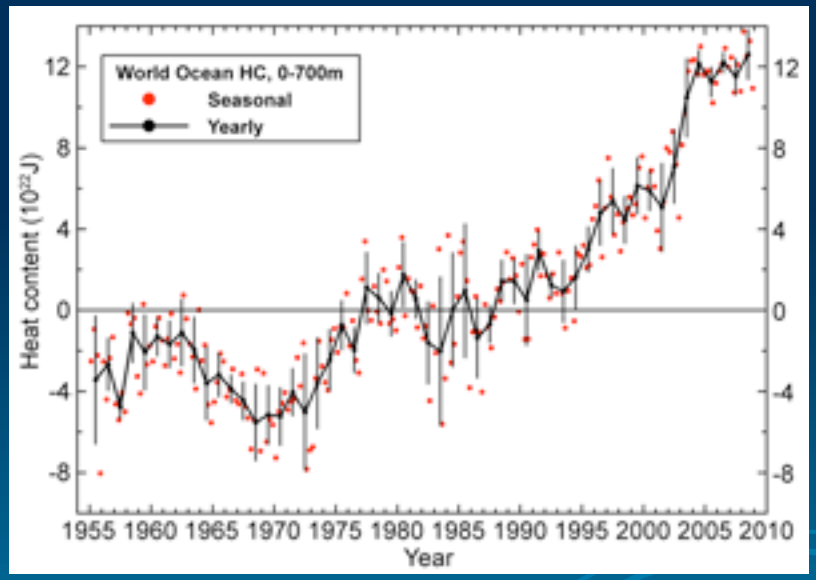


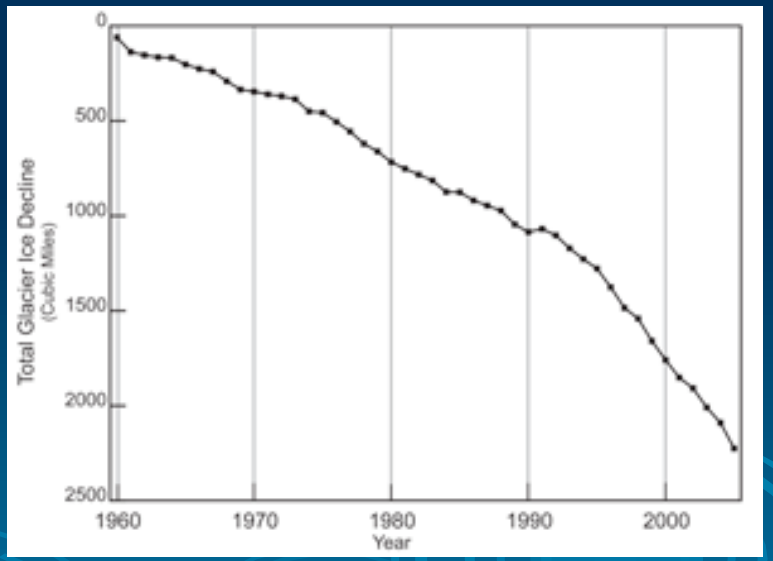


The solar constant is 1368 Wm^{-2}

The Greenhouse Gases

- ✓ Global upper ocean heat content is rising
- ✓ Glacier volume is shrinking
- ✓ Our best understanding from climate models is that the climate change is in fact due to increases in greenhouse gases



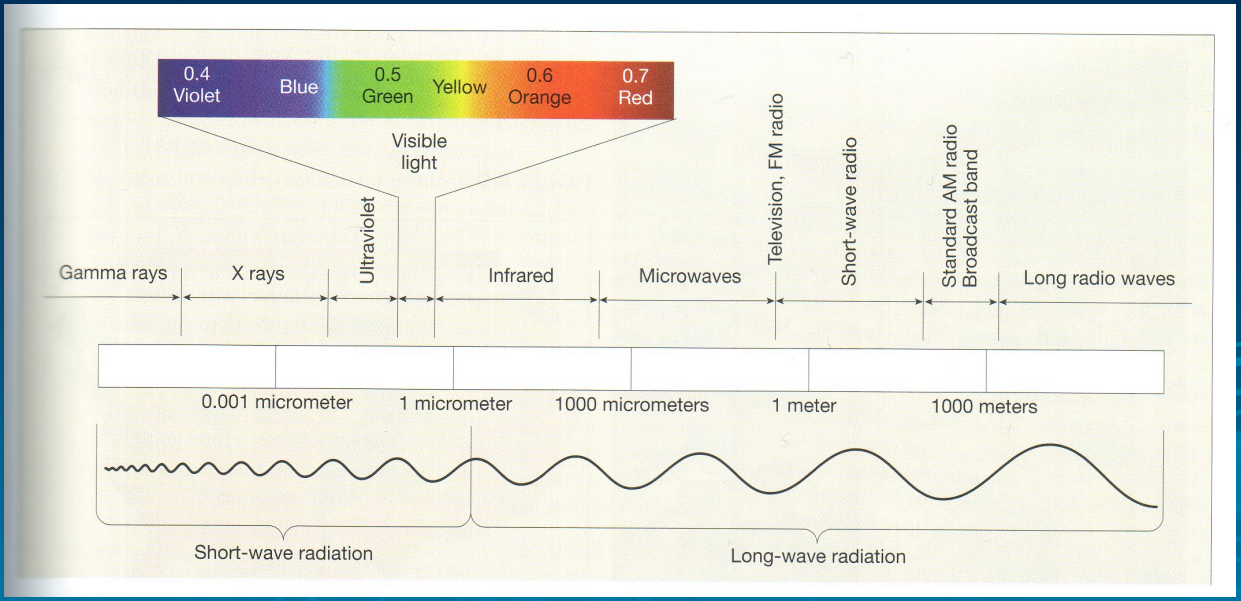


The Greenhouse Gases (Radiation)

- ✓ The main source of heat to the Earth is solar energy
  - ✓ Transmitted from Sun to the Earth by shortwave (SW) radiation
  - ✓ Converted to heat at the Erath's surface
- ✓ To balance this input of solar radiation
  - ✓ Earth emits longwave (LW) terrestrial radiation to space
  - ✓ Some of this radiation is trapped by greenhouse gases, resulting in the warming of the surface
  - ✓ Trapping of LW terrestrial radiation by naturally occurring greenhouse gases is essential for maintaining the Earth's surface temperature above the freezing point

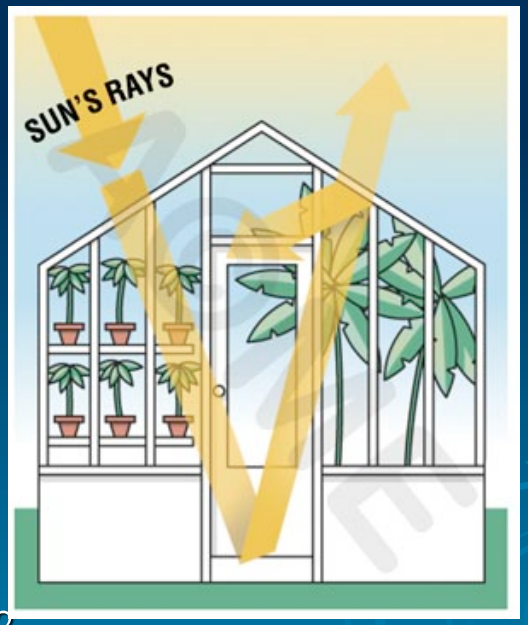
The Greenhouse Gases (Radiation)

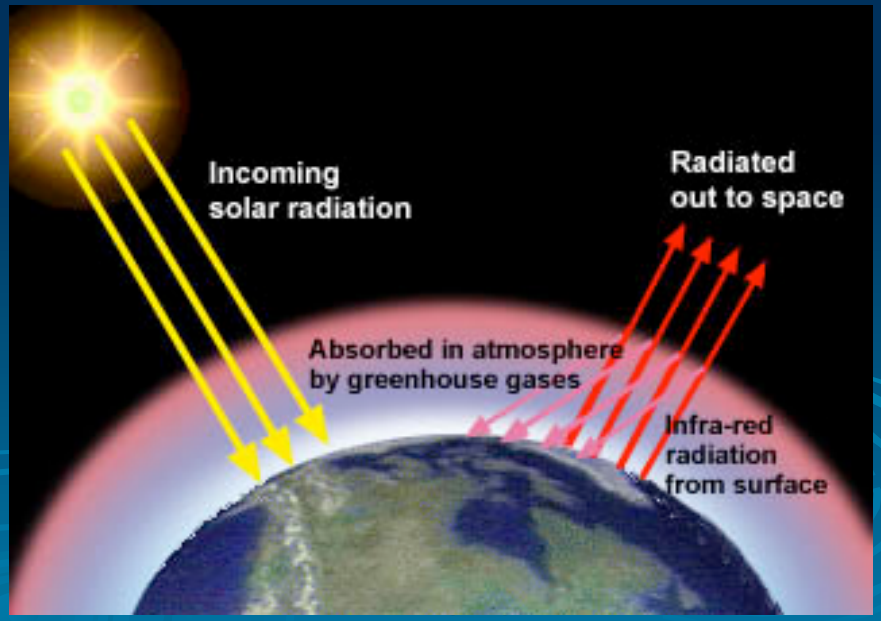
- Over 95 % of all solar radiation is emitted in wavelenghts between 0.1 and 2.5 micrometers (visible and near-visible, UV & IR)
  - visible 43 percent
  - 49 percent infrared (IR)
  - 7 percent ultraviolent (UV)
  - Less than 1 percent X rays, gamma rays and radio waves.



The Greenhouse Gases

- Sunlight brings energy into the climate system; most of it is absorbed by the oceans and land.
- Some of the infrared energy is absorbed by greenhouse gases in the atmosphere, which emits the energy in all directions.
- Some of the infrared energy further warms the Earth.





The Spectrum of Radiation

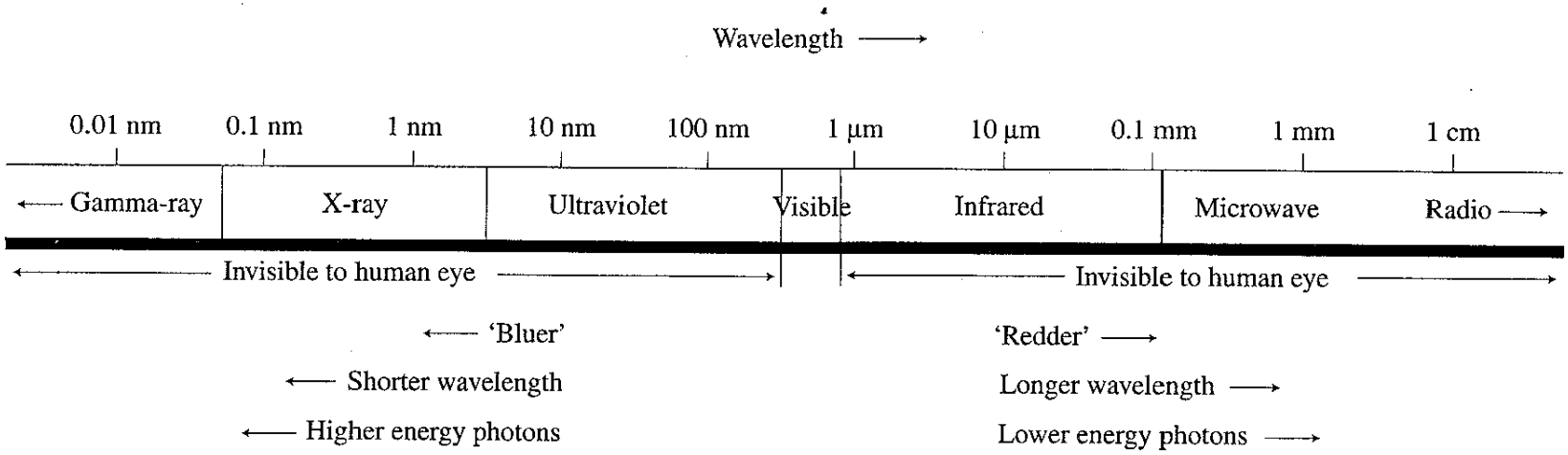


FIGURE 3.1 The electromagnetic spectrum. (Adapted from Hartmann 1989)

$c = 2.998 \times 10^8$ ms^{-1} speed of electromagnetic radiation

λ = wavelength

$k = 1/\lambda$ = wavenumber

ν = frequency

$$c = \lambda\nu = \frac{\nu}{k}$$

- We will be predomoninantly concerned with radiation in the IR, visible, and UV ranges

Planck's Law

- The amount of radiation emitted by a blackbody (a perfect absorber and emitter) is uniquely determined by its temperature:

$$B_\lambda(T) = \frac{2hc^2}{\lambda^5 (e^{hc/K\lambda T} - 1)}$$

h = 6.6262×10^{-34} J s (Planck's Constant)

K = 1.3807×10^{-23} J K^{-1} (Boltzmann's Constant)

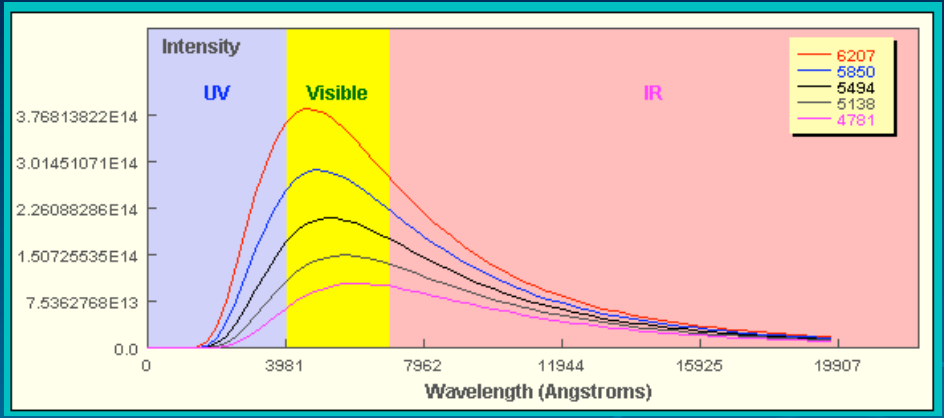
c = 2.998×10^8 ms^{-1} speed of electromagnetic radiation

λ = wavelength

- This yields the smooth curves of intensity as a function of wavelength for an emitter at a given temperature.

Blackbody curves

- Normalized curves for the sun and earth (unnormalized the radiation from a body the temperature of the earth would be so feeble that it would not show up on the same plot with the sun), and
- Several intensity curves for bodies with a range of surface temperatures typical of medium-sized stars like the sun.



Blackbody radiation curves at five different temperatures (K; see legend in upper right corner).

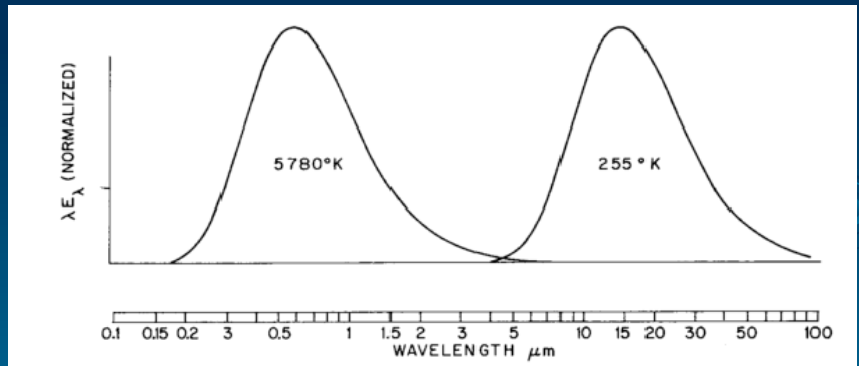


Fig. 6.4 Normalized blackbody spectra representative of the sun (left) and earth (right), plotted on a logarithmic wavelength scale. The ordinate is multiplied by wavelength in order to make area under the curves proportional to irradiance. [Adapted from R. M. Goody, "Atmospheric Radiation," Oxford Univ. Press (1964), p. 4.]

Wien's Displacement Law

- The wavelength of the peak in the thermal spectrum of an object (i.e., max emission) is inversely proportional to its temperature.

$$\frac{\partial B_\lambda(T)}{\partial \lambda} = 0$$

$$\lambda_{\max} = \frac{2897}{T}$$

T in degrees K, and λ in micrometers.

Earth's average T = 287 K, so $\lambda_{max} \approx 10$ microns

Sun's T = 5780 K, so $\lambda_{max} \approx 0.50$ microns

Stefan-Boltzmann Law

If we integrate the Planck function across all wavelengths, it reduces nicely to:

$$B(T) = bT^4, \quad \text{where} \quad b = \frac{2\pi^4 K^4}{15c^2h^3}$$

Since blackbody radiation is isotropic, we can define the flux density (integrating over the entire spherical solid angle):

The flux of radiation (R) emitted by such a body given by the ***Stefan-Boltzmann Law***

$$R = \sigma T^4$$

where $\sigma = 5.67 \times 10^{-8}$ W m^{-2} K^{-4} is the Stefan-Boltzmann constant and T is the surface temperature of the body in absolute (K) units..

Kirchhoff's Law

A body absorbs and emits energy at a given wavelength with equal efficiency. For a blackbody:

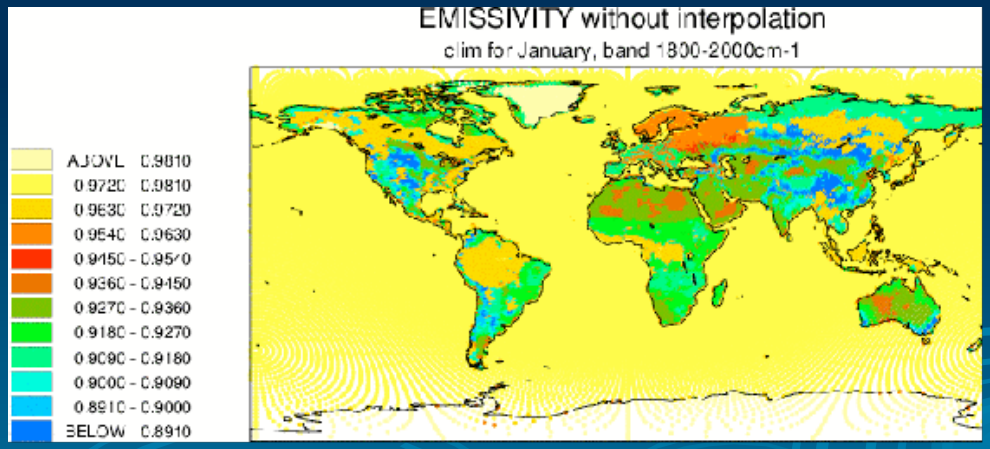
$$A_\lambda = \varepsilon_\lambda = 1$$

Where A_λ is the absorptivity, and ε_λ is the emissivity. If the object is not a blackbody, then:

$$A_\lambda = \varepsilon_\lambda < 1$$

Scattering of radiation (e.g. reflection) is the main contributor.

Emissivity in the 5-5.5 μm band primarily from MODIS and ASTER



Radiative properties of natural surfaces

- Natural surfaces are not perfect radiators or blackbodies, but are, in general, gray bodies. They are generally characterized by several different radiative properties, which are defined as follows
  - Emissivity
  - Absoptivity
  - Reflectivity
  - Transmissivity

Radiative properties of natural surfaces

- Natural surfaces are not perfect radiators or blackbodies, but are, in general, gray bodies. They are generally characterized by several different radiative properties, which are defined as follows
- **Emissivity (ε)** is defined as the ratio of the energy flux emitted by the surface at a given wavelength and temperature to that emitted by a blackbody at the same wavelength and temperature
- **Absoptivity (α)**is defined as the ratio of the amount of radiant energy absorbed by the surface material to the total amount of energy incident on the surface
- **Reflectivity (r)** is defined as the ratio of the amount of radiation reflected to the total amount incident upon the surface
- **Transmissivity (t)** is defined as the ratio of the radiation transmitted to the subsurface medium to the total amount incident upon the surface

Radiative properties of natural surfaces

- The term "**albedo**" is used to represent the integrated reflectivity of the surface for shortwave (0.15-4 micrometer) radiation
- For natural surfaces, the emission of shortwave radiation is usually neglected, and the emission of longwave radiative flux is given by the modified Stefan-Boltzmann Law

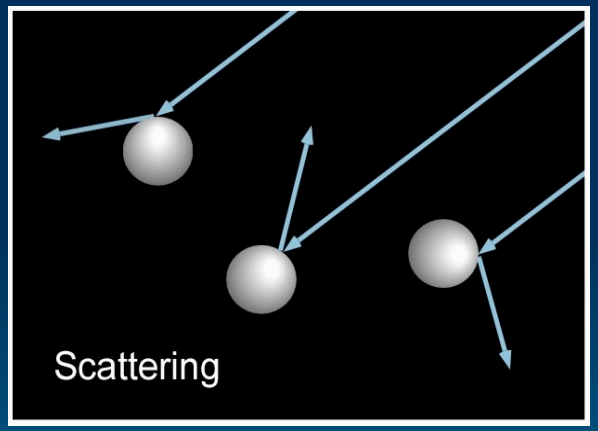
$$R_L = -\varepsilon\sigma T^4$$

Atmospheric Scattering by Particles

Particle Size Parameter

$$x = \frac{2\pi r}{\lambda}$$

(r = radius of particle)



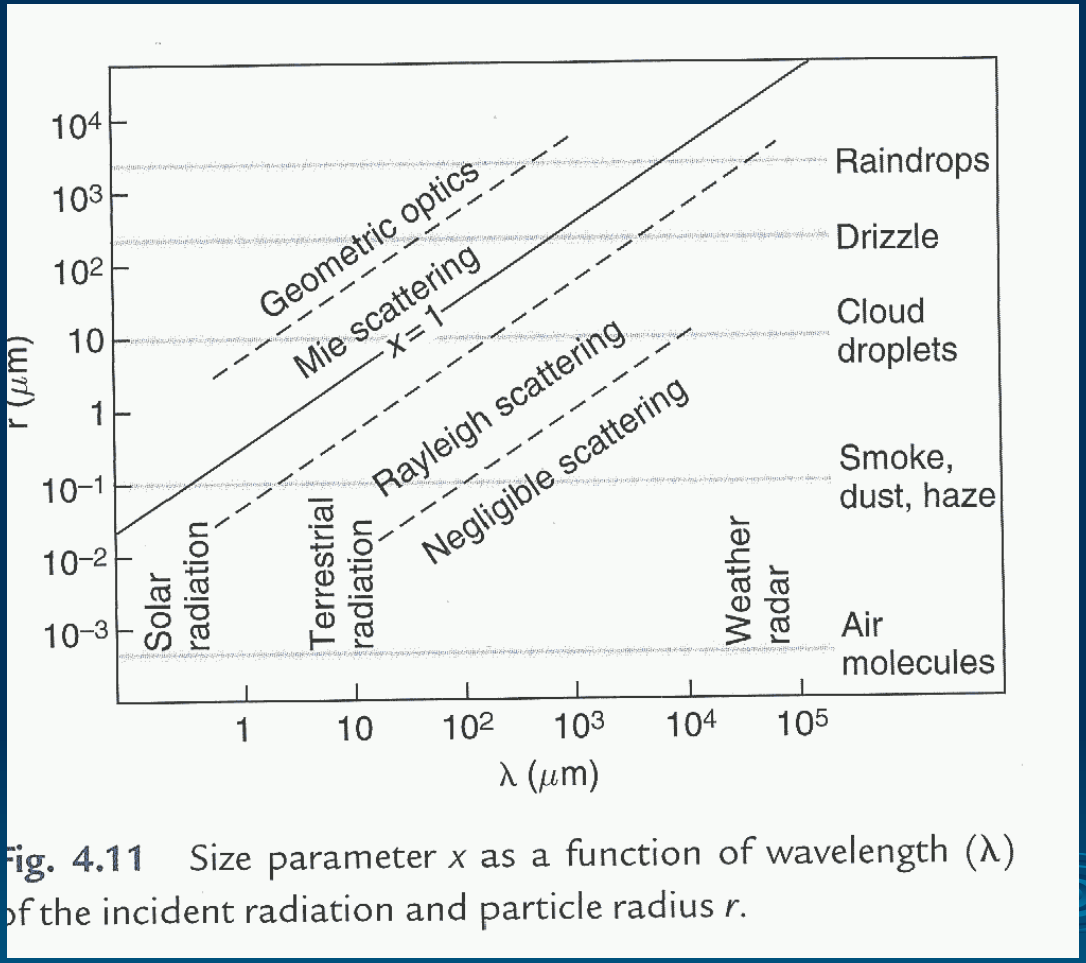


Fig. 4.11 Size parameter x as a function of wavelength (λ) of the incident radiation and particle radius r.

Particle Scattering

Rayleigh Scattering (x << λ)

$$K_\lambda \propto \frac{1}{\lambda^4}$$

Small particles are much more efficient at scattering than larger particles.

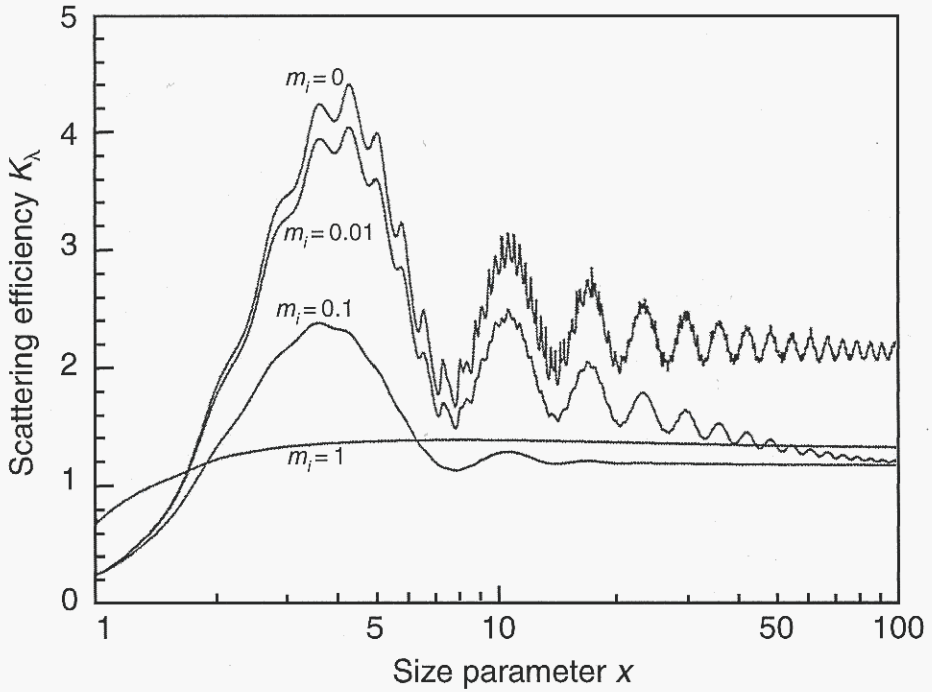
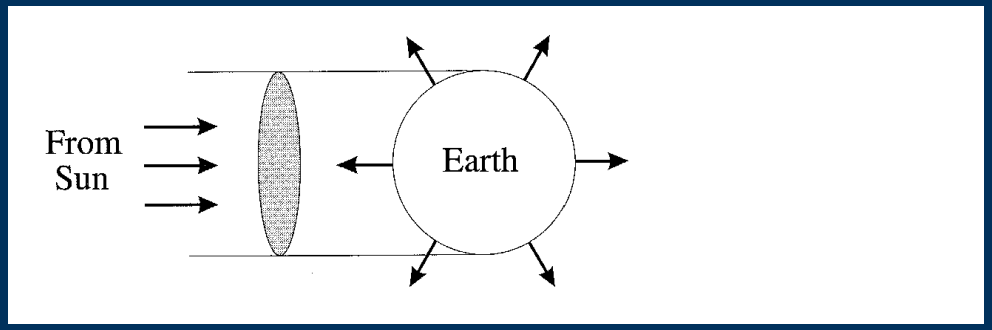


Fig. 4.13 Scattering efficiency K_λ as a function of size parameter x, plotted on a logarithmic scale, for four different refractive indices with $m_r = 1.5$ and m_i ranging from 0 to 1, as indicated. [From K. N. Liou, *An Introduction to Atmospheric Radiation*, Academic Press, p. 191, Copyright (2002), with permission from Elsevier.]

The Effective Temperature of the Earth & Planets



Incoming Solar Radiation

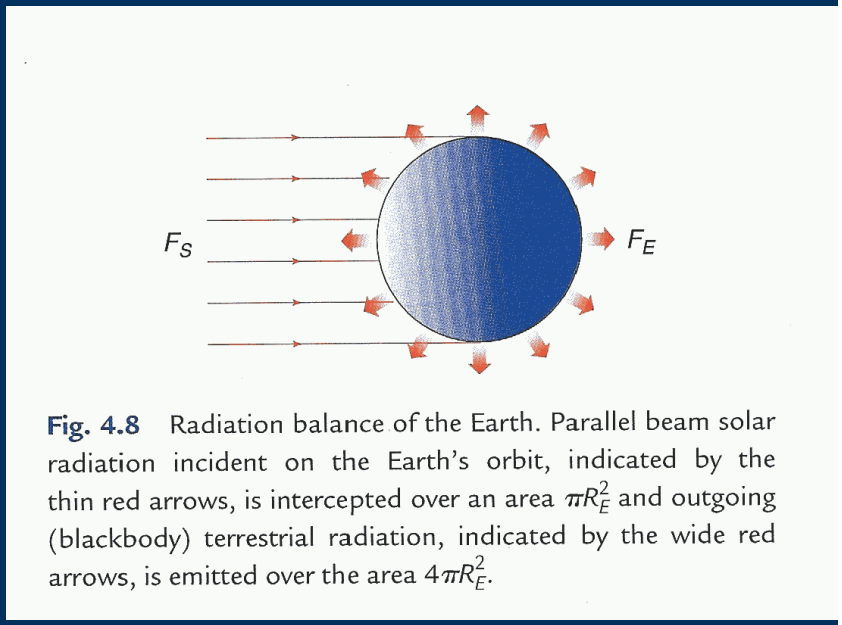


Fig. 4.8 Radiation balance of the Earth. Parallel beam solar radiation incident on the Earth's orbit, indicated by the thin red arrows, is intercepted over an area πR_E^2 and outgoing (blackbody) terrestrial radiation, indicated by the wide red arrows, is emitted over the area $4\pi R_E^2$.

Outgoing Terrestrial IR Radiation

Stefan-Boltzmann Law
Energy Flux from a Blackbody = σT^4
Energy Flux from a non-BB = σT_{eff}^4
Albedo of Surface (Reflectivity) = A

Luminosity of Sun at Earth: L_s = 1370 Watts m^{-2}
Energy Flux from Sun at Distance D
(in astronomical units) = L_s/D^2

Earth:
T_{eff} = 255 K
T_{avg} = 287 K

Equilibrium Temperature of a Planet of radius R:

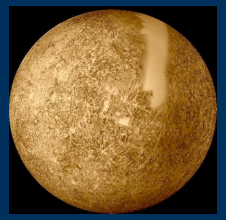
$4\pi R^2 \sigma T_e^4 = (1 - A)\, \pi R^2 L_s/D^2$

$$T_e = [(1 - A)L_s/4\sigma D^2]^{1/4}$$

Temperature vs. Distance From Sun



Sun:
T_{eff} = 5780 K



Mercury:
T_{eff} = 439 K
T_{surf} = 445 K



Venus:
T_{eff} = 226 K
T_{surf} = 740 K



Earth:
T_{eff} = 255 K
T_{surf} = 287 K



Mars:
T_{eff} = 216 K
T_{surf} = 225 K

$$T_e = [(1 - A)L_s/4D^2]^{1/4}$$

When the average temperature is larger compared to effective temperature, it must have an internal energy source. So that it is radiating more energy than it receives from the sun.

Planet	Distance from sun[a]	F_s (W m^{-2})	A	T_E (K)
Mercury	0.39	8994	0.06	439
Venus	0.72	2639	0.78	225
Earth	1.00	1368	0.30	255
Mars	1.52	592	0.17	216
Jupiter	5.18	51	0.45	105

[a] Astronomical units are multiples of Earth–Sun distance.

The Greenhouse Gases (Radiative Forcing)

- "Radiative forcing" is a measure of the influence a factor has in altering the balance of incoming and outgoing energy in the Earth-atmosphere system
- Radiative forcing can be used to estimate a subsequent change in equilibrium temperature

$$\Delta T_s = \lambda \Delta F$$

$\Delta T_s = equilibrium\ surface\ temperature$

$\Delta F = radiative\ forcing$

$\lambda = c\lim ate\ sensitivity\ coefficinet$

The Greenhouse Gases (Forcing Due To Atmospheric Gas)

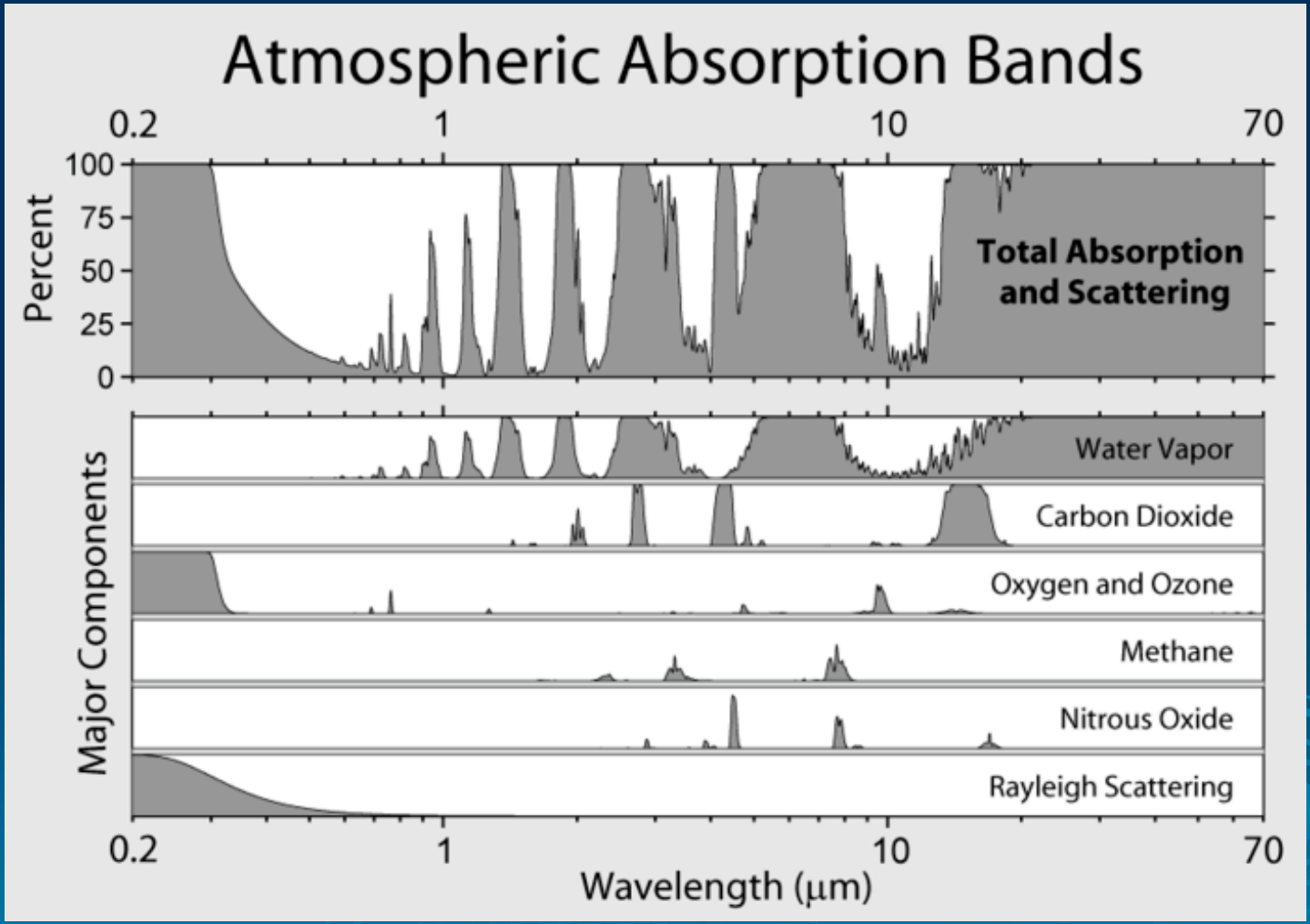
- For a greenhouse gas radiative forcing can be calculated as function of changing concentration
- These calculations can be often be simplified into an algebraic formulation that is specific to that gas
- For example, C is the CO_2 concentration in ppm by volume and C_0 is the reference concentration

$$\Delta T_s = \lambda \Delta F$$

$$\Delta F = 5.35 x \ln \frac{C}{C_0} \quad Wm^{-2}$$

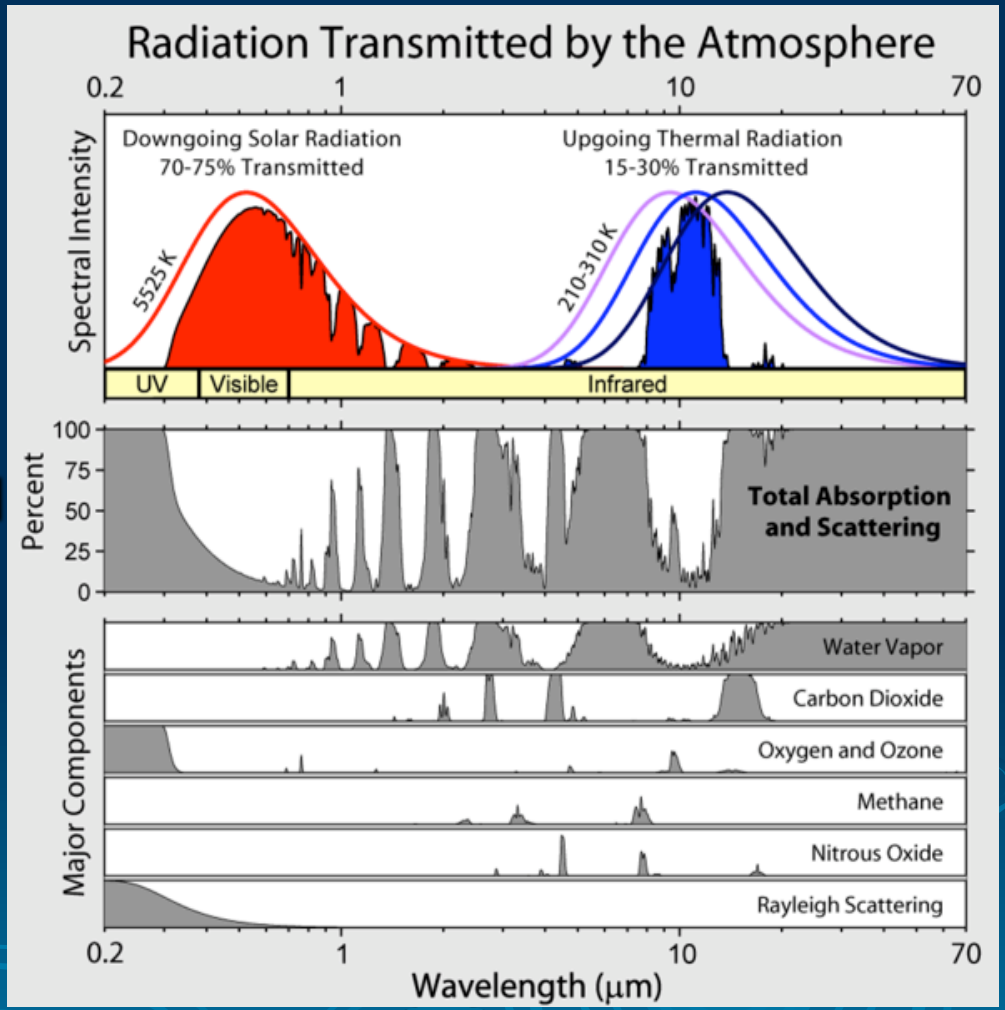
The Greenhouse Gases

- Over 95 percent of Earth's radiation has wavelengths between 2.5 and 30 micrometers.



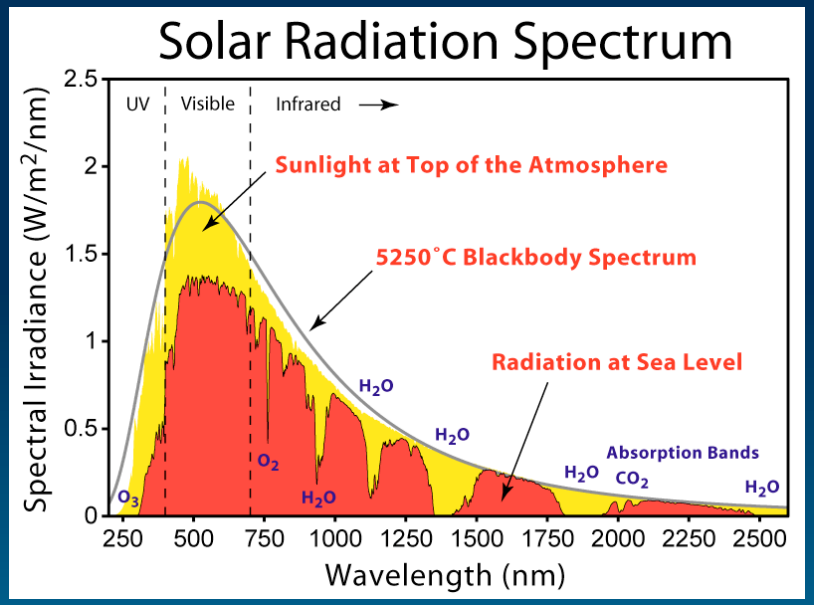
The Greenhouse Gases

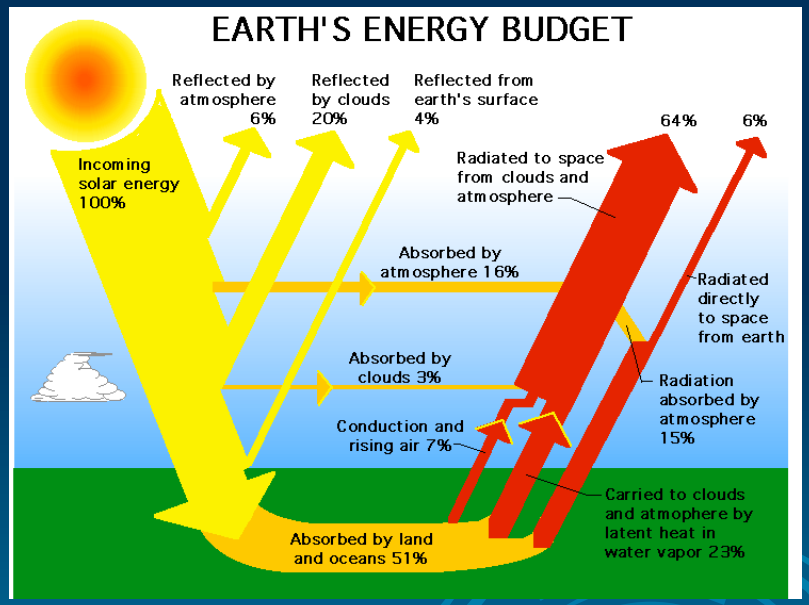
- The gab between the solar radiation and the Earth's radiation is important in understanding of how our atmosphere is heated.
- The atmosphere is heated from the ground up, instead of vice versa.
- This explains the general drop in temperature with increase altitude in the troposphere (lapse rate 6.5 °C /km).



The Greenhouse Gases

- The best estimate solar constant is 1368 Wm^{-2}
- The solar flux density received at the surface of the earth is smaller than their values at the top of atmosphere, because of the depletion of solar radiation in passing through the atmosphere

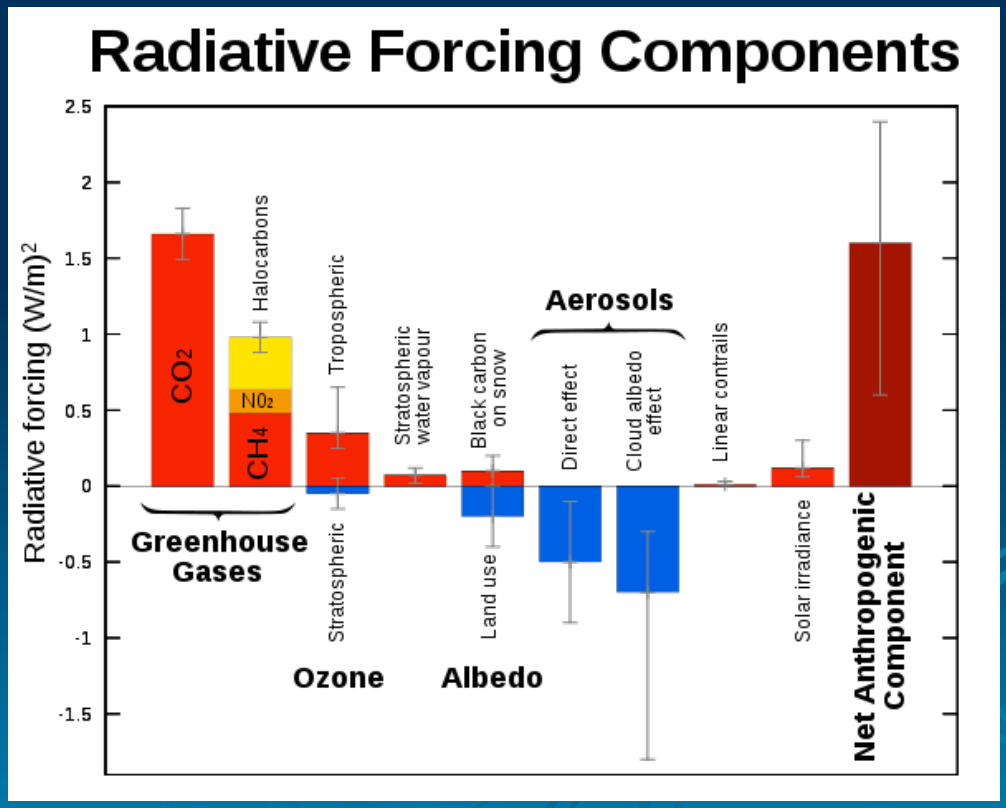




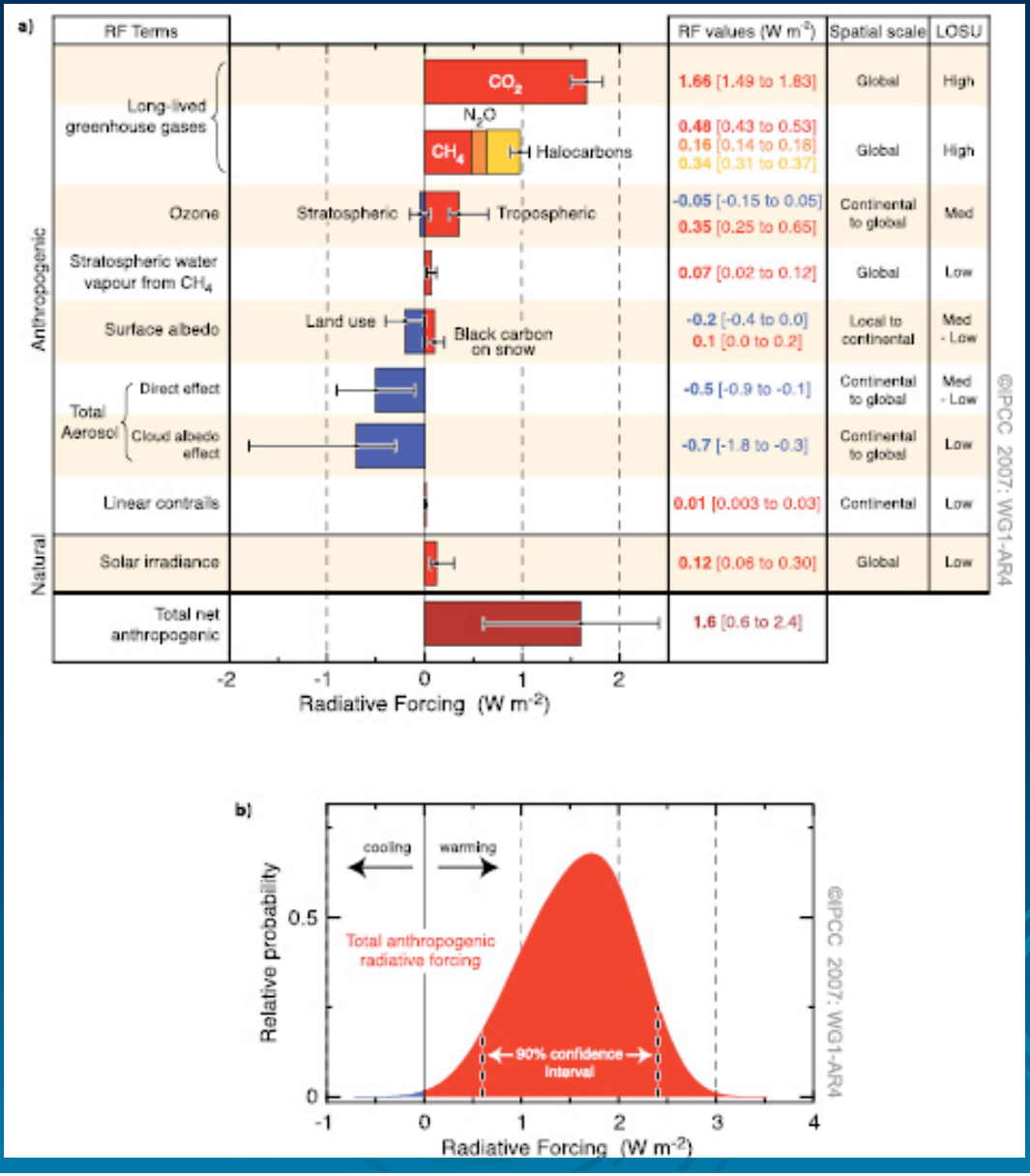
Deviations from blackbody due to absorption by the solar atmosphere, absorption and scattering by the earth's atmosphere (above).

The Greenhouse Gases

- "Radiative forcing" is relatively simple quantity to calculate
- Radiative forcing values are for changes relative to preindustrial conditions defined at 1750 and are expressed in Watts per square meter (W/m^2)

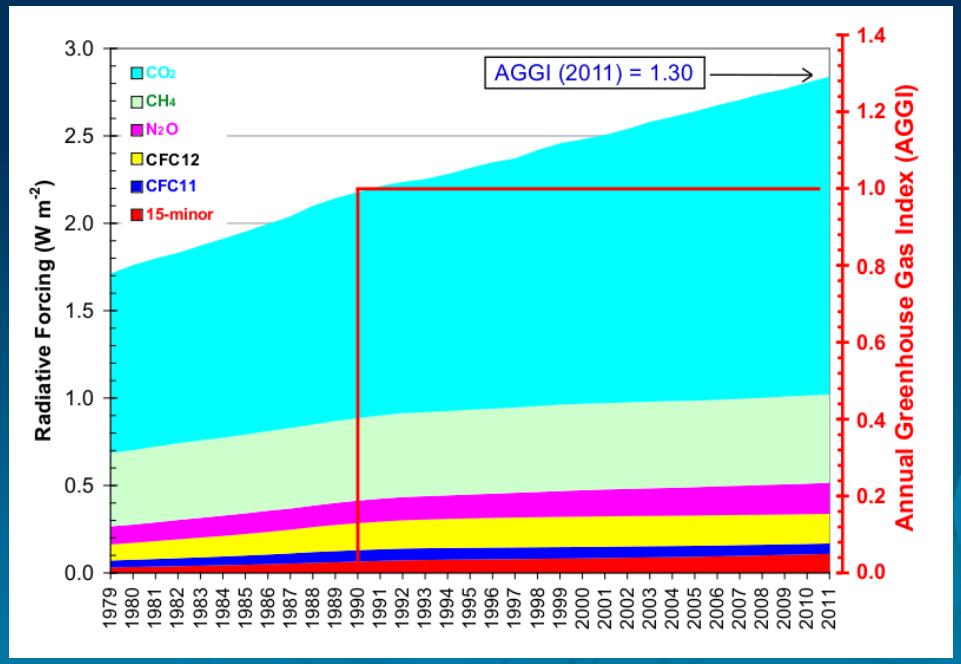


The Greenhouse Gases



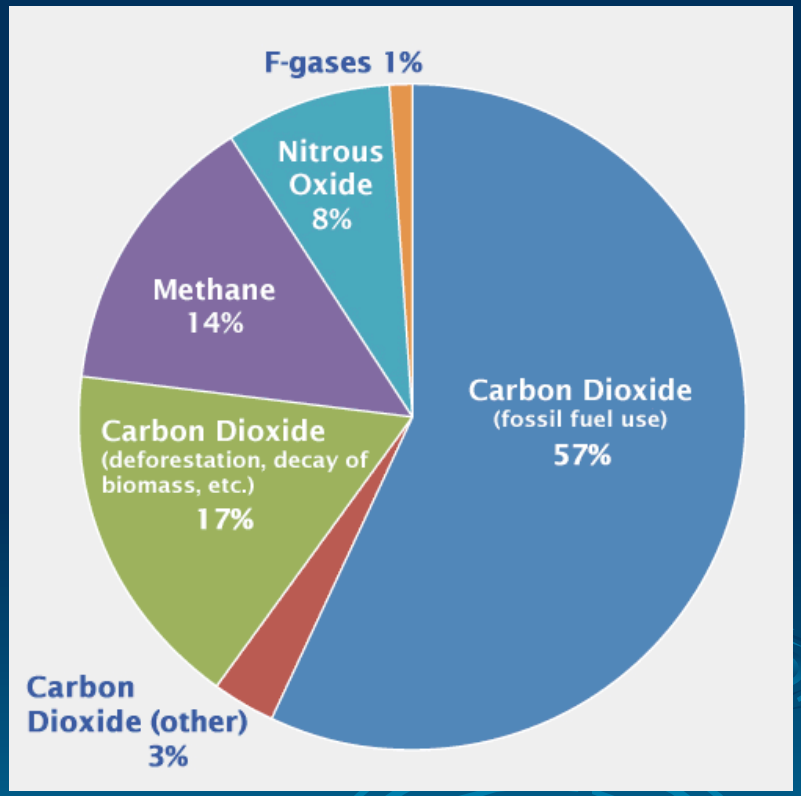
The Greenhouse Effect Gases

- ✓ Radiative forcing of all the long-lived greenhouse gases
- ✓ The five major greenhouse gases account for about 96% of the direct radiative forcing
- ✓ The remaining 4% is contributed by the minor halogenated gases
- ✓ Annual Greenhouse Gases Index is indexed to 1 for 1990 (The Kyoto Protocol)



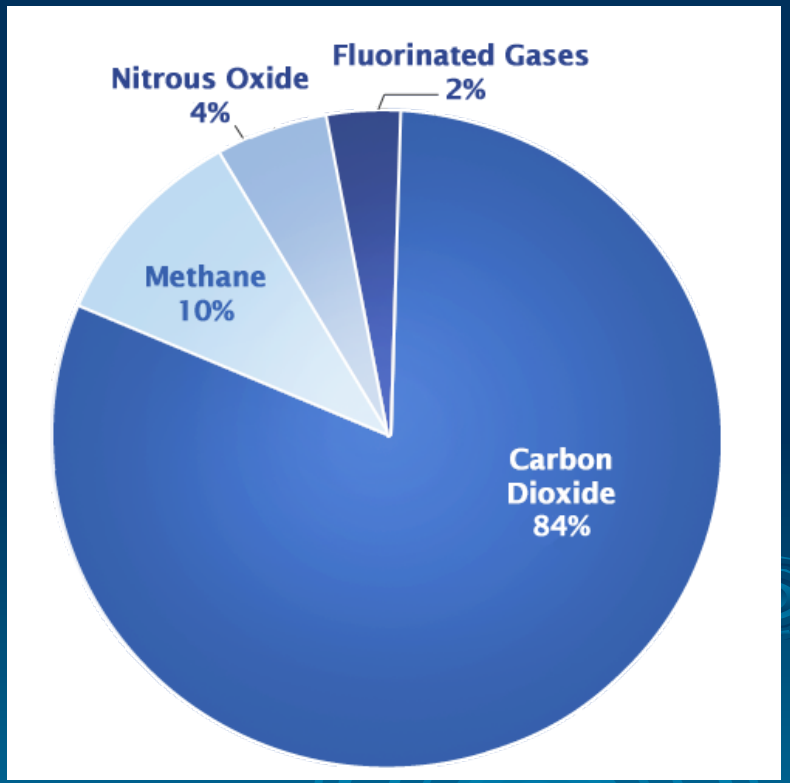
The Greenhouse Gases (Global Emissions)

- Fossil fuel is the primary source of CO2
- The way in which people use land is also an important source of CO2
- Agricultural activities, waste management, and energy use all contribute to CH4 emissions
- Agricultural activities, such as fertilizer use are the primary source of N2O emissions
- Industrial processes, refrigeration, and the use of a variety of consumer products contributes to emissions of Fluorinated gases (such as hydrofluorocarbons, perfluorocarbons)



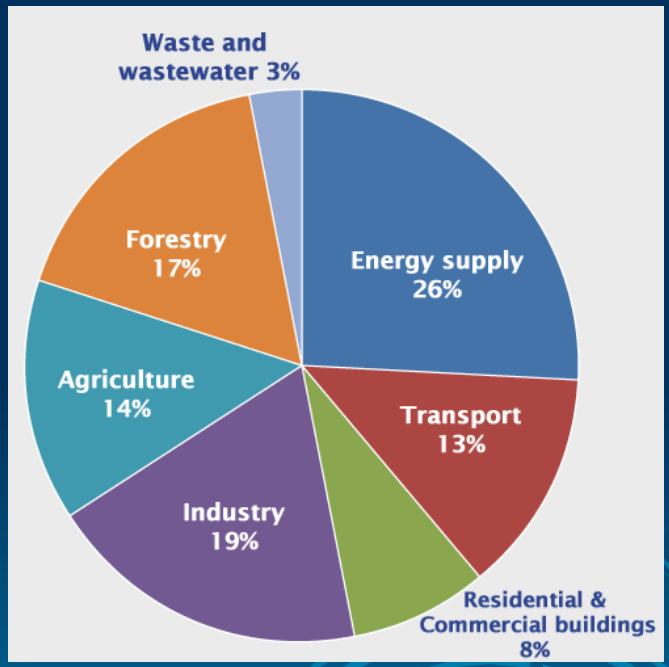
The Greenhouse Gases (National, U.S. Emissions)

- Carbon dioxide emissions by burning fossil fuels (coal, natural gas and oil), solid waste, trees and wood products, and also as a result of certain chemical reactions (e.g., manufacture of cement)
- Methane is emitted during the production and transport of coal, natural gas, and oil.
- Nitrous oxide is emitted during agricultural and industrial activities, as well as during combustion of fossil fuels and solid waste.
- Fluorinated gases emitted from a variety of industrial processes



The Greenhouse Gases (Global Emissions by Source)

- The burning of coal, natural gas, and oil for electricity and heat is the largest source of global greenhouse gas emissions
- Greenhouse gas emissions from industry and transportation primarily also involve fossil fuels burning



The Greenhouse Gases (Global Emissions by Countries)

- ~32 billion metric tons of CO_2 emissions globally
- Deforestation can account for 5 billion metric tons of CO_2 emissions or about 16% of emissions
- Tropical deforestation in Africa, Asia, and South America are thought to be the the largest contributors

