Global Atmospheric Change

Changha Lee

School of Chemical and Biological Engineering
Seoul National University

The Earth's Atmosphere

√ **The Earth's atmosphere**

- Relatively small compartment (0.3% of the ocean's mass)
- Easy to contaminate (little dilution)
- Greenhouse gases CO_2, CFCs, CH_4, N_2O affect global climate changes.
- Largely made up of N_2 (79%) and O_2 (21%)
- Other gases present in small concentrations (trace gases)
- Human's activities much more likely to affect trace gas concentrations than O_2 and N_2

Global Temperature

√ **Global temperature**

- Interested in the history of the earth's temperature in order to understand the system and make predictions

- Climatologists study
  - Tree rings
  - Ice volume
  - Fossil pollen
  - Oxygen isotopes (most reliable)

Oxygen Isotopes

√ Oxygen isotopes

- H_2O evaporating from sea has

  ^{18}O (0.20%) + ^{16}O(99.76%)

- It is easier to vaporize a light molecule (^{16}O).

- Water vapor tends to move towards the poles, and then precipitates into the ice cap.

  - Always, $^{18}O/^{16}O$ ice sample < $^{18}O/^{16}O$ standard

- The separation of light isotopes from heavier ones is temperature-dependent.

  -Cold: less ^{18}O makes it to the poles. $\Rightarrow$ low $^{18}O/^{16}O$ in sample $\Rightarrow$ high (negative) $\delta^{18}O$

  -Warm: more ^{18}O makes it to the poles. $\Rightarrow$ high $^{18}O/^{16}O$ in sample $\Rightarrow$ low (negative) $\delta^{18}O$

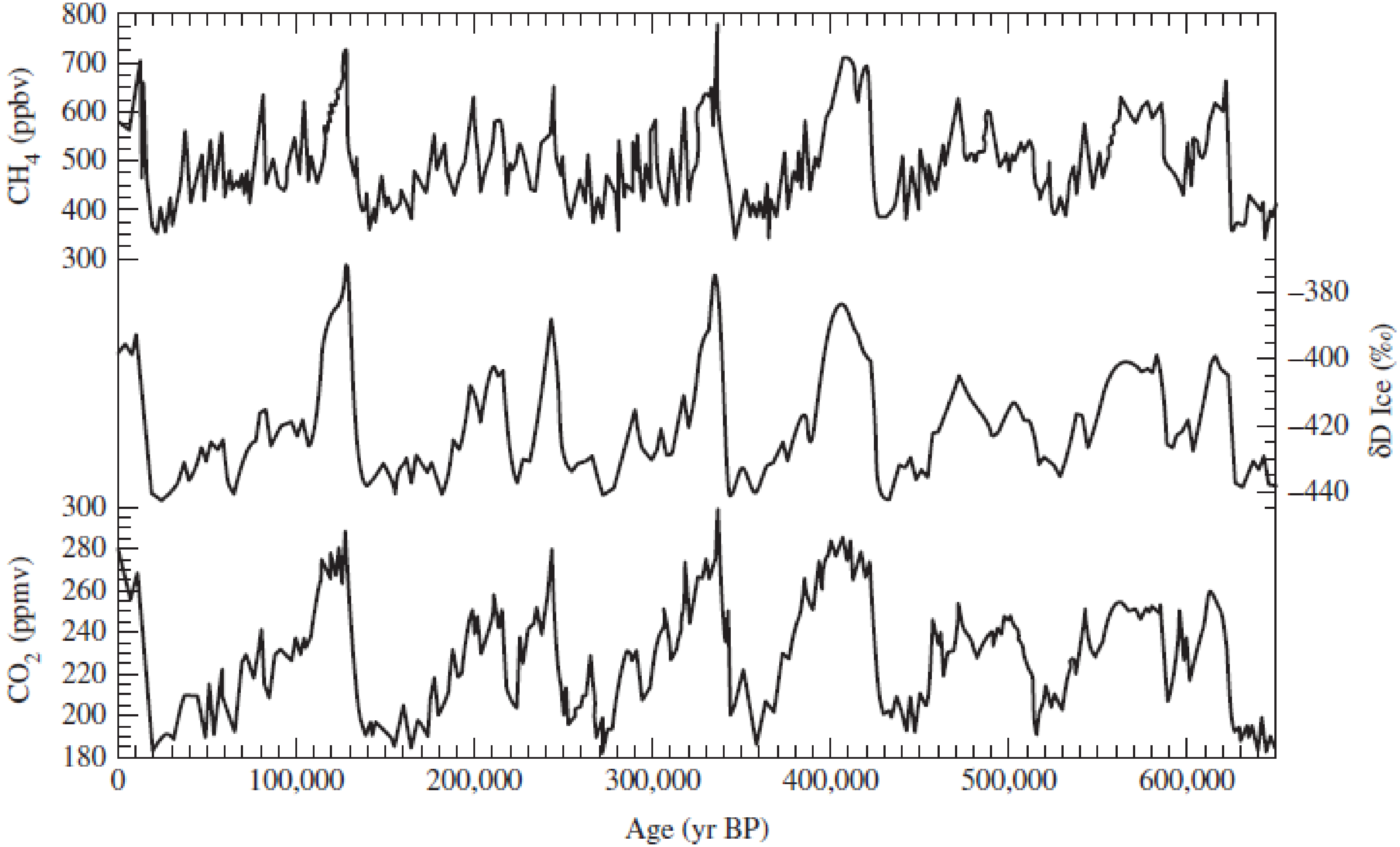
$$\delta^{18}O(^0/_{00}) = \left[\frac{(^{18}O/^{16}O)\ \text{sample}}{(^{18}O/^{16}O)\ \text{standard}} - 1 \right] \times 10^3$$

Oxygen Isotopes

√ **Ice cores**

- Layering of the ice provides a time record.
- Oxygen isotopes act as a “historical thermometer” of past temperatures.
- By examining air bubbles sealed in (Antarctic) polar ice at different depths, the historical concentration of trace gases can be determined.
- A correlation between CO_2 and CH_4 concentrations in air bubbles and temperature (per $^{18}O/^{16}O$ in ice) is seen.

Ice Cores

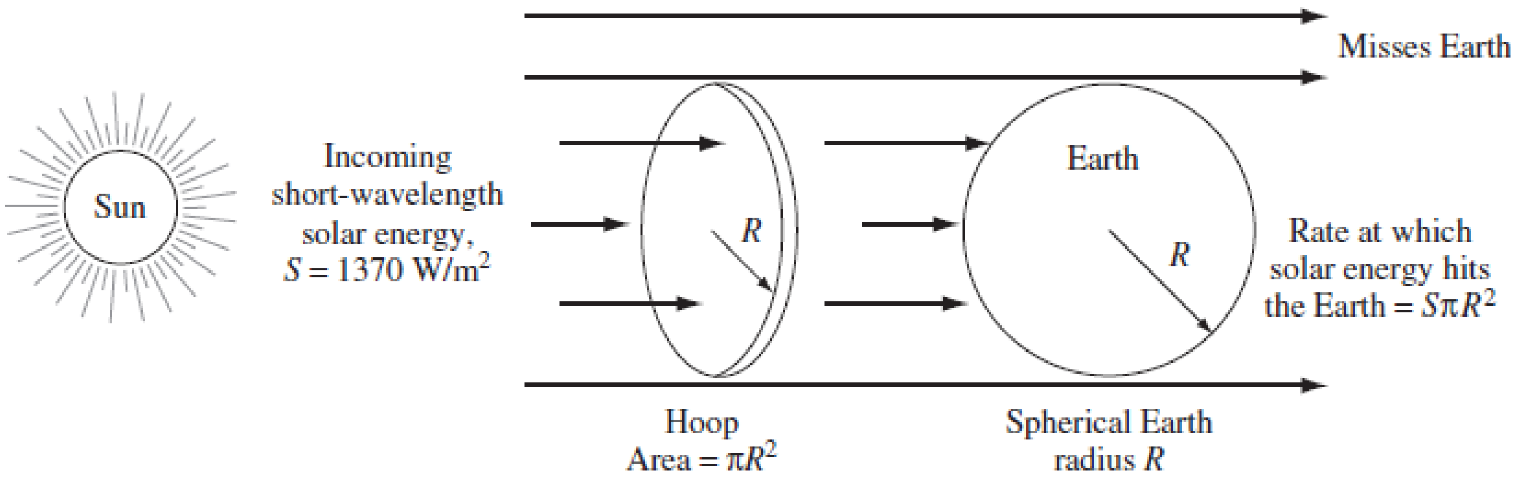


800
700
600
500
400
300
CH4 (ppbv)
−380
−400
−420
−440
δD Ice (‰)
300
280
260
240
220
200
180
CO2 (ppmv)
0
100,000
200,000
300,000
400,000
500,000
600,000
Age (yr BP)

The Globe as a Blackbody

√ The Globe as a Blackbody

- To predict the effect of changes in CO_2 concentrations researchers use *general circulation models (GCMs)*
- The starting point is a model that describes how radiation and the earth interact – the blackbody model



The Globe as a Blackbody

√ **The Globe as a Blackbody**

- A blackbody absorbs all of the radiation that impinges upon it.
- Energy is emitted from a blackbody due to its temperature.
- Rate at which solar energy strikes the earth $= S\pi R^2$

  Where

  - S = the solar radiation, 1370 W/m^2
  - R = the radius of the earth (m)

- Stefan-Boltzmann equation for blackbody radiation

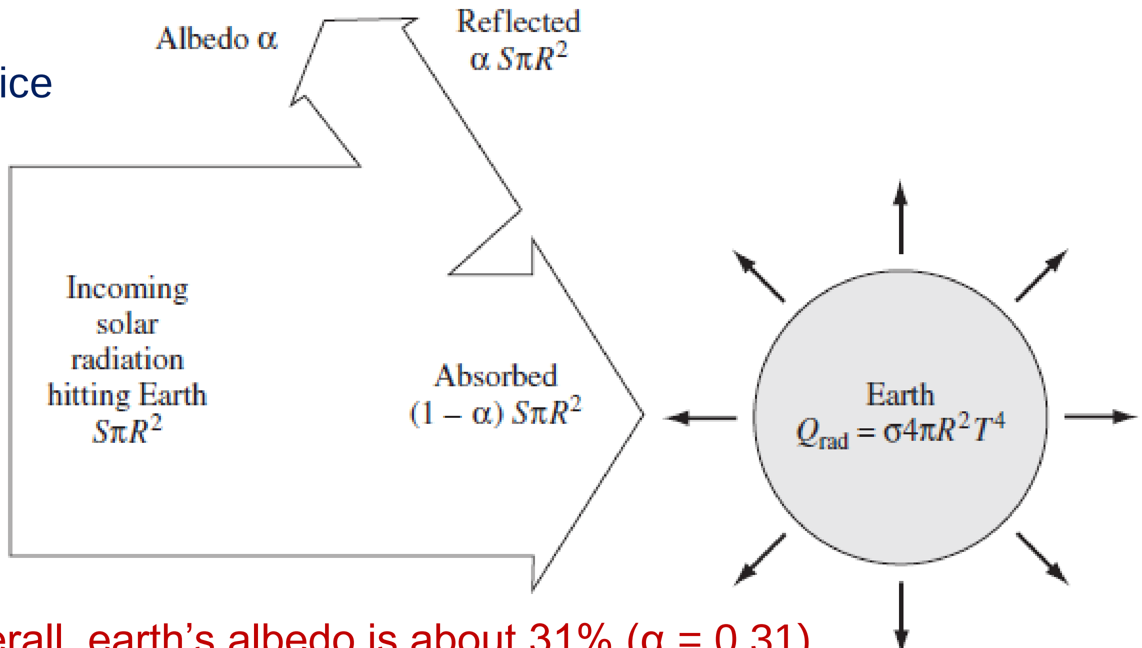
$$\text{Energy radiated back to space by earth} = \sigma 4\pi R^2 T_e^4$$

- Where
  - σ = Stefan-Boltzmann constant, 5.67 x 10^{-18} (W/m^2-K^4)
  - T_e = “effective” blackbody temperature (K)

The Globe as a Blackbody

√ **Albedo**

- However,
  - Some incoming radiation is reflected off the surface
  - Thus, it does not contribute to the Earth's warming
- The fraction of radiation that is reflected is called the albedo, α (i.e., reflectivity)
  - Low for oceans
  - Moderate for land
  - Highest for snow and ice



Overall, earth's albedo is about 31% (α = 0.31)

The Globe as a Blackbody

√ **The Earth's effective blackbody temperature**

- Using equations to describe the radiation balance, accounting for
  - Incoming radiation
  - Albedo
  - Blackbody emission
- Energy balance:

$$S\pi R^2(1 - \alpha) = \sigma 4\pi R^2 T_e^4$$

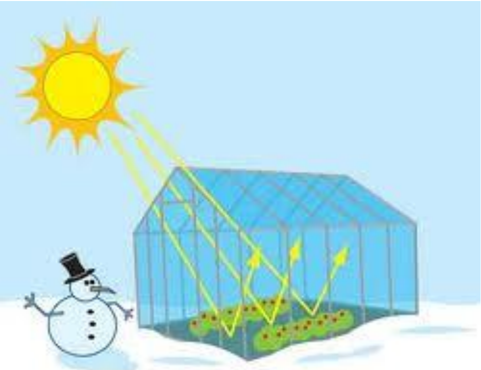
- Solve for T, then

$$T_e = \left[\frac{S(1 - \alpha)}{4\sigma}\right]^{1/4}$$

- The earth's predicted average temperature is 254 K (i.e., -19°C)
- The actual average temperature is about 288 K (15°C) about 34°C higher than predicted
- The inaccuracies are related to the greenhouse effect that were not accounted for in energy balance.

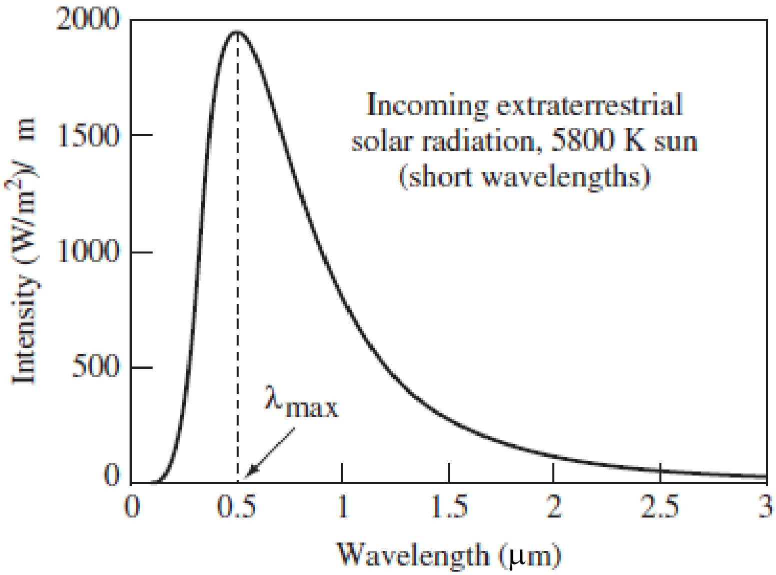
The Greenhouse Effect

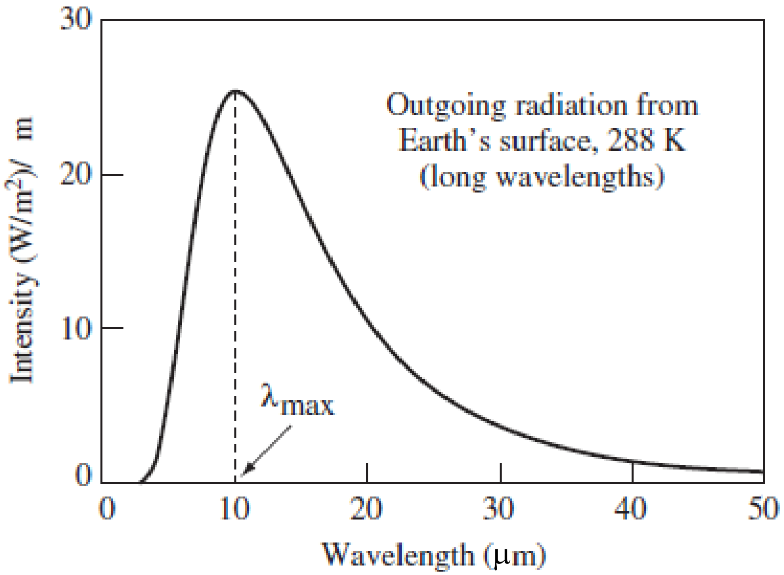
√ **Incoming and outgoing radiation**



- The radiation emitted by the sun is primarily between 0.15 and 3 μm (short wave)
- The radiation emitted by the Earth is between 3 and 50 μm (long wave)

$$\lambda_{max}\,(\mu m) = \frac{2{,}898}{T(K)}$$

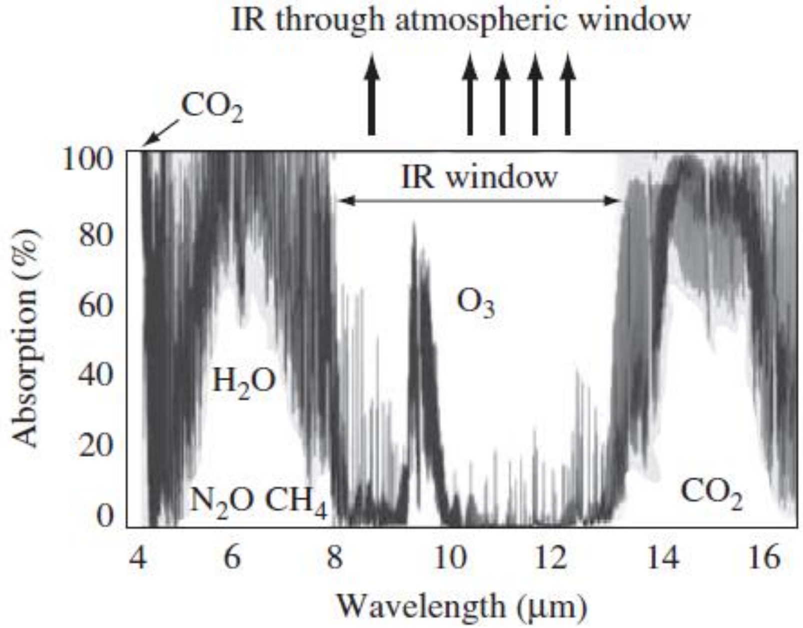


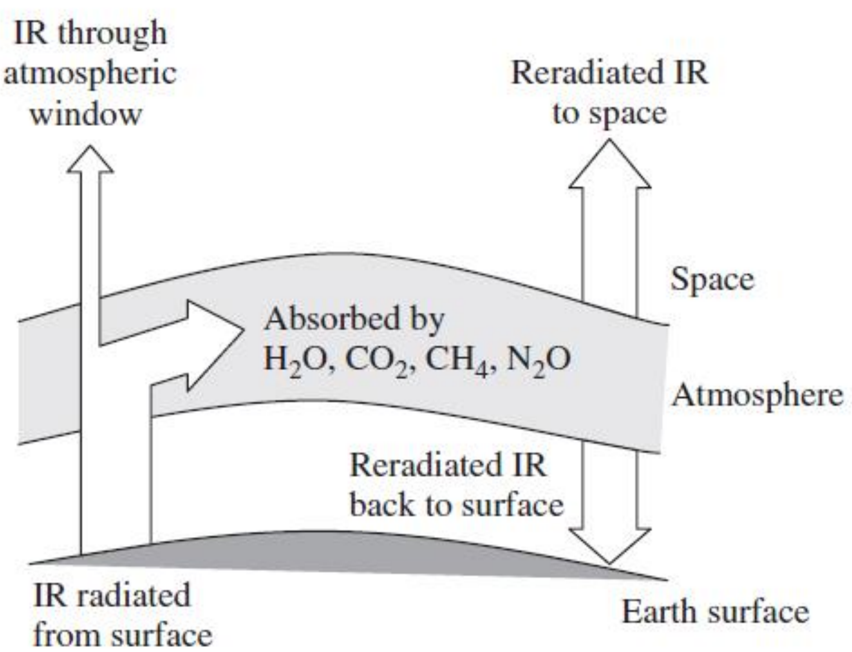


The Greenhouse Effect

√ The Greenhouse effect

- Many atmospheric gases absorb radiation.
  - Water absorbs radiation <8 μm & >18 μm
  - CO_2 strongly absorbs between 13 and 18 μm
  - There is an atmospheric radiative window: 7-13 μm
- The atmosphere radiates energy back to earth and to space.
- This greenhouse effect raises the average surface temperature of the earth by 34°C.





Greenhouse Effect Enhancement

√ Greenhouse effect enhancement

- The gases in the atmosphere that absorb radiation are important to maintaining a temperature that is conducive to life as we know it
- The greenhouse effect is a naturally occurring phenomenon, but....
- What happens as the concentration of greenhouse gases changes?
- How and why are the concentrations changing?

√ Gases of concern: CO_2, CFCs, CH_4, N_2O

- CO_2
  - Produced by fossil fuel combustion
  - Deforestation removes a CO_2 sink
- CFCs (Foams, refrigerants, solvents)
- CH_4 (Wetlands, rice paddies, livestock)
- N_2O (Fuels, fertilizers)

Greenhouse Effect Enhancement

The main greenhouse gases

Greenhouse gases	Chemical formula	Pre-industrial concentration	Concentration in 1994	Atmospheric lifetime (years)***	Anthropogenic sources	Global warming potential (GWP)*
Carbon-dioxide	CO_2	278 000 ppbv	358 000 ppbv	Variable	Fossil fuel combustion Land use conversion Cement production	1
Methane	CH_4	700 ppbv	1721 ppbv	12,2 +/- 3	Fossil fuels Rice paddies Waste dumps Livestock	21 **
Nitrous oxide	N_2O	275 ppbv	311 ppbv	120	Fertilizer industrial processes combustion	310
CFC-12	CCl_2F_2	0	0,503 ppbv	102	Liquid coolants. Foams	6200-7100 ****
HCFC-22	$CHClF_2$	0	0,105 ppbv	12,1	Liquid coolants	1300-1400 ****
Perfluoromethane	CF_4	0	0,070 ppbv	50 000	Production of aluminium	6 500
Sulphur hexa-fluoride	SF_6	0	0,032 ppbv	3 200	Dielectric fluid	23 900

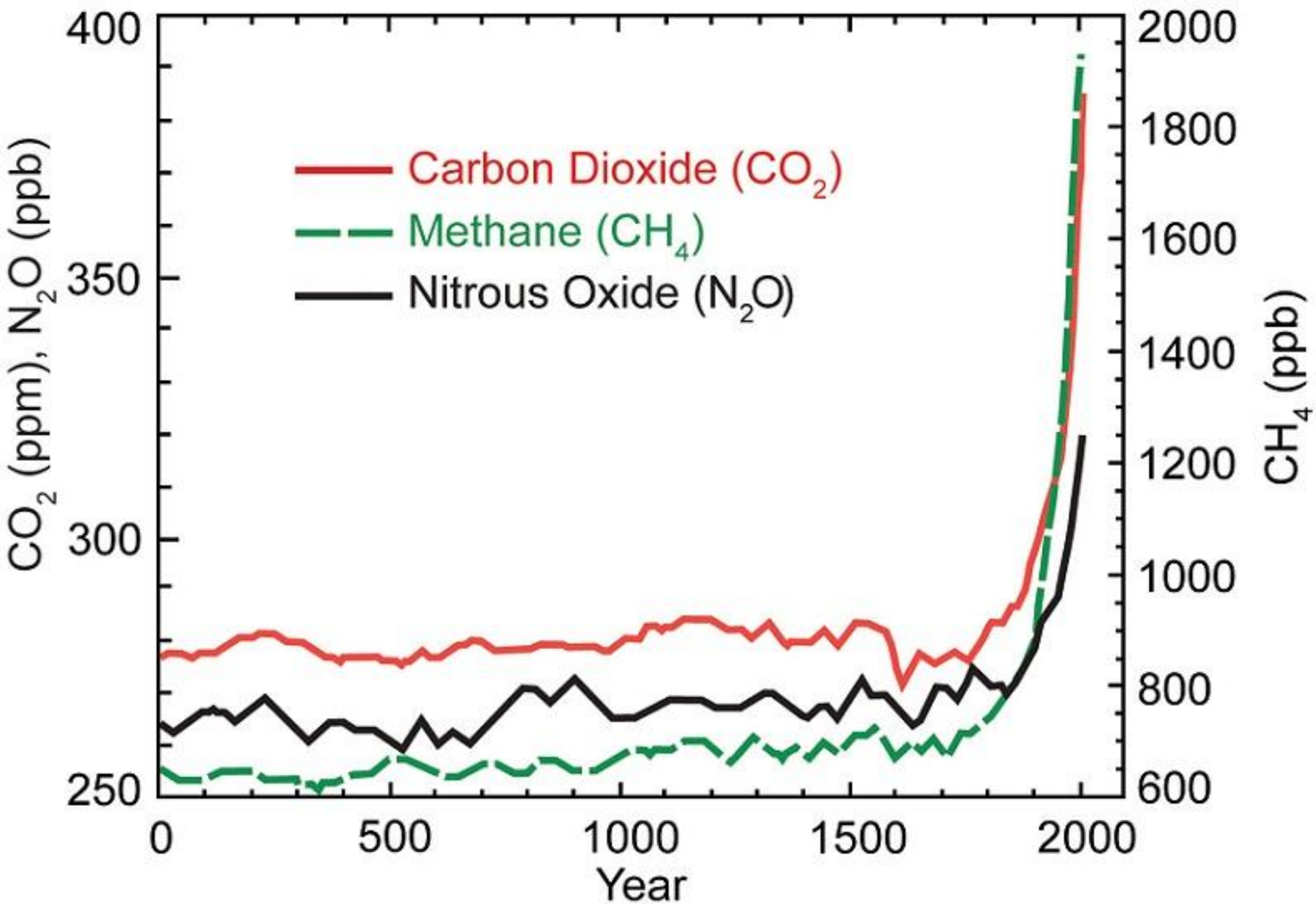
Note : pptv= 1 part per trillion by volume; ppbv= 1 part per billion by volume, ppmv= 1 part per million by volume

* GWP for 100 year time horizon. ** Includes indirect effects of tropospheric ozone production and stratospheric water vapour production. *** On page 15 of the IPCC SAR. No single lifetime for CO_2 can be defined because of the different rates of uptake by different sink processes. **** Net global warming potential (i.e., including the indirect effect due to ozone depletion).

Source: IPCC radiative forcing report ; Climate change 1995, The science of climate change, contribution of working groupe 1 to the second assessment report of the intergovernmental panel on climate change, UNEP and WMO, Cambridge press university, 1996.

CO_2 is the least potent but it is the greatest overall contributor (60%) due to higher conc.

Greenhouse Effect Enhancement



Development and Climate Change

“Developed countries produced most of the greenhouse gas emissions of the past and have high per capita emissions. They *must lead in both reducing emissions and financing mitigation and adaptation*.

Yet globally, most future emissions will be generated in the developing world. Those countries *need adequate investments and technology so they can pursue lower-carbon paths* without jeopardizing economic growth.”

Bierbaum and Zoellick SCIENCE VOL 326 6 NOVEMBER 2009

Global Warming and Climate Change

√ **Effects of global warming, and climate change**

- Increased average temperature
- Change in length and time of seasons
- Melting of polar caps – raising sea level
- Change in precipitation patterns – food security
- Increase frequency and intensity of extreme weather events - natural disasters (floods, hurricanes)

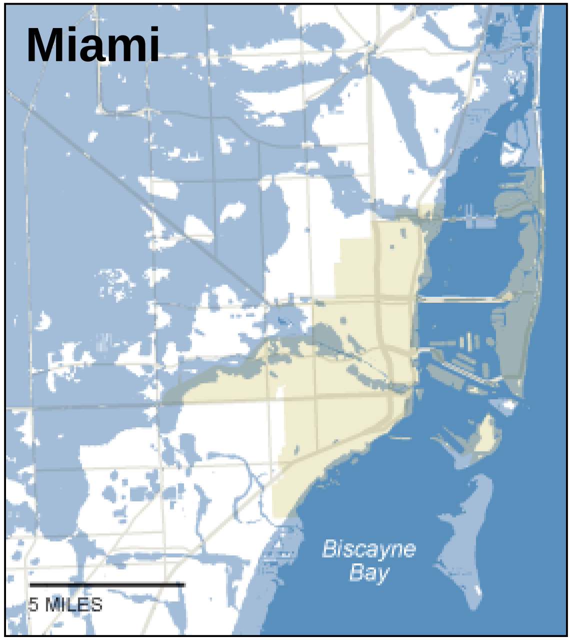
And so many more, secondary and tertiary effects!!!

Global Warming and Climate Change

√ **What Could Disappear with 5 ft. Sea Level Rise**
(Probable in 100-300 years)

Logan Airport starts to disappear. Boston Harbor begins to encroach on downtown; the Charles River floods southern Cambridge.

If levees breach, almost all of the city would flood. The surrounding region is also mostly flooded.



Much of suburban Miami and the area's barrier islands, including Miami Beach, are submerged.

Global Warming and Climate Change

√ **Climate Change?**

- **Global warming** is happening and is correlated to human emission of greenhouse gases.
- Uncertainty about the extent it induces **climate variability**, or our ability to change anything *(correlation does not prove causation)*
- **Consensus** does not mean certainty.
- Most important decisions in life are made under **uncertainty.**

Global Warming and Climate Change

√ Effects of global climate change

- What can we do about it?

- **Adaptation**

피할 수 없으면 즐겨라?

(manage the unavoidable)

  - Move people
  - Build protective systems

- **Prevention**

즐길 수 없으면 피해라?

(avoid the unmanageable)

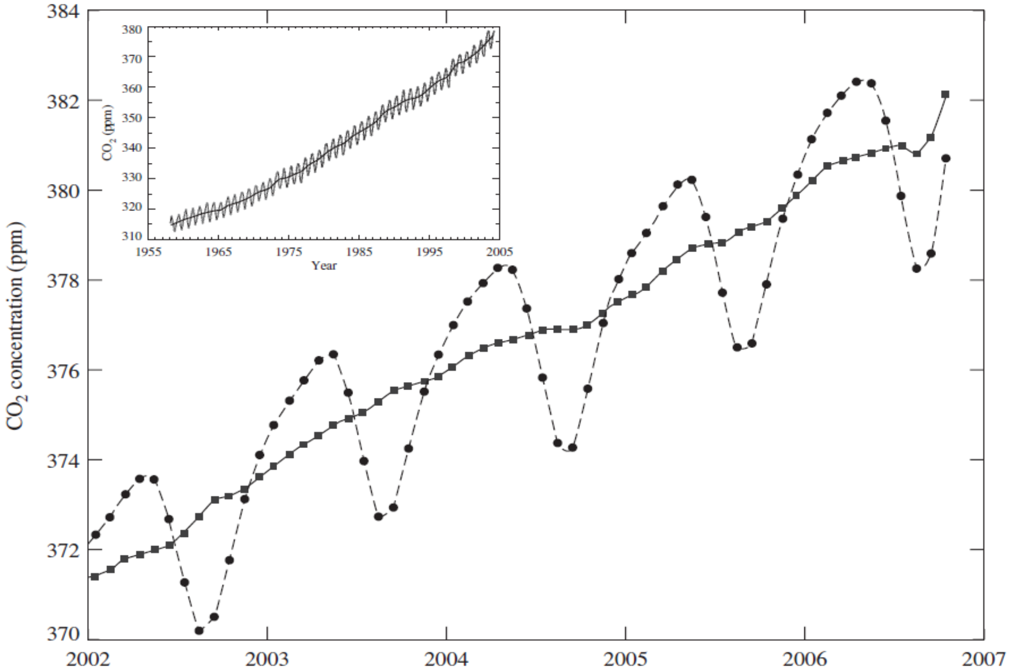
  - Reduce emissions
  - Reforestation

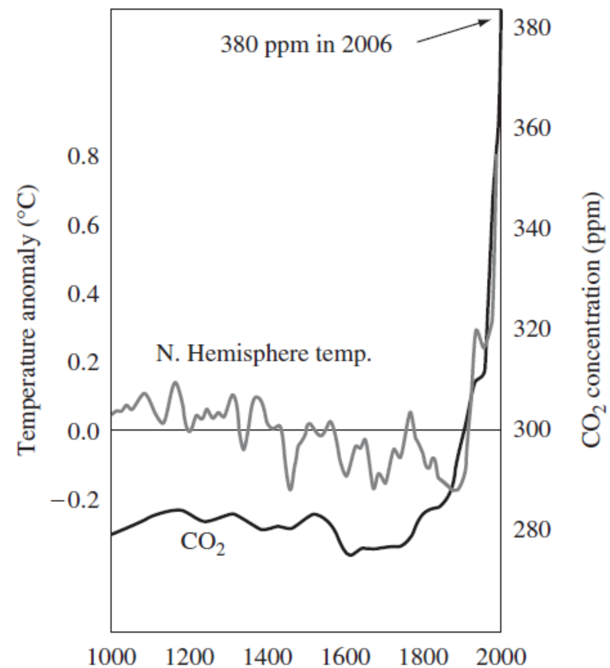
Global Warming and Climate Change

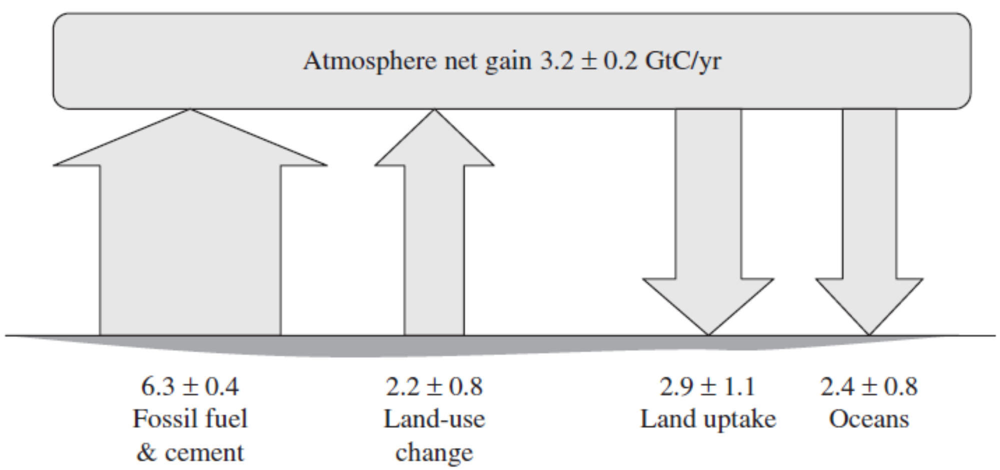
√ Precautionary principle (Wingspread statement, 1998)

- There is considerable uncertainty regarding anthropogenic effects on global climate, but…
- "When an activity raises threats of harm to human health or the environment, precautionary measures should be taken even if some cause-and-effect relations are not fully established scientifically"
- "If we live as if it matters and it doesn't matter, it doesn't matter. If we live as if it doesn't matter and it matters, then it matters"

CO_2 Emissions

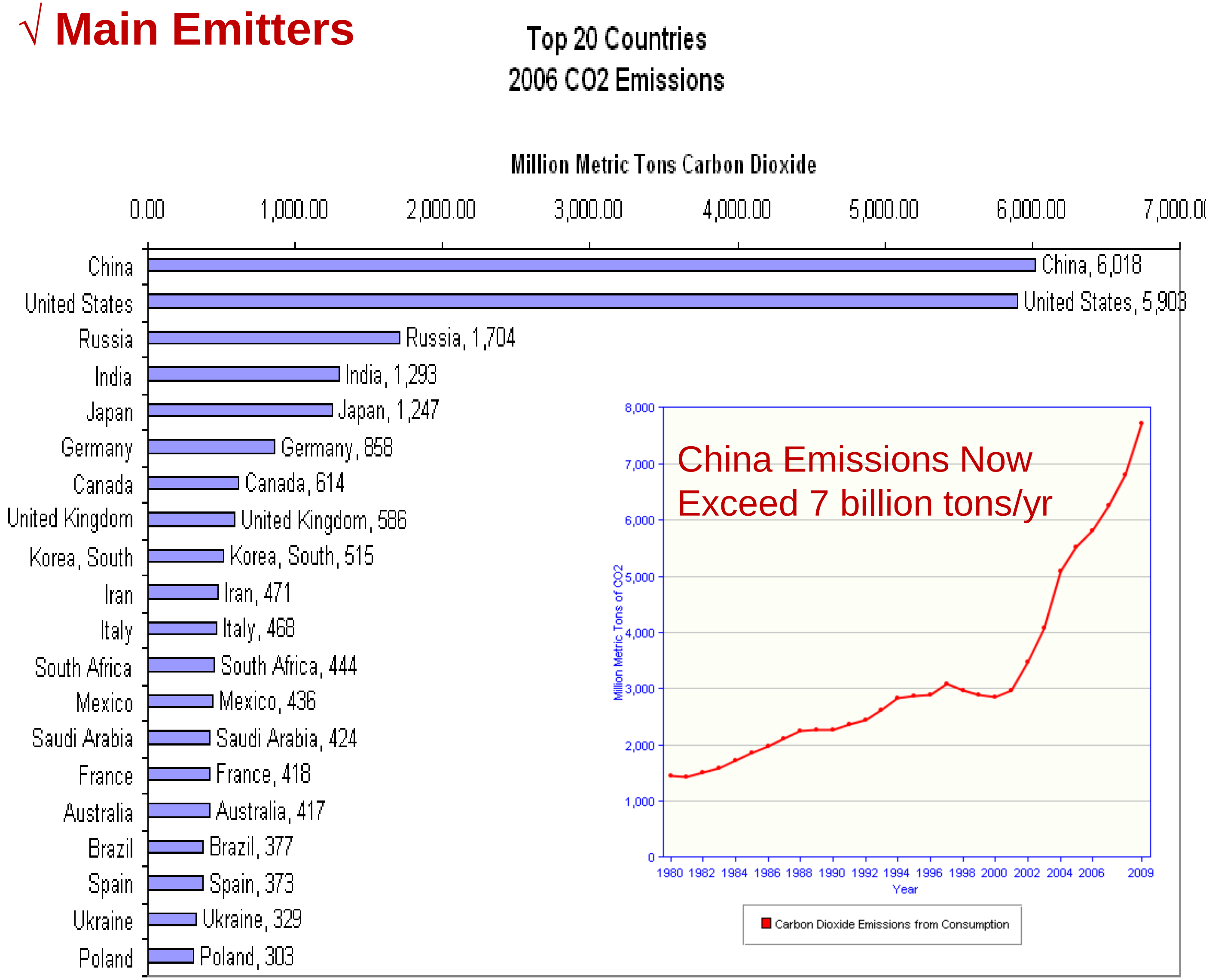






CO_2 Emissions

√ Main Emitters




Take action for our future
– reduce your CO2-emissions
This is the size of
ONE TONNE CO2
Take up the challenge
- reduce every way YOU can.
Now!
LOXAM

Example 1

- **How much CO_2 mass emitted corresponds to a 1 ppm_v increase in atmospheric concentration?**

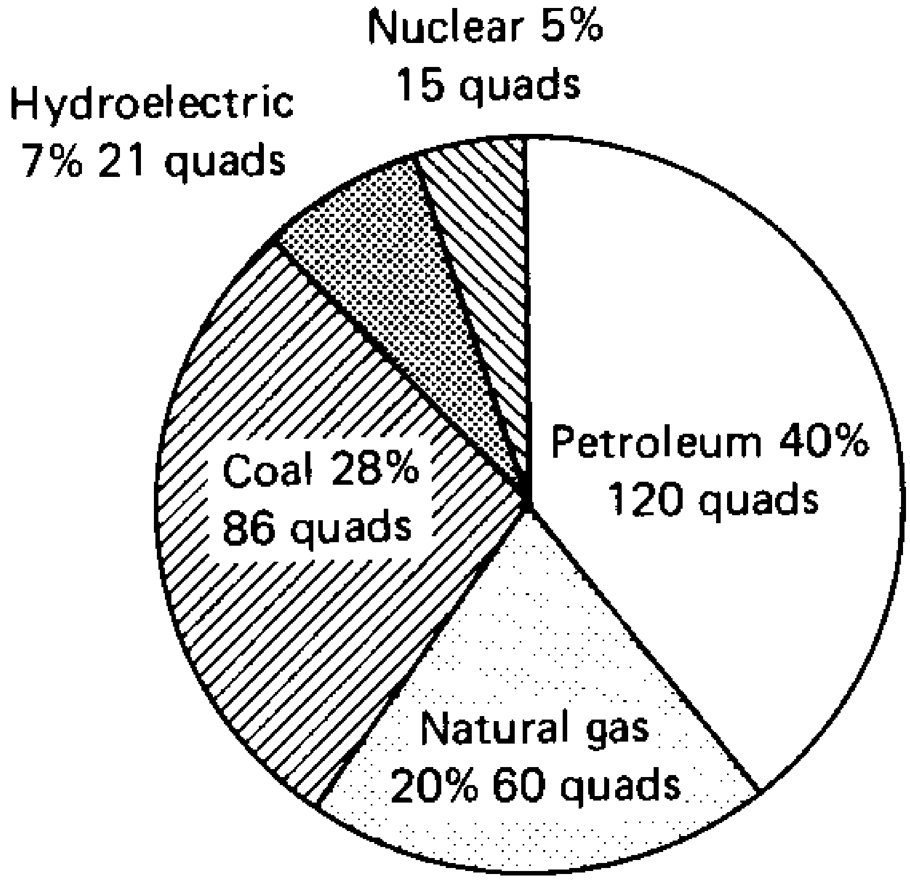
Assume STP and ideal gas.

The total mass of air equals 5.1 x 10^{18} kg.

The density of air at STP is 1.29 kg/m^3.

CO_2 Emissions and Energy

- World uses 266 quads (quadrillion BTUs ≈ exajoules (10^{18} J)) from fossil fuels (88% of total energy needs)



CO_2 Emissions and Energy

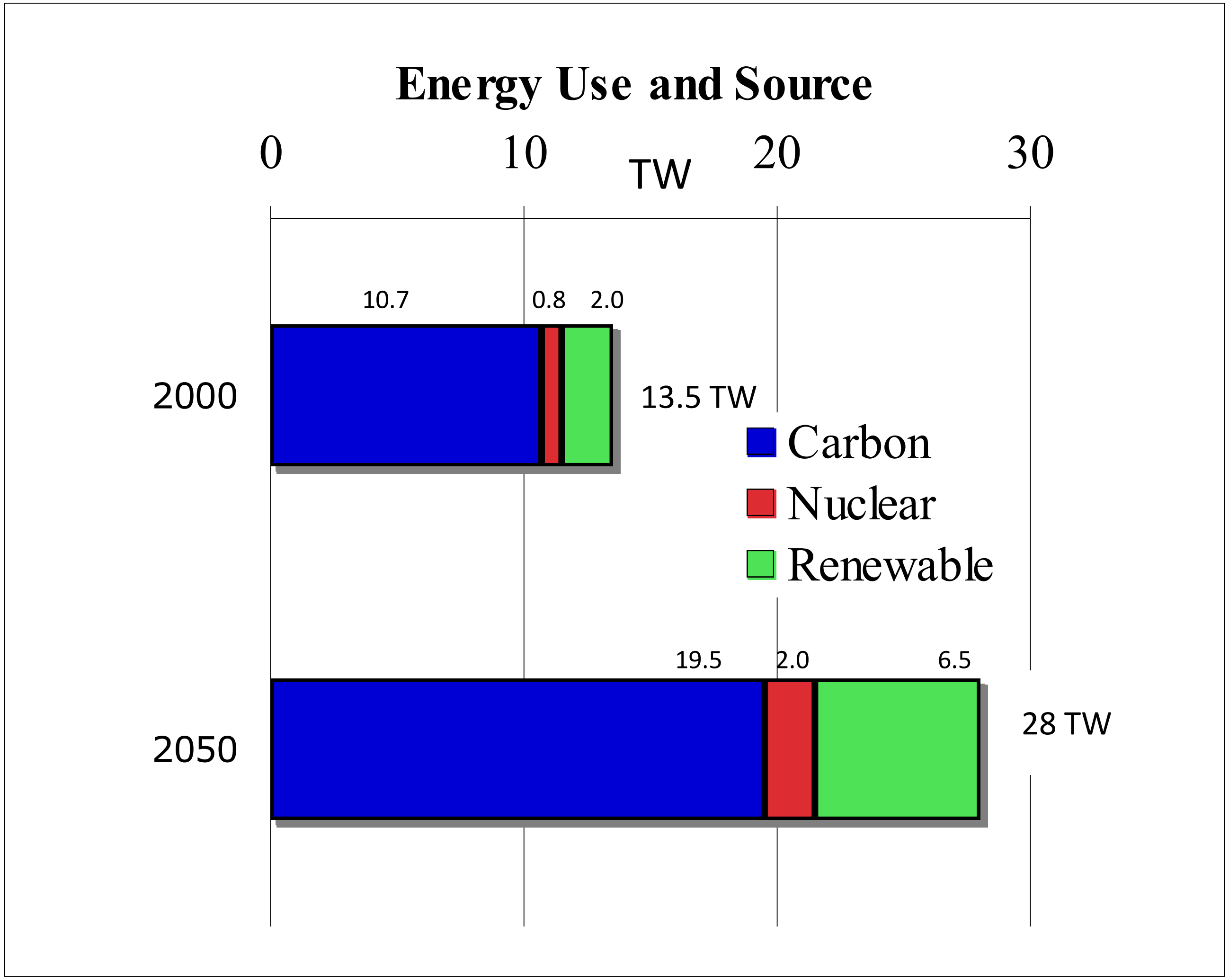
- Different fuels have different energy contents, and therefore varying emissions of carbon per unit energy
- For example, when burning natural gas, 14.5 million tons of C are emitted per quad of energy
- If fuel source is coal, 25.2 million tons C emitted/quad
- These numbers suggest ways to reduce C emissions.
- Therefore it is important to know what the source of energy is/will be

				Synthetic fuels			
Factor	Natural gas	Conventional oil	Coal	Oil from shale	Oil from coal	Gas from coal	Non-fossil fuel
10^6 ton C/quad	14.5	20.8	25.2	50.2	40.7	42.9	0
Quads/yr	60	120	86	0	0	0	36
Carbon emissions (Gt C/yr)	0.9	2.5	2.2	0	0	0	0

Source: Data from Seidel and Keyes (1983) and EIA (1986).

Natural gas is cleaner than coal and oil.

Energy Alternatives



Energy Alternatives

- Conventional alternatives:
  (Need about 28 TW new by 2050)

- Nuclear
  - Need 10,000 new reactors to provide 10 TW
  - Requires uranium extraction from sea water

- Hydropower
  - Approximately 1.5 TW global potential
  - Environmental concerns

Energy Alternatives

√ **Renewable alternatives:**

- Geothermal
  - Potential is 11.6 TW
- Wind
  - Potential is 2 TW
- Biomass
  - Potential is 5 to 7 TW
- Oceans
  - Potential is unknown

Energy Alternatives

- Solar
  - Theoretical potential is 12,000 TW
  - One hour of the light striking the Earth provides 10 TW
  - Practical estimates: up to 600 TW
  - Currently not cost competitive
  - Provides electricity but not compatible with existing transportation infrastructure
    - Hydrogen (?), Electric vehicles (?)

A Model for Carbon Emissions Growth

- One model for C emissions assumes that a number of factors are involved.

Wealth — Efficiency — Fuel Quality

$$\text{C emissions} = \text{Pop} \times \frac{\text{GNP}}{\text{Person}} \times \frac{\text{Energy}}{\text{GNP}} \times \frac{\text{C emissions}}{\text{Energy}}$$

- To estimate emission changes, we can look at each factor, perhaps on a regional basis.

- Population
  - Population growth rate worldwide is 1.1%/yr (peaked at 2.2% in 1963).
  - In more developed countries, rate is 0.6%.
  - Less developed other than China grow at 2.4%.
  - China's growth rate is about 0.5%, USA is 0.9%.

A Model for Carbon Emissions Growth

- Per capita GNP
  - This factor tells us something about economic growth.
  - Most projections are in the range of 1-2%/yr.
  - Note that developing countries may grow quickly in the next half century
- Energy per GNP
  - An indicator of how energy efficient a nation is.
  - Previously, economic growth meant growth in energy needs.
  - Since the 1970's, US has become more energy efficient, and this factor has fallen.
  - Some predict a decrease of 2% per year.
  - Developing countries could use more efficient technologies, but it may be expensive.
- Emissions per energy
  - Low for natural gas, high for coal
  - Will decrease gradually.

A Model for Carbon Emissions Growth

- Let's assume
  - Population growth slows to 1% per yr
  - Per capita GNP grows at 1.2% per yr
  - Globally, we become no more energy efficient (0%)
  - C emissions/energy decrease 0.2% per yr

- What will the emissions be in 2020 if we emitted 6 Gt/yr carbon in 1995?

- The model for C emissions can be analyzed using the aggregated growth model.
- Exponential law: $E = E_0 e^{rt}$, $E_0 = 6$ Gt/yr
- And in aggregated growth, when one multiplies exponential factors, the overall aggregate rate $r = r_1 + r_2 + r_3 + r_4 = 1 + 1.2 + 0 - 0.2 = 2.0$ % per year
- $E = 6.0\ e^{(0.02)(2020-1995)} = 9.9$ Gt/year in 2020

A Model for Carbon Emissions Growth

√ **Total (Cumulative) emissions**

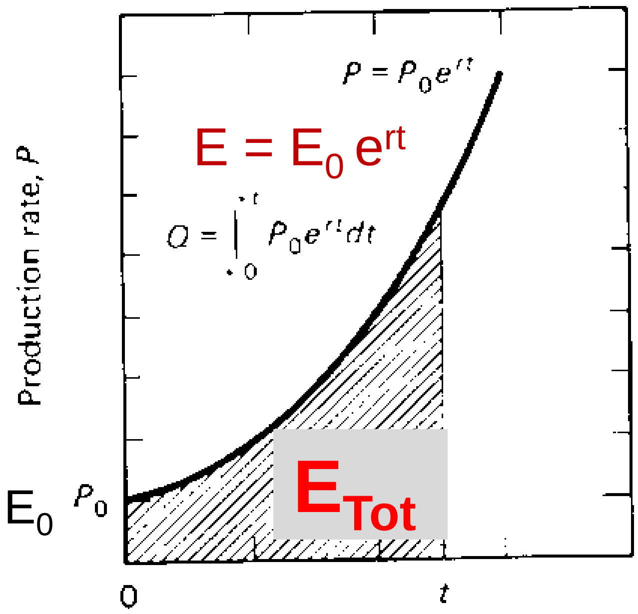
- The emission rate tells us nothing about the change in CO_2 concentration. To know total cumulative emissions over the time period is important.

- We need the integrated form.

$$E_{Tot} = \frac{E_0}{r}(e^{rt} - 1)$$

Where

- E_{Tot} is the total amount of CO_2 emitted
- E_0 is the initial emission rate



A Model for Carbon Emissions Growth

- The cumulative emissions over those 25 yr would be

$$E_{Tot} = \frac{6}{0.02}(e^{0.02\times 25} - 1) = 195 \text{ Gt}$$

- If half of the emissions remain in the atmosphere, 97.5 Gt C would be added to the atmosphere

- In the previous example, 1 ppm_v CO_2 increase is produced by about 7.66 Gt CO_2 (2.12 Gt C), so this addition of 97.5 Gt C would raise the CO_2 concentration in the atmosphere by **97.5/2.12 = 46 ppm_v**.

CO_2 Concentration and Temperature Change

- Estimates use complex global circulation models (GCM)

- Present estimates:
  - If the CO_2 concentrations double, temperatures will rise 1.5 to 4.5 degrees (^{o}C).

- Temperature change uses a logarithmic model

$$\Delta \mathrm{T} = \frac{\Delta T_d}{\ln 2} \ln\left[\frac{(CO_2)}{(CO_2)_0} \right]$$

Where ΔT_d = T change for doubling CO_2 = **1.5 to 4.5 ^{o}C**

Example

- What would the equilibrium temperature change corresponding to a CO_2 increase from 280 ppm_v in 1850 to 345 ppm_v in 1984, if a doubling of CO_2 is predicted to produce a 3.0^oC increase?

Other Greenhouse Gases

Global Warming Potentials (GWPs) Relative to Carbon Dioxide (kilograms of CO_2 per kilogram of gas)

Chemical Species	Chemical Formula	Lifetime (yrs)	Global Warming Potential (Time Horizon in Years) 20-yr	100-yr	500-yr
Carbon dioxide	CO_2	50–200	1	1	1
Methane	CH_4	12	62	23	7
Nitrous oxide	N_2O	114	275	296	156
CFC-11	$CFCl_3$	45	6,300	4,600	1,600
CFC-12	CF_2Cl_2	100	10,200	10,600	5,200
CFC-113	$CF_2ClCFCl_2$	85	6,100	6,000	2,700
CFC-115	CF_3CClF_2	1,700	4,900	7,200	9,900
HCFC-22	CHF_2Cl	12	4,800	1,700	540
HCFC-141b	CH_3CFCl_2	9.3	2,100	700	220
HCFC-142b	CH_3CF_2Cl	19	5,200	2,400	740
HFC-23	CHF_3	270	9,400	11,700	10,000
HFC-134a	CH_2FCF_3	14	3,300	1,300	400
HFC-152a	CH_3CHF_2	1.4	410	120	37
Tetrafluoromethane	CF_4	50,000	3,900	5,700	8,900
Hexafluoroethane	C_2F_6	10,000	8,000	11,900	18,000
Sulfur hexafluoride	SF_6	3,200	15,100	22,200	32,400
Carbon tetrachloride	CCl_4	35	2,700	1,800	580
Methyl bromide	CH_3Br	1	16	5	1
Halon-1301	CF_3Br	65	7,900	6,900	2,700

Source: IPCC, 3rd Assessment, 2001.

Stratospheric Ozone

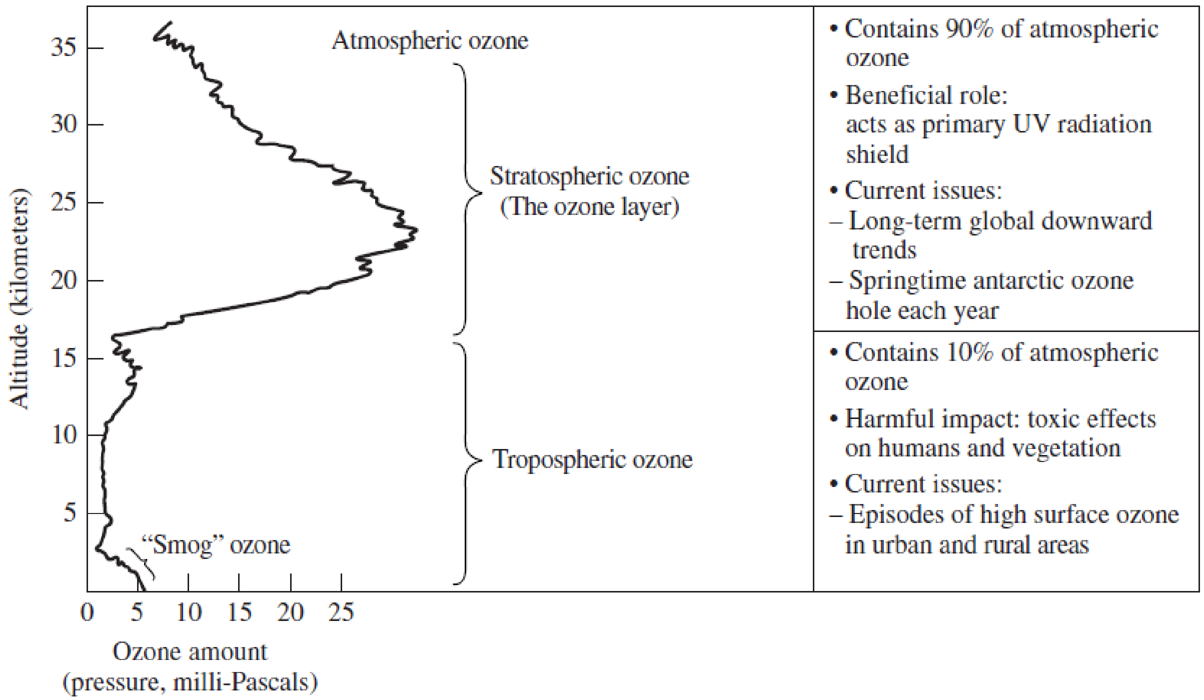
- Ozone is naturally formed and decomposed in the stratosphere by photochemical reactions.
- The central reactions:

$$O_2 + h\nu \rightarrow O + O$$

$$O + O_2 + M \rightarrow O_3 + M$$

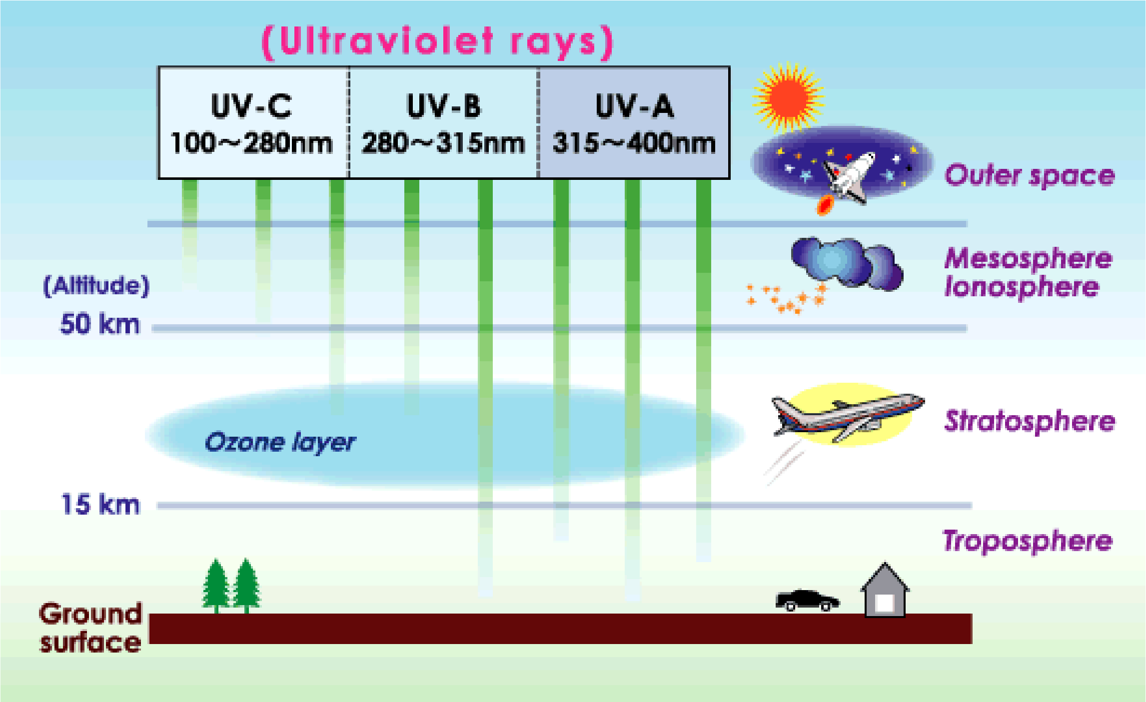
$$O_3 + h\nu \rightarrow O_2 + O$$

Where M represents a third body (N_2 or O_2) needed to carry away energy released in the reaction.



Stratospheric Ozone

- The ozone in the stratosphere absorbs UV radiation that can be biologically damaging.
- Almost all radiation less than 295 nm is absorbed.
- Note UV-B radiation (less than 320 nm) is the biologically damaging fraction (sunburn, skin cancer).



Removal of Stratospheric Ozone

- Nitric oxide (NO), chlorine, and bromine react catalytically with O_3.

- Let's look at chlorine, which an be released from CFCs.

  $Cl + O_3 \rightarrow ClO + O_2$ chlorine monoxide formed

  $ClO + NO_2 \rightarrow ClONO_2$ which is inactive

- In winter, polar ice clouds form, surface reactions occur.

  $H_2O + ClONO_2 \rightarrow HOCl + HNO_3$ (hypochlorous + nitric)

Removal of Stratospheric Ozone

- When sun appears

$HOCl + hv \rightarrow Cl + OH$

- Then the reactions with ozone begin

$Cl + O_3 \rightarrow ClO + O_2$

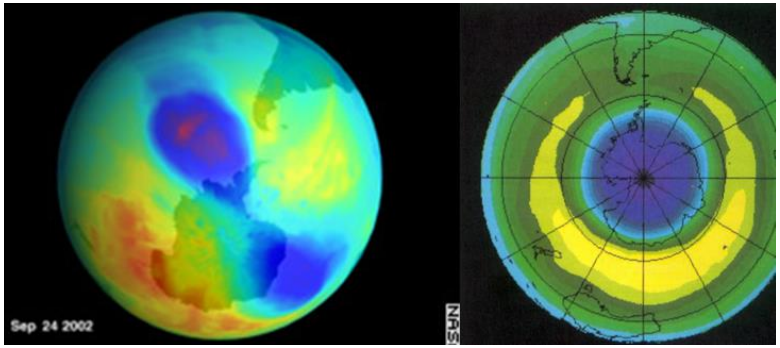
$OH + O_3 \rightarrow HO_2 + O_2$ (hydroperoxyl)

$ClO + HO_2 \rightarrow HOCl + O_2$

Net:
$$2O_3 \rightarrow 3O_2$$

Effects of Stratospheric Ozone Depletion

- Satellite measurements show depletion of O_3 from the polar region over Antarctica in August to November.



- Changes in the UV spectrum that reaches the earth will have biological effects.
  - DNA effects such as human skin cancer
  - Ocular damage (cataracts and retinal degeneration)
  - Damage to crop yield and quantity

- However, effects will be regional.

How to Solve or Mitigate Global Warming?

√ We Need Cohesive and Decisive Action to…

- Transition to environmentally sound energy sources (reduce CO_2 emissions)
- Halt tropical deforestation and reforest the globe
- Sustainably manage fisheries, forests, agriculture, biodiversity, and other ecosystem services
- Develop technologies for long-term CO_2 sequestration
- Recognize our Joint and differential responsibilities

How to Solve or Mitigate Global Warming?

" We have arrived at a turning point in human history.

The future habitability of our planet will be determined

by decisions made and actions taken by this generation,

by the people who are alive today.

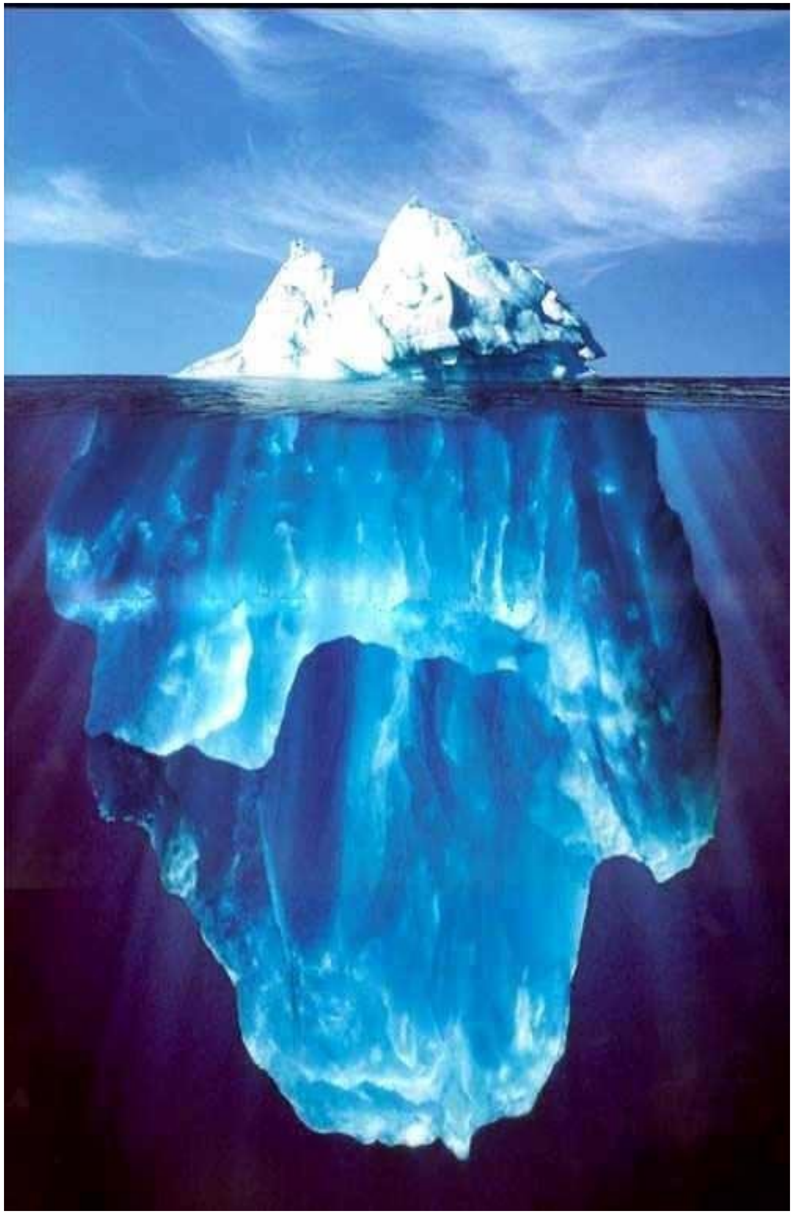
Our problems have solutions, and we all have our parts

to play."

Report of the World Commission on Environment and Development:

Our Common Future

How to Solve or Mitigate Global Warming?



Never doubt that a small group of thoughtful, committed citizens can change the world; indeed, it is the only thing that ever has.

Margaret Mead