Methods of pollution control and waste management

Lecture 5

The Earth's atmosphere and air pollution (Part 1)

Composition and regions of the atmosphere

- The earth’s atmosphere is a thin shell of gases sorrounding the globe.

  Major components of the dry atmosphere near the surface of the earth.

Component	Mixing ratio [%]
Nitrogen	78.08
Oxygen	20.95
Argon	0.93
Carbon dioxide	0.037 (increasing)

The water is a fifth major component but it’s concentration is variable, ranging from 0.5 to 3.5%

G. W. vanLoon, S. J. Duffy Environmental Chemistry, Oxford Press, 2011

Composition and regions of the atmosphere

Regions of the Earth’s atmosphere

Troposphere – 0 -15 km, temperature decreases with altitude

Stratosphere – 15 – 50 km, temperature increases with altitude

Mesosphere – 50 – 85 km, temperature decreases with altitude

Thermosphere – 85 – 500 km, temperature increases with altitude

Composition and regions of the atmosphere

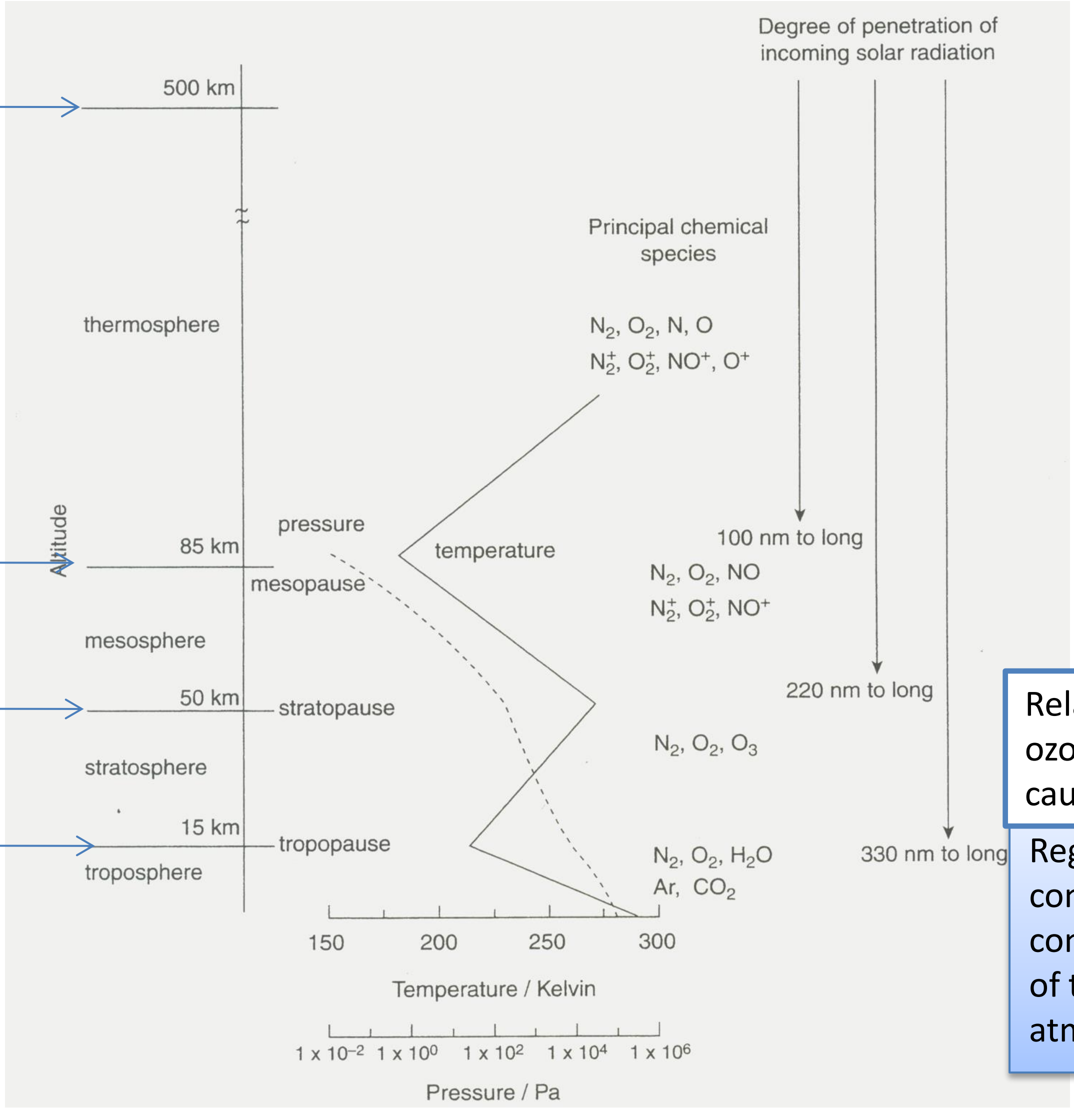
+1200^{0}C

Reversals:

-92 ^{0}C

-2^{0}C

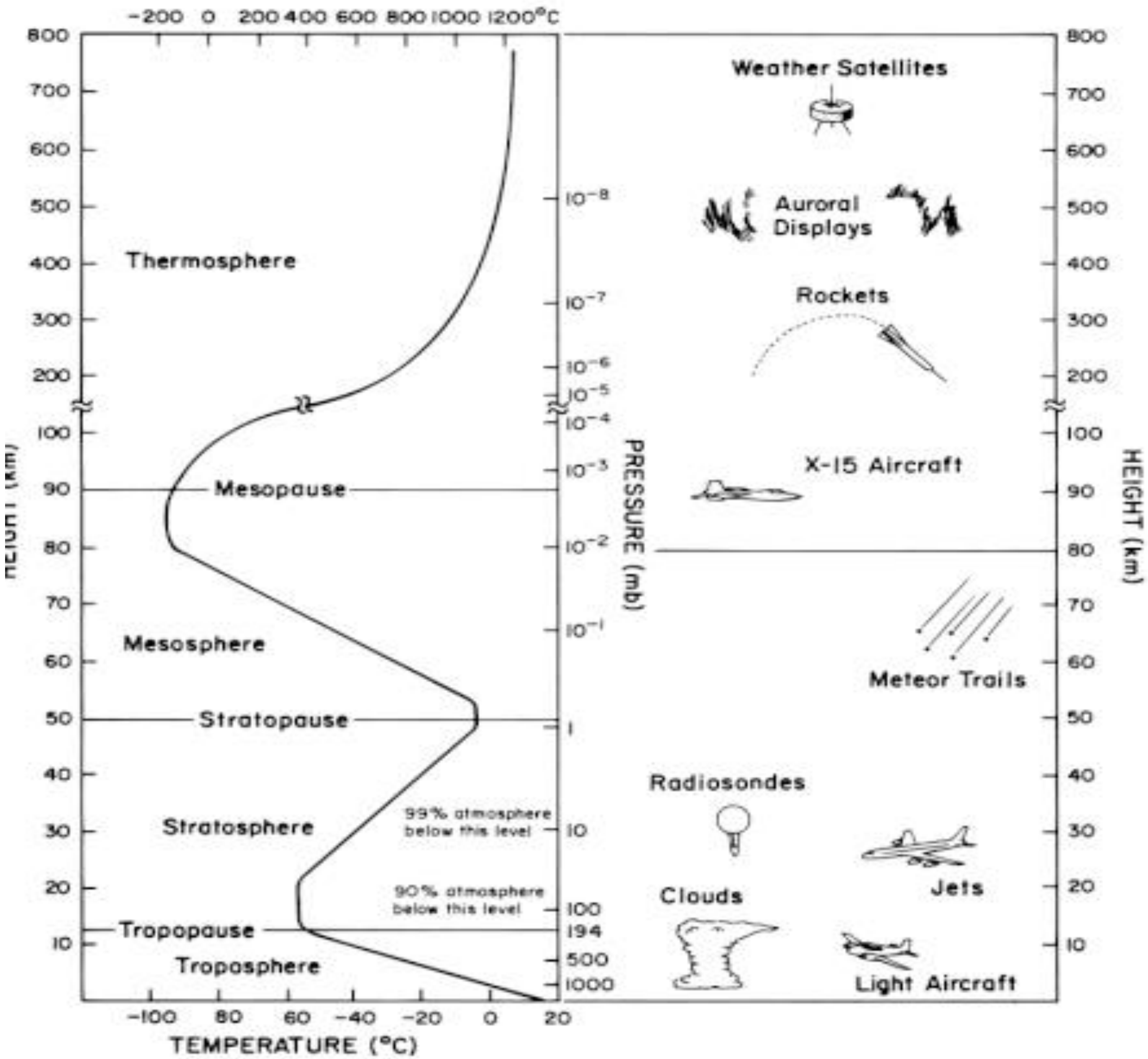
-56^{0}C



Relatively stable region, ozone absorbs UV and causes increse of temp

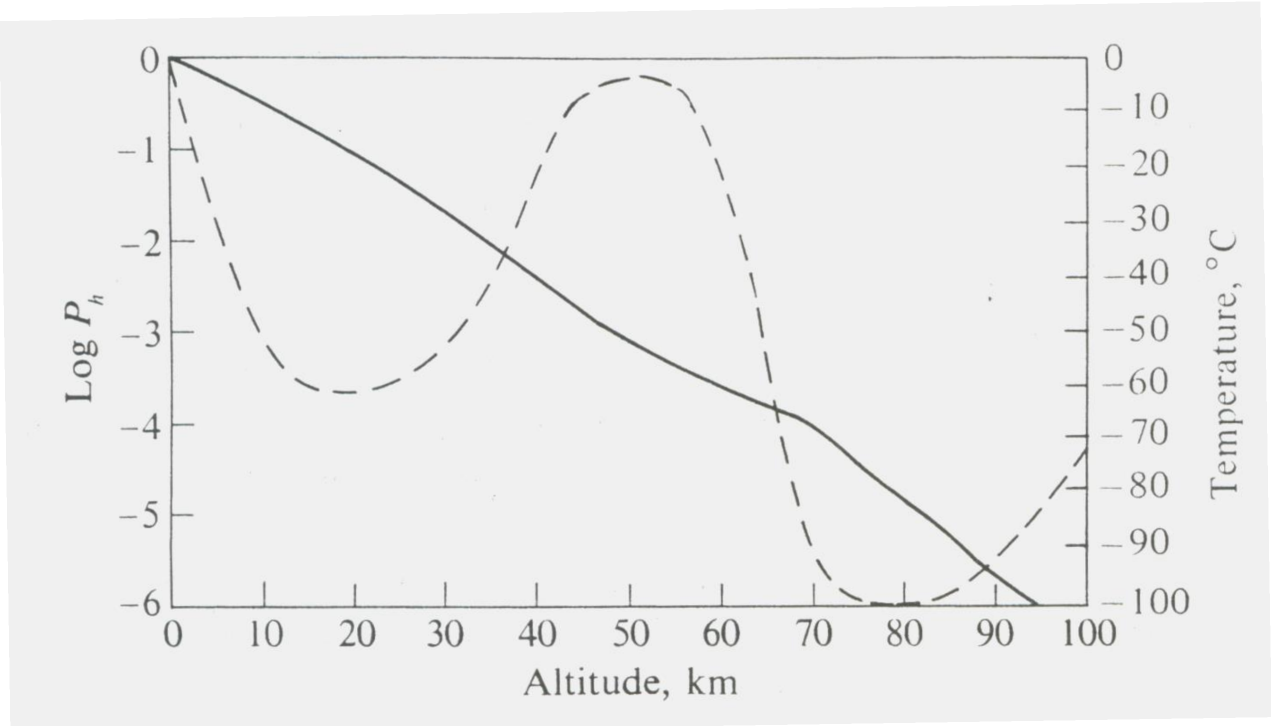
Region of intense convective mixing, contains 85% by mass of the entire atmosphere

G. W. vanLoon, S. J. Duffy Environmental Chemistry, Oxford Press, 2011



J. R. Eagleman, Meteorology: The Atmosphere in Action. *Wadsworth.*

Variation of atmospheric temperature and pressure with altitude



Atmospheric pressure decreases as an approximate exponential function with altitude

P_0(sea level) = 101 325 Pa   P (85 km)= 10^{-2} Pa

S. E. Manahan „Environmental Chemistry" Brooks/Cole Publishing Company , 1984

The earth's heat balance

Energy from the Sun – surface temperature of Sun is 5800 K, thus solar radiation spans part of **near –ultraviolet**, all of **visible** and part of the **infrared** regions of electromagnetic spectrum

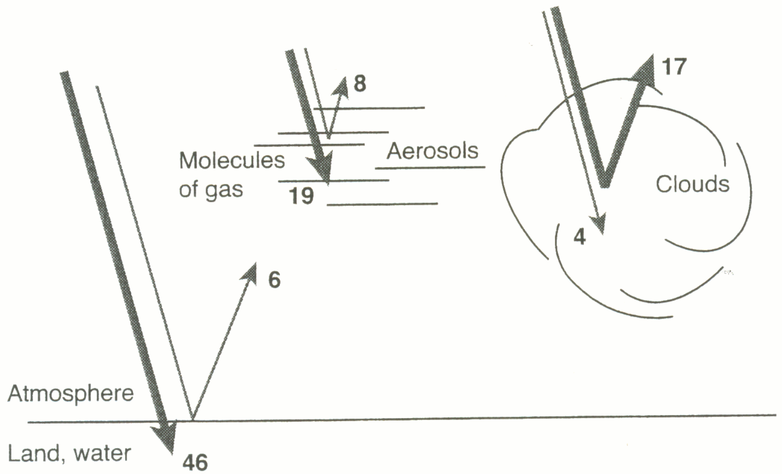


Fig. 8.4 Relative energy flows of solar radiation into the Earth's environment (based on 100 units). Arrows show solar energy that is absorbed or reflected by components of the Earth's environment.

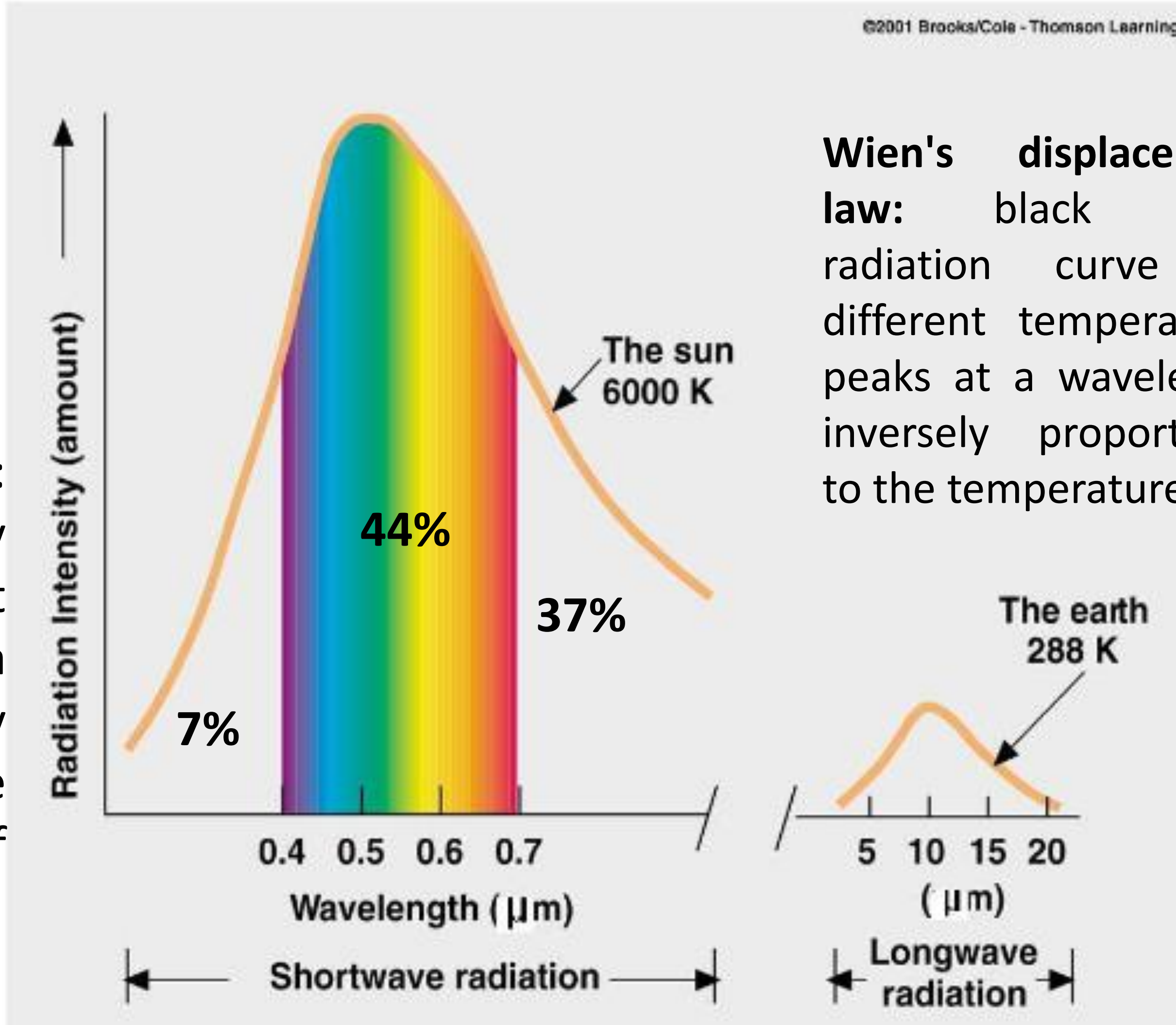
If the total solar flux represented as 100 %
The reflected portion includes:
6% from the earth surface
17% due to clouds
8% by aerosols
Total reflectivity of the Earth is 31% it's called the Earth albedo („Earth radiation")

Solar vs. Terrestrial ("Earth") Radiation

Sun is much hotter than the Earth, therefore sunlight is emitted more intensely at shorter wavelengths than Earth's radiation

Stefan-Boltzman law: the total energy radiated per unit surface area of a black body is directly proportional to the fourth power of temperature:

$$\Phi=\sigma T^4$$



Wien's displacement law: black body radiation curve for different temperatures peaks at a wavelength inversely proportional to the temperature

Black body radiation diagrams for Sun and Earth

Greenhouse effect

- If all of radiation emitted from earth could escape into space the average global surface temperature should be -19^{0}C, in fact the measured average surface temperature is +17^{0}C.

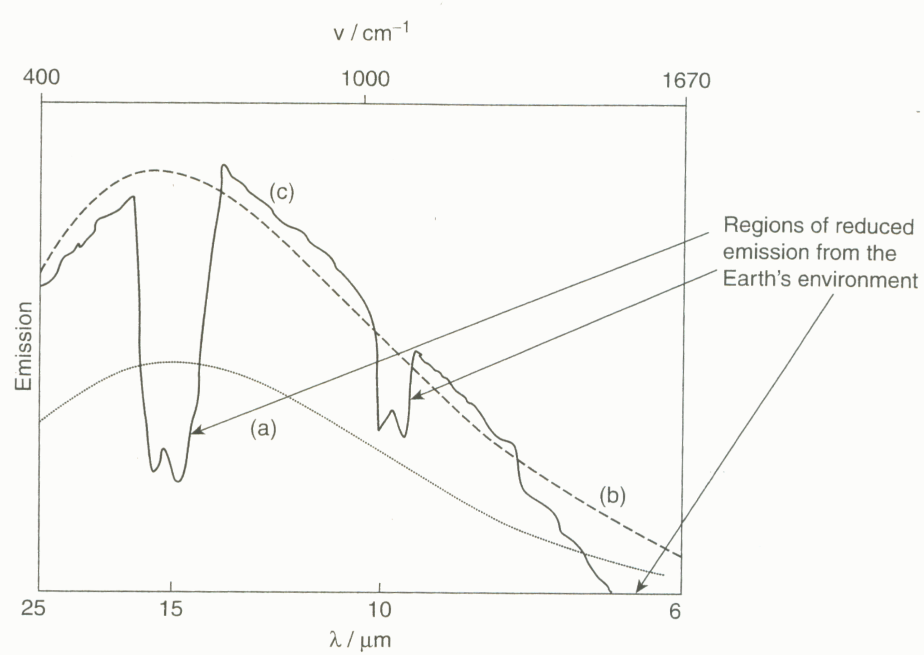
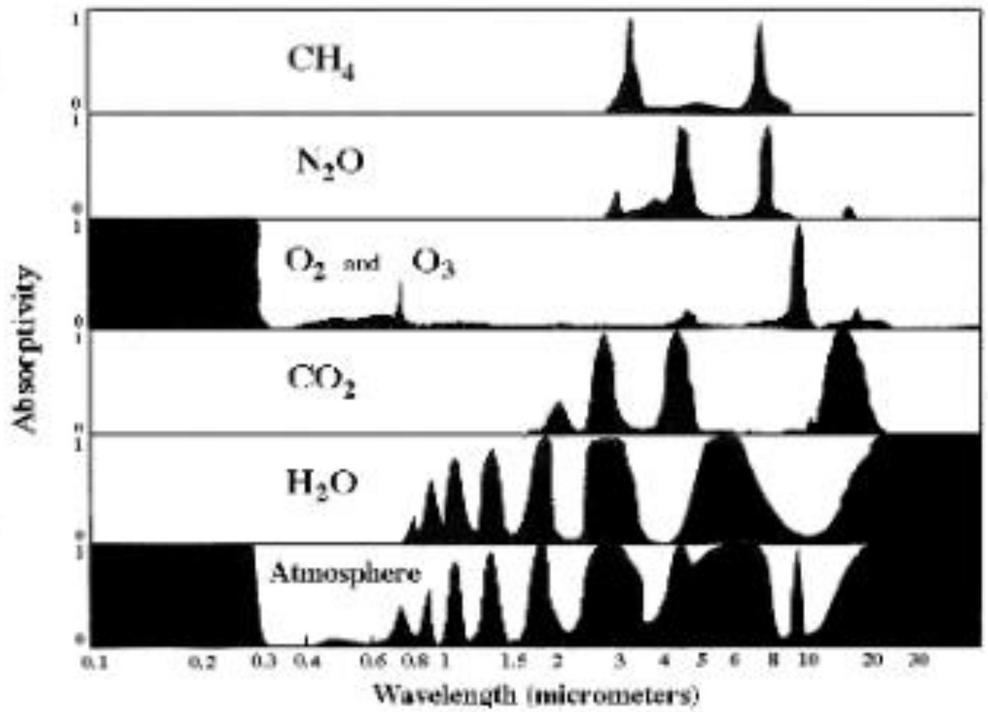


Fig. 8.6 Infra-red emission spectra for black-body radiators at (a) 240 K, (b) 280 K, and (c) t Earth. (Redrawn from Wayne, R.P., *Chemistry of atmospheres*. Clarendon Press, Oxford; 199

The significant portion of the radiation that is re-emitted from the planet's surface is absorbed by gases in the planetary atmosphere, particularly the lower troposphere, it contributes to warming which called „greenhouse effect".

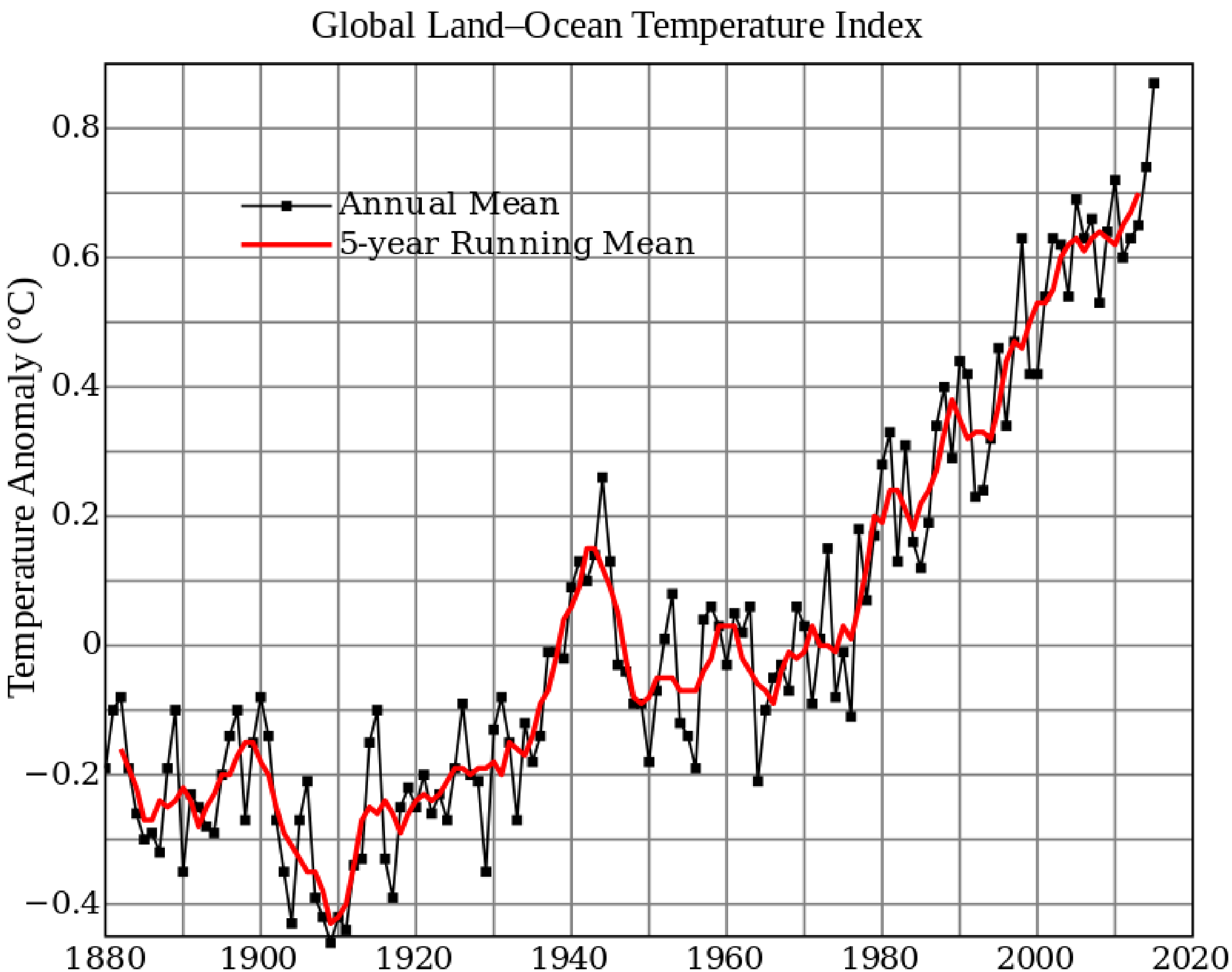
Greenhouse gases GHG

The greenhouse effect occurs because the atmosphere is relatively **transparent to the wavelengths of solar radiation, while it absorbs infrared radiation**



Greenhouse effect

- The greenhouse effect is a naturally-occurring phenomenon on the earth. The enhancement of this effect by increasing greenhouse gases associated with man-made activities is the reason for concern about climate change (global warming).
- Increased emissions of GHGs the last 100+ years have increased GHG concentrations in the atmosphere. This is believed by the consensus of climate scientists to have amplified the greenhouse effect, and therefore the main reason behind the global warming experienced the last 100+ years
- Is Anthropogenic Climate Change Real? Unlike the Greenhouse Effect, the validity and more accurately, the magnitude of ACC is still in debate.

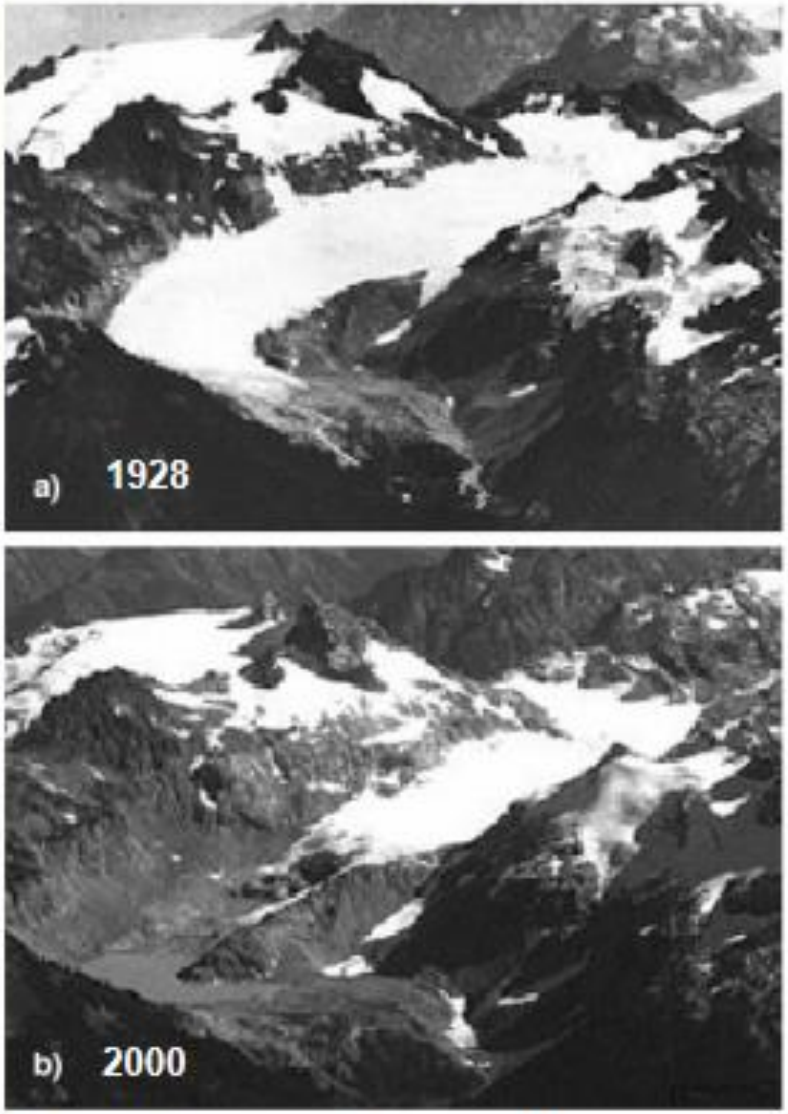


GMSTC
based on surface air measurements over land, sea and ocean surface

Global mean surface temperature change (GMSTC) from 1880 to 2015, relative to the 1951–1980 mean. The black line is the annual mean and the red line is the 5-year running mean.
Source: NASA GISS.

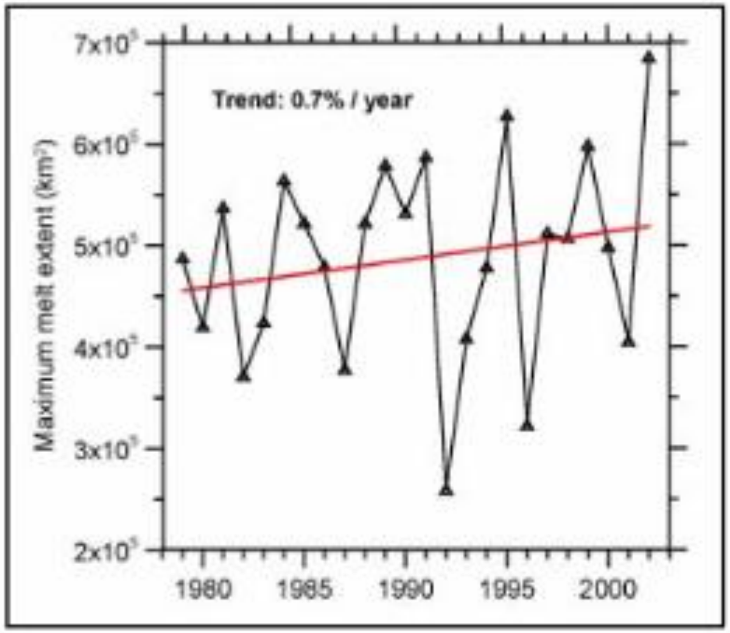
Evidence of global warming

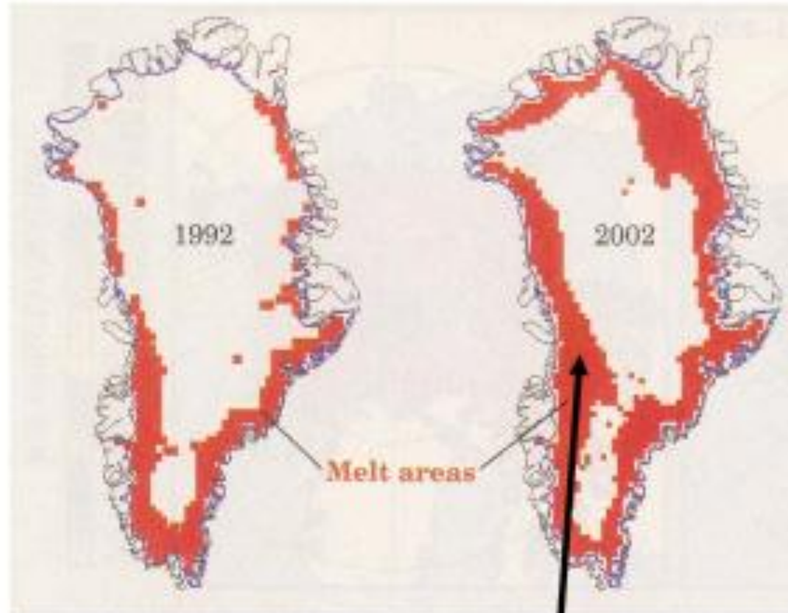
The South Cascade Glacier has been closely monitored by glaciologists studying the effects of climate on glaciers. Between 1958 and 2009 South Cascade Glacier lost nearly a half of its volume.



South Cascade Glacier, Washington

Increasing Melt Area on Greenland



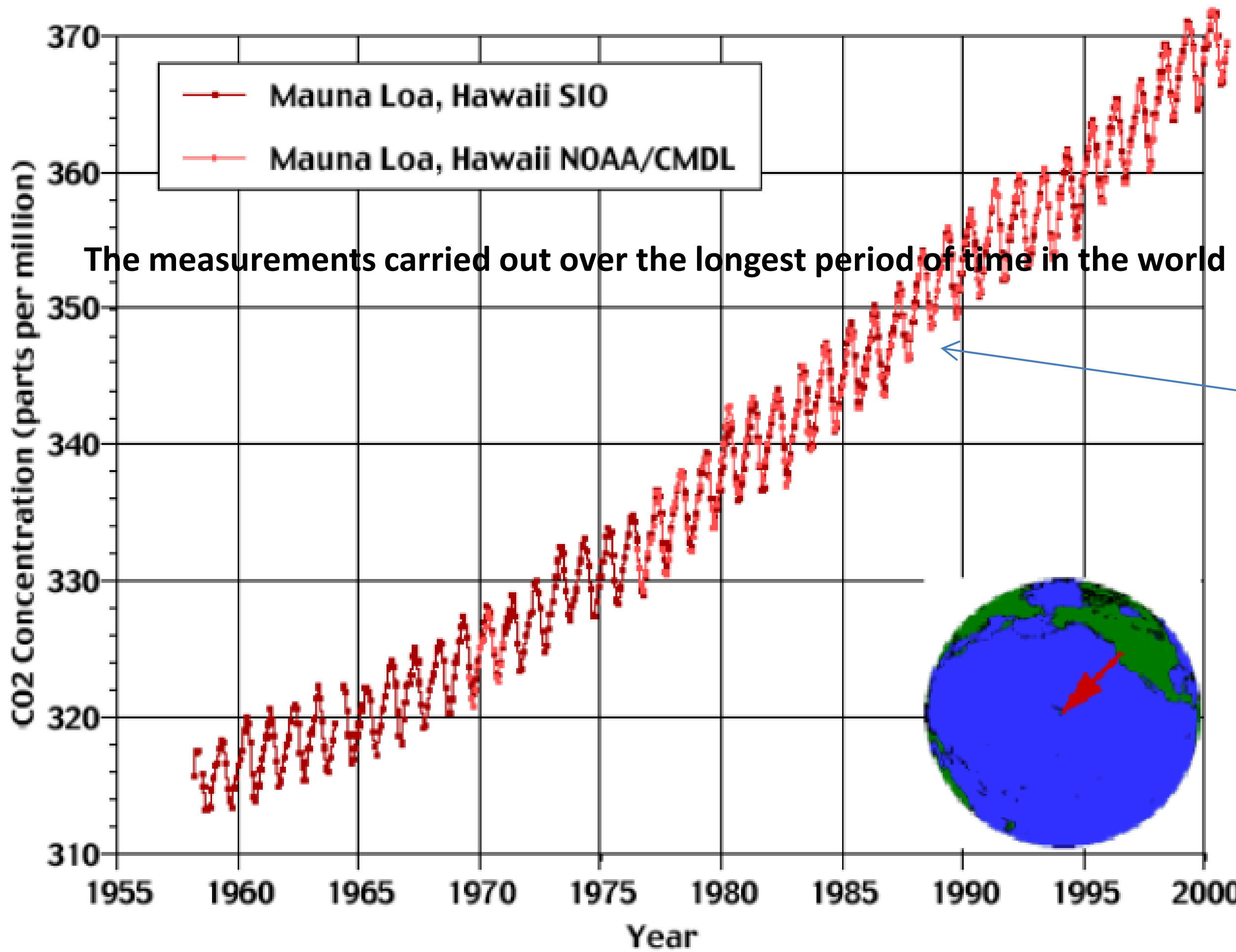


- 2002 all-time record melt area
- Melting up to elevation of 2000 m
- 16% increase from 1979 to 2002

70 meters thinning in 5 years

Satellite-era record melt of 2002 was exceeded in 2005.

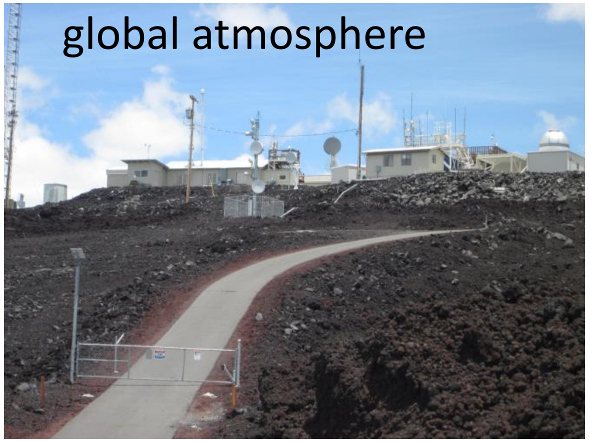
Source: Waleed Abdalati, Goddard Space Flight Center



The Keeling Curve

The Keeling Curve shows that atmospheric carbon dioxide levels are increasing, and at a faster rate each year.

MLO monitors the global atmosphere



Atmospheric concentrations of CO_2 measured at Mauna Loa in Hawaii.

Why is CO_2 rising?

Main reasons: fossil fuel combustion and deforestatio??

Graphic copied from http://chemistry.beloit.edu/Warming/pdf/CO2

Greenhouse gases GHG

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

Gaseous compound	Tropospheric concentration		Contribution to radiative forcing / $W\ m^{-2}$
	Before 1750	At present	
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	
CFC-12	0 pptv	544 pptv	
CFC-113	0 pptv	80 pptv	
Carbon tetrachloride	0 pptv	94 pptv	
Methyl chloroform	0 pptv	34 pptv	0.34 total for all halocarbons
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

[a] Average additional energy in watts per square meter associated with the increase in concentration of each gas

G. W. vanLoon, S. J. Duffy Environmental Chemistry, Oxford Press, 2011

The relative contribution of emissions of different greenhouse gases

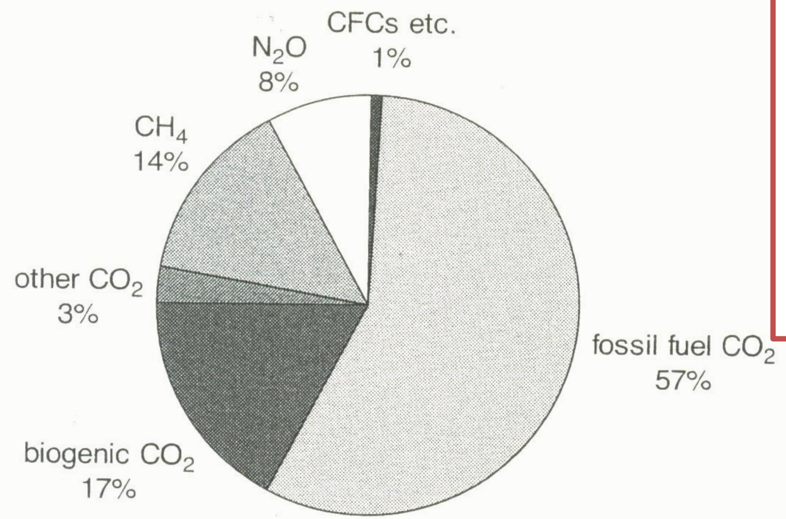


Fig. 8.13 Share of different greenhouse gases of anthropogenic origin to global emissions in 2004. All values take into account quantity of emissions and relative instantaneous radiative forcing. Redrawn from *Climate change 2007: Synthesis report*.

With including three factors:
- the concentration of the species
- the wavelength of absorption
- the strength of absorption

G. W. vanLoon, S. J. Duffy Environmental Chemistry, Oxford Press, 2011

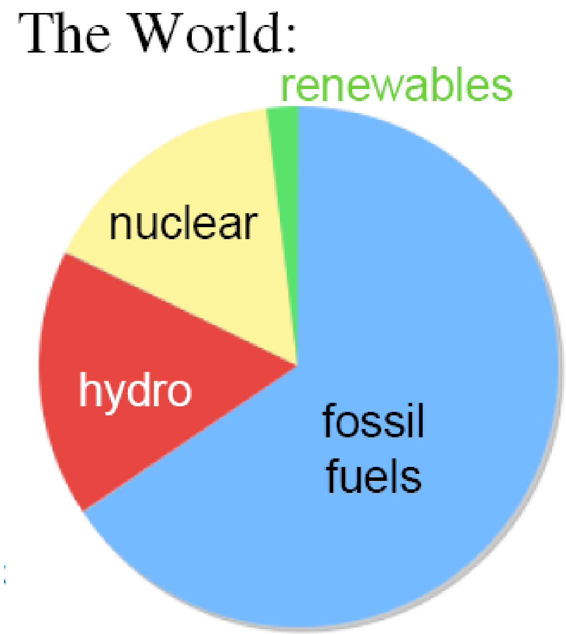
Energy sources

•2/3 of the world's power comes from fossil fuel combustion

•30 Gt CO_2/year emissions

•No uncertainty that rising CO_2 levels are causing climate change

•Great uncertainty in the extent of changes to expect and course of action to minimize negative effects



http://www.eia.doe.gov/emeu/international/electricitygeneration.html

Kyoto Protocol

- The protocol to **United Nations Framework Convention on Climate Change** (UNFCCC) to reduce global warming, initially adopted on 11 December 1997 in Kyoto and entered into force on 16 February 2005.
- Assumes reduction (ca 5 % against 1999 level to 2012) of emission of four greenhouse gases (GHG) (carbon dioxide, methane, nitrous oxide, sulphur hexafluoride) and two groups of gases (hydrofluorocarbons and perfluorocarbons) in 37 countries. This protocol has expired in 2012. A second commitment period was proposed in 2012, known as the Doha Amendment, which would commit only Europe to further CO_2 reductions until 2020. Negotiations are currently under way.
- Paris, 2016 ADOPTION OF THE PARIS AGREEMENT to achieve < 2^oC anomaly temperature (in comparison with the pre-industrial time), signed by 195 countries

Carbon dioxide capture and storage (CCS)

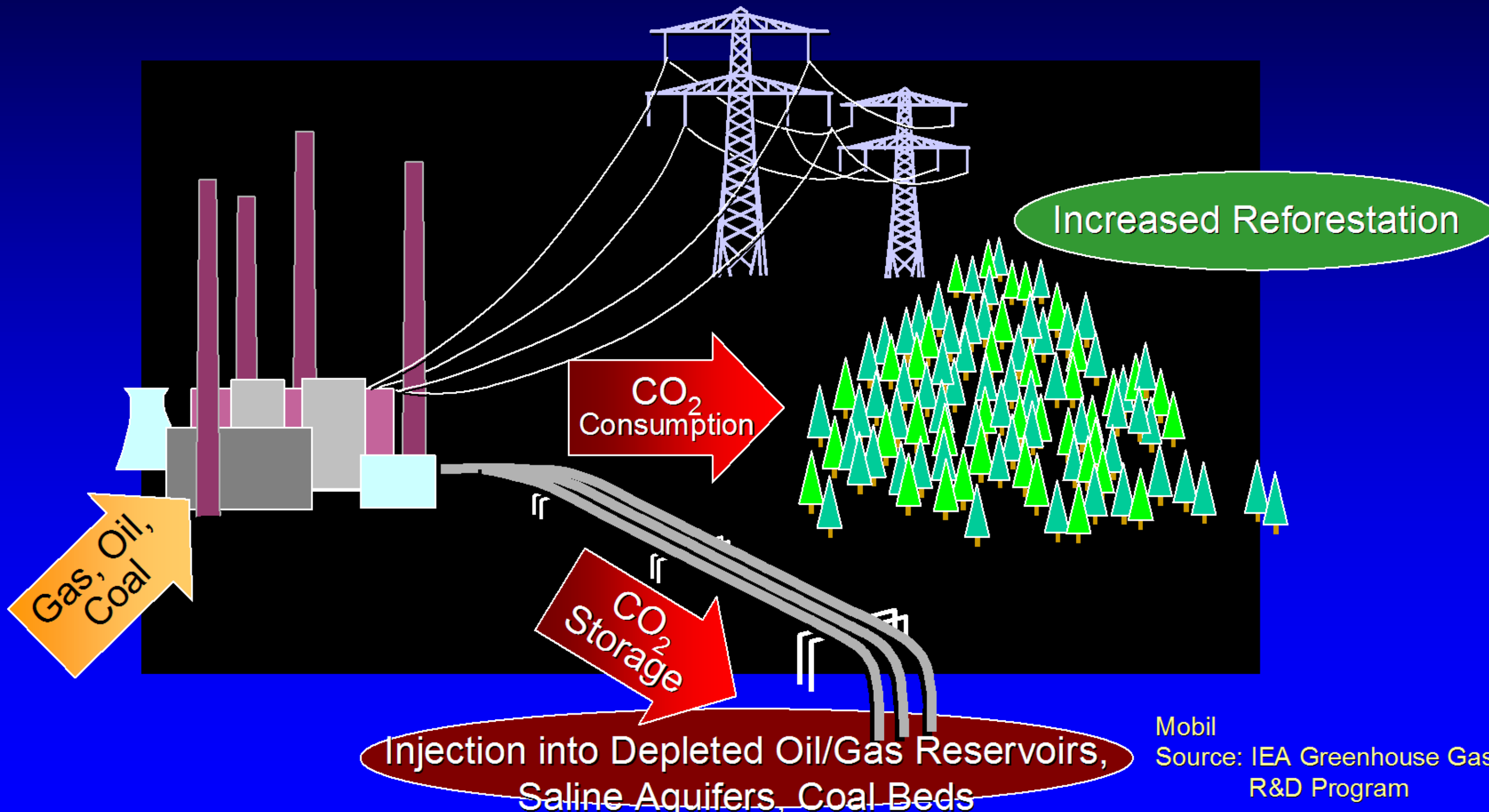
- *Carbon dioxide (CO_2) capture and storage (CCS) –* ***sequestration*** *is a process consisting of the* ***separation of CO_2 from industrial and energy-related sources, transport to a storage location and long-term isolation from the atmosphere.***

- *The CO_2 would then be* ***compressed*** *and* ***transported for storage in geological formations, in the ocean, in mineral carbonates, or for use in industrial processes****.*

- *The International Energy Agency (IEA) (2008) suggests that carbon capture and storage (CCS) can potentially make a significant contribution to reduce anthropogenic carbon dioxide (CO_2) emissions to the atmosphere by 2050.*

CO_2 Capture and Storage

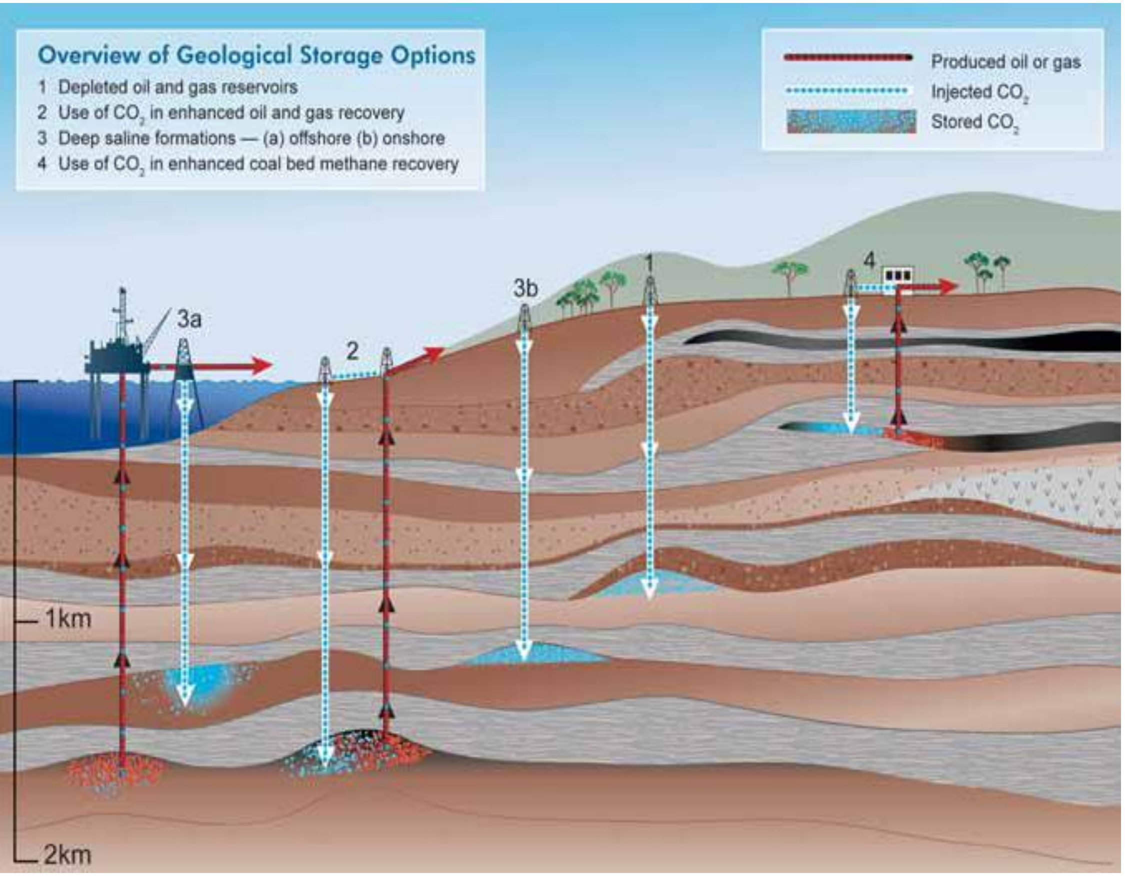
Potential for Reducing CO_2 Emissions from Fossil Fuel Power Generation



Mobil
Source: IEA Greenhouse Gas R&D Program

JMA

Carbon dioxide capture and storage (CCS)



*Storage of CO_2 in deep, in **geological formations** uses many of the same technologies that have been developed by the oil and gas industry.*

•In depleted gas and oil wells

•Above 800 m in saline formations that can sequester and retain large quantities of CO_2

Intergovernmental Panel on Climate Change, special report „**Carbon Dioxide Capture and Storage" 2005**

Carbon dioxide capture and storage (CCS)

Geological storage seems most promising

- **Oil and Gas Fields**

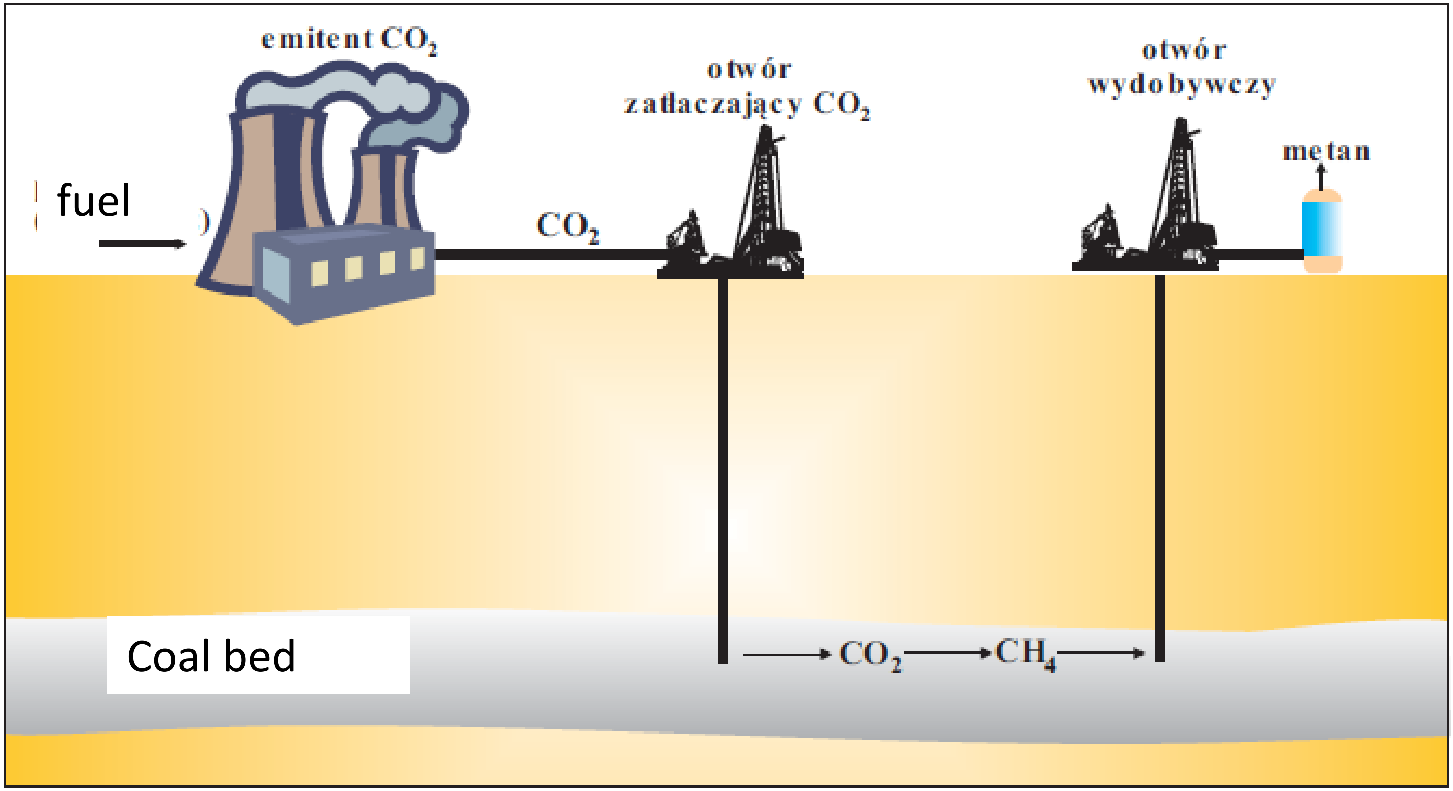
  Can be enhanced by pumping CO_2 gas into the reservoir to push out the product, which is called enhanced oil recovery. The United States is the world leader in enhanced oil recovery technology, using about 32 million tons of CO_2 per year.

Carbon dioxide capture and storage (CCS)

- **Coal Beds - Enhanced Coal Bed Methane**

  Injection of carbon dioxide gas into the coal bed. Tests have shown that the adsorption rate for CO_2 to be approximately twice that of methane, giving it the potential to efficiently displace methane and remain sequestered in the bed. CO_2 recovery of coal bed methane has been demonstrated in limited field tests, but much more work is necessary to understand and optimize the process.

Enhanced Coal Bed Methane (ECBM)



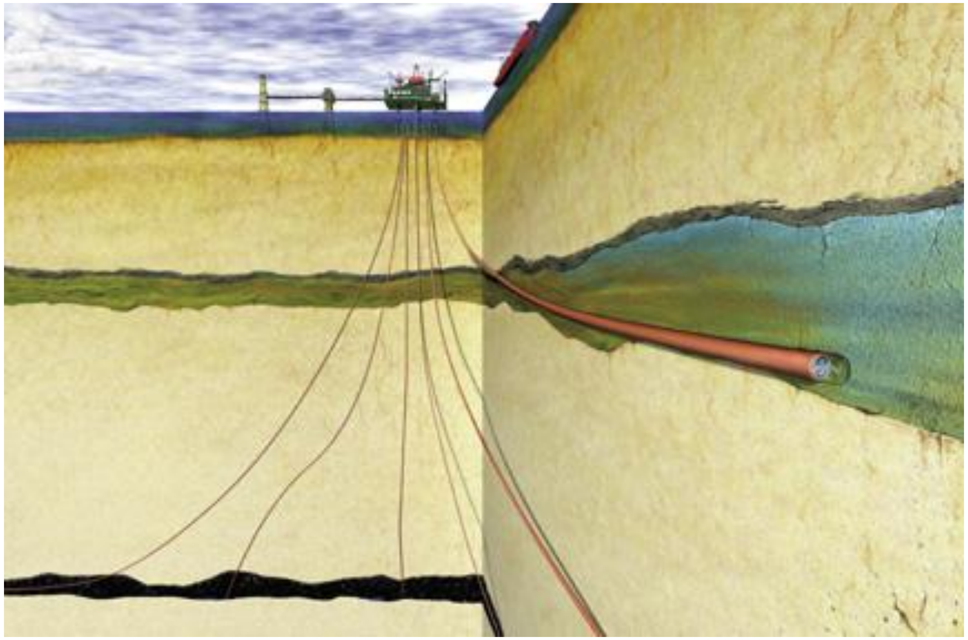
Rys. 26. Składowanie CO_2 w pokładach węgla z intensyfikacją wydobycia metanu (Putting... 2001)

Fig. 26. CO_2 storage in coal seams with ECBM (Putting… 2001)

R. Tarkowski, „Geologiczna sekwestracja CO_2" Wydawnictwo Instytutu Gospodarki Surowcami Mineralnymi , Kraków 2005

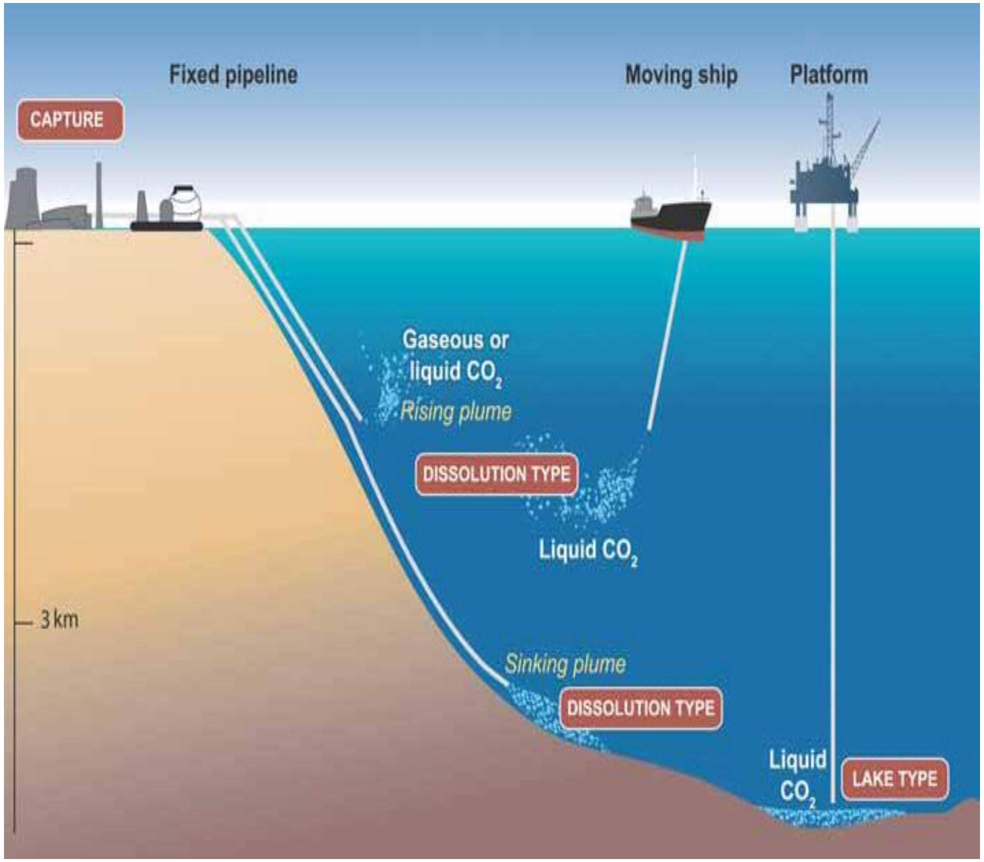
Carbon dioxide capture and storage (CCS)

- **Deep Saline Aquifers**



Sequestration of CO_2 in deep saline formations.
The Norwegian oil company, Statoil, is injecting approximately one million tonnes per year of recovered CO_2 into the Utsira Sand, a saline formation under the sea associated with the Sleipner West Heimdel gas reservoir.(Since 1996)

Carbon dioxide capture and storage (CCS)



Ocean storage potentially could be done in two ways:

•by injecting and dissolving CO_2 into the water (at depth below 1000 m) or onto the sea floor

• at depths below 3,000 m, where liquid CO_2 (as supercritical fluid) denser than water forms a "lake" that would delay dissolution of CO_2

Ocean storage are still in the research phase, currently not favored.

Intergovernmental Panel on Climate Change, special report „**Carbon Dioxide Capture and Storage" 2005**

Important questions related to CCS

- How long will the CO_2 remain underground?
- What happens if the CO_2 eventually leaks into the atmosphere?
- What if the CO_2 eventually spreads?
- Could it affect on drinking water from underground sources?

At very high *concentrations* (a factor of 100 or more higher than its atmospheric *concentration*), ***carbon dioxide*** **can be** ***toxic.***

Carbon dioxide capture by chemical absorption

- **Chemical absorpion** $NaOH_{(aq)}$, $CH_3CH_2NH_{2(aq)}$ (Monoethylamine - MEA)

$$CO_2 + OH^- \rightleftharpoons HCO_3^-$$

$$HCO_3^- + OH^- \rightleftharpoons CO_3^{2-} + H_2O$$

$$CH_3CH_2NH_2 + CO_2 \rightleftharpoons CH_3CH_2NHCOO^- + H^+$$

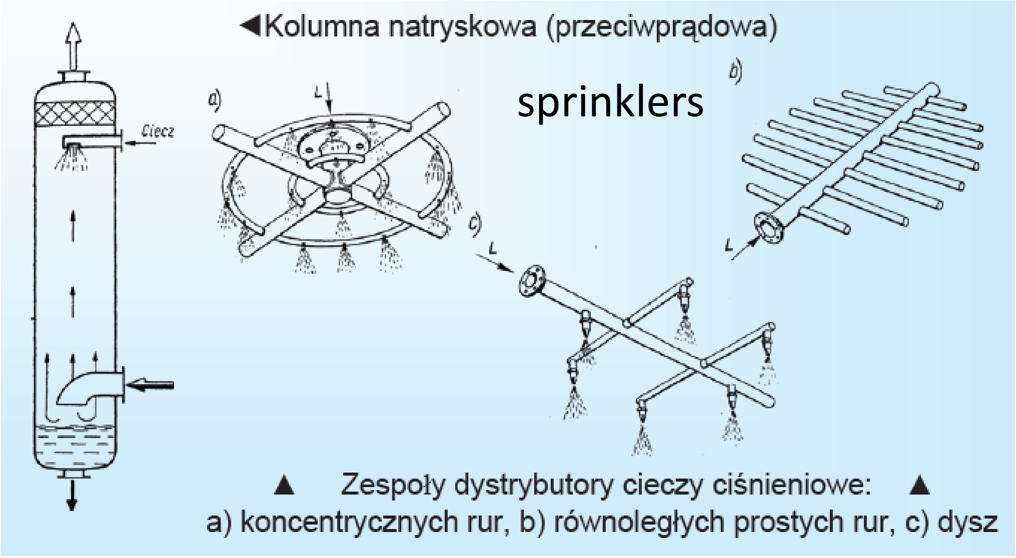
$$CH_3CH_2NH_2 + H^+ \rightleftharpoons CH_3CH_2NH_3^+$$

Gas absorption is the process whereby a pollutants (in gas or vapor form) are removed from air or another gaseous stream by contact with a flowing liquid phase.

Absorption is the process by which atoms, molecules, or ions enter a bulk phase (liquid, gas, solid).

Carbon dioxide capture by chemical absorption

- In order to increase the surface area available for mass transfer, the operation is almost always conducted inside a tower or column packed with high surface-area filling material
- Industrial-scale gas absorbers are often referred to as "scrubbers„



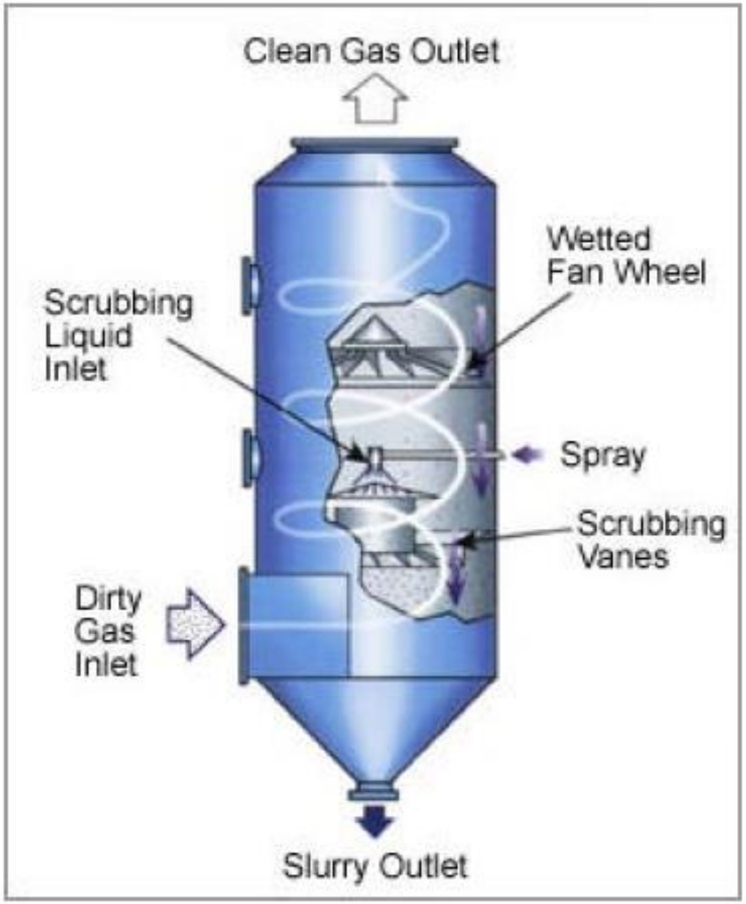
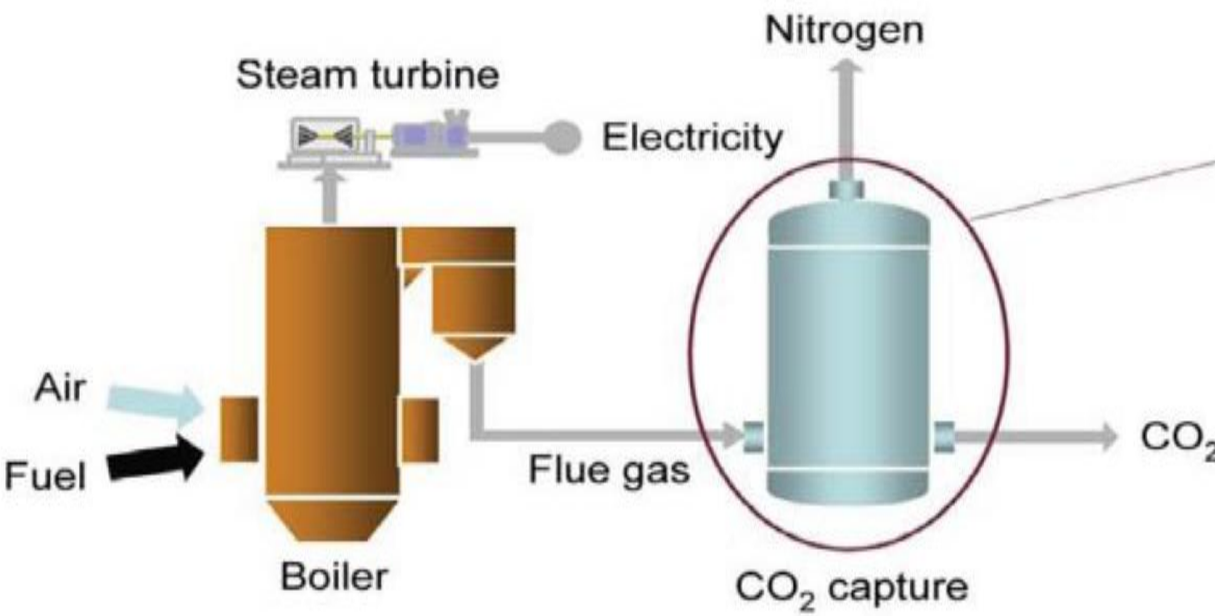


Figure 4: example of wet scrubber [ref. 34]

Carbon dioxide capture by chemical absorption

Electric plant



Flue gas from fuel combusting is directed to absorption tower where CO_2 is captured, nitrogen is directed to atmosphere and after absorption solution is heated with steam to reverse the CO_2 absorption reaction and afterwards CO_2 is compressed for transport.

Intergovernmental Panel on Climate Change, special report „**Carbon Dioxide Capture and Storage" 2005**

Carbon dioxide capture by chemical absorption

CO_2 post-combustion capture at a plant in Malaysia. This plant employs a chemical absorption process to separate 0.2 $MtCO_2$ per year from the flue gas stream plant for urea production (Courtesy of Mitsubishi Heavy Industries).

Intergovernmental Panel on Climate Change, special report „**Carbon Dioxide Capture and Storage" 2005**

Biological sequestration and biomass based fuels

- Plants can remove carbon dioxide from atmosphere or from water as they are growing. Biomass is organic material produced as the solid product.

$$6\ CO_2 + 6\ H_2O \longrightarrow C_6H_{12}O_6 + 6\ O_2 \quad \text{(photosynthesis)}$$

Dry biomass can be used **as fuel** to provide energy. Biomass can be regard as **renewable resource** because energy of the Sun remains constant and crops can be grown and harvested year after year.