EUROPEAN UNION
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MINISTRY OF EDUCATION, YOUTH AND SPORTS

ATMOSPHERIC CHEMISTRY

Lecture No.: 6

Marek Staf, MSc., Ph.D., Department of gaseous and solid fuels and air protection

Organisation of study

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  e-learning:

  https://e-learning.vscht.cz/course/view.php?id=106

- Scale of subject: winter semester

  14 lectures, 14 weeks, 2 hours/week

- Classification: Exam - written + oral form (depending on result of the test)

Scope of lecture 6

Pollutants and important chemical agents in the air – introduction to the problematics of greenhouse gases

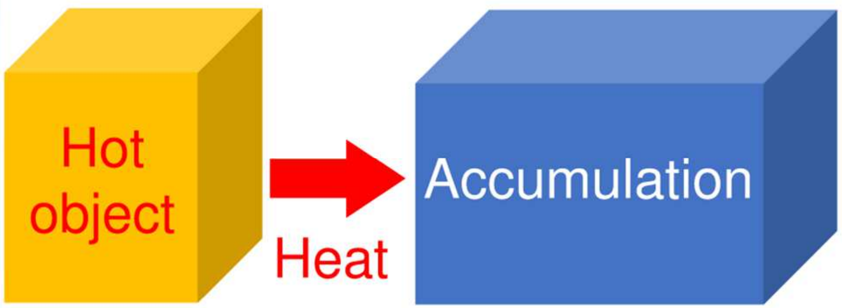
- General classification of all types of pollutants according to their effects
- Overview of the main greenhouse gases
- Mechanism of greenhouse gas impacts
- Global warming potential, its importance and calculation
- Radiative forcing and radiative forcing capacity
- National greenhouse gas inventory plan and economical branches contributing to GHG emissions
- General relationship between economic activities and GHG emissions
- Worldwide emissions of major GHGs according to their chemical properties and industrial sectors

Distribution of pollutants

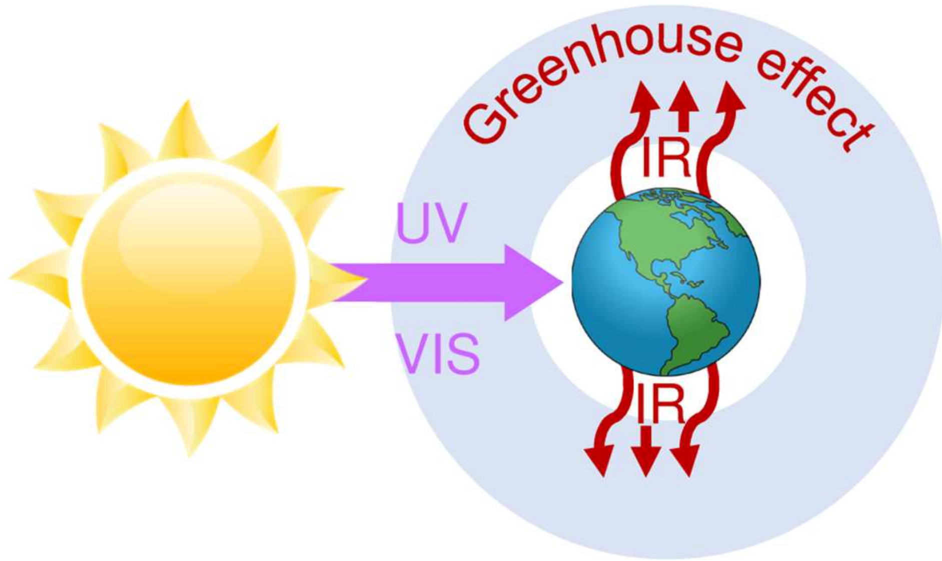
- Pollutants can be divided into following fundamental groups:
  - Substances with acidic reaction - decrease atmospheric pH and subsequently acidify soil and water;
  - Toxic substances - damage health of plants and animals chemically, physically or due to their radioactivity ;
  - Substances damaging O_3 - decompose stratospheric ozone layer;
  - Greenhouse gases - change a balance between heat absorption and radiation from the atmosphere;
  - Precursors - their initial form has no dangerous properties, but undergo changes resulting in the above mentioned properties, or allow other compounds to be transformed into dangerous.

Greenhouse effect

- The greenhouse effect **is not** simply the accumulation of heat.
- Principle: The Earth absorbs UV and VIS and emits IR, but specific gases retain it in the atmosphere.
- Gases capable of this process = greenhouse gases (GHGs).



$$\delta Q = mc\Delta T$$



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Greenhouse gases

- Main greenhouse gases:
  - Generally:
    - H_2O (vapour)
    - CO_2
    - C_xH_y (especially CH_4)
    - N_2O
    - F-gases and ClF-gases = CFC, HFC, PFC a SF_6
    - O_3
  - Substances reported within National GHG Inventory:
    - CO_2
    - N_2O
    - CH_4
    - F-gases = HFC, PFC and SF_6
  - Substances involved in emission trading within EU ETS:
    - CO_2
    - N_2O
    - Perfluorinated hydrocarbons (PFC)

Greenhouse gases

What is their origin:

H_2O (vapor)	NATURAL	
CO_2	NATURAL	ANTHROPOGENIC
C_xH_y (especially CH_4)	NATURAL	ANTHROPOGENIC
N_2O	NATURAL	ANTHROPOGENIC
F-gases a ClF-gases:		
CFCs (chlorofluorocarbons)		ANTHROPOGENIC
HFCs (hydrofluorocarbons)		ANTHROPOGENIC
PFCs (perfluorocarbons)		ANTHROPOGENIC
SF_6 (sulfur fluoride)		ANTHROPOGENIC
O_3	NATURAL	ANTHROPOGENIC

Effects of greenhouse gases

- Mechanism of GHG impact:

1 - Greenhouse gases must absorb radiation in IR part of spectrum; (quantum transition during IR absorption = values of molecular vibrations)

2 - Molecules must change their dipole moment due to IR absorption;

→ Symmetric di-atomic molecules, like H_2, N_2, O_2, do not change their dipole moment ⇒ they are IR inactive;

→ Molecules with different partial charges on the atoms, like CO, CO_2, N_2O, NO, HCl, change the dipole moment ⇒ they are IR active;

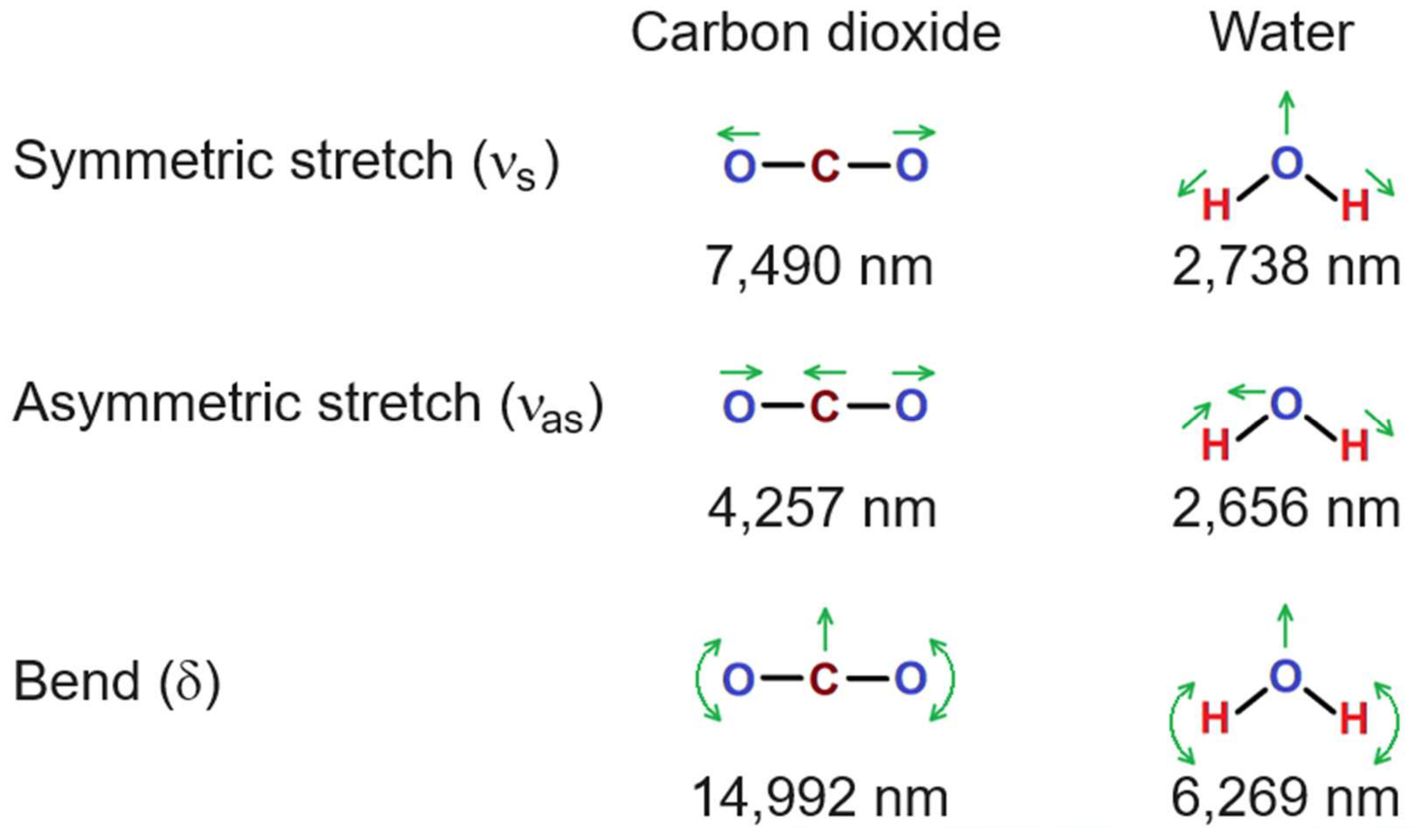
3 - GHG molecules must have sufficient lifetime in the atmosphere

4 - GHG must be present at sufficient concentrations (e.g. average content of H_2O = 0.4 % vol., average content of CO_2 > 0.04 % vol.).

2023 highest CO_2 value = 424 ppm !

Effects of greenhouse gases

- Mechanism of GHG impact:
  - Each molecular vibration has its specific wavelength value, but 1 molecular vibration induces high number of various rotation levels ⇒ extension of absorption belt width.
  - Example – molecular vibrations of CO_2 and H_2O:



Effects of greenhouse gases

- Mechanism of GHG impact:
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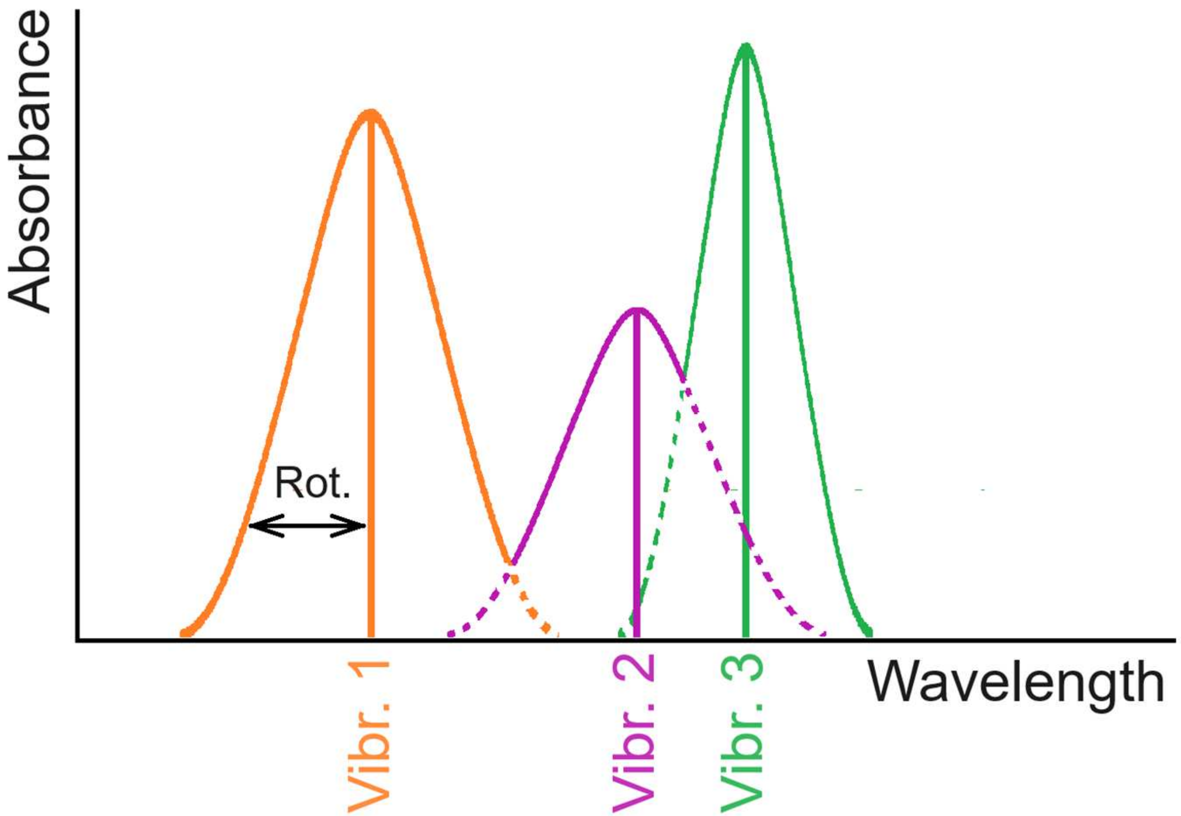
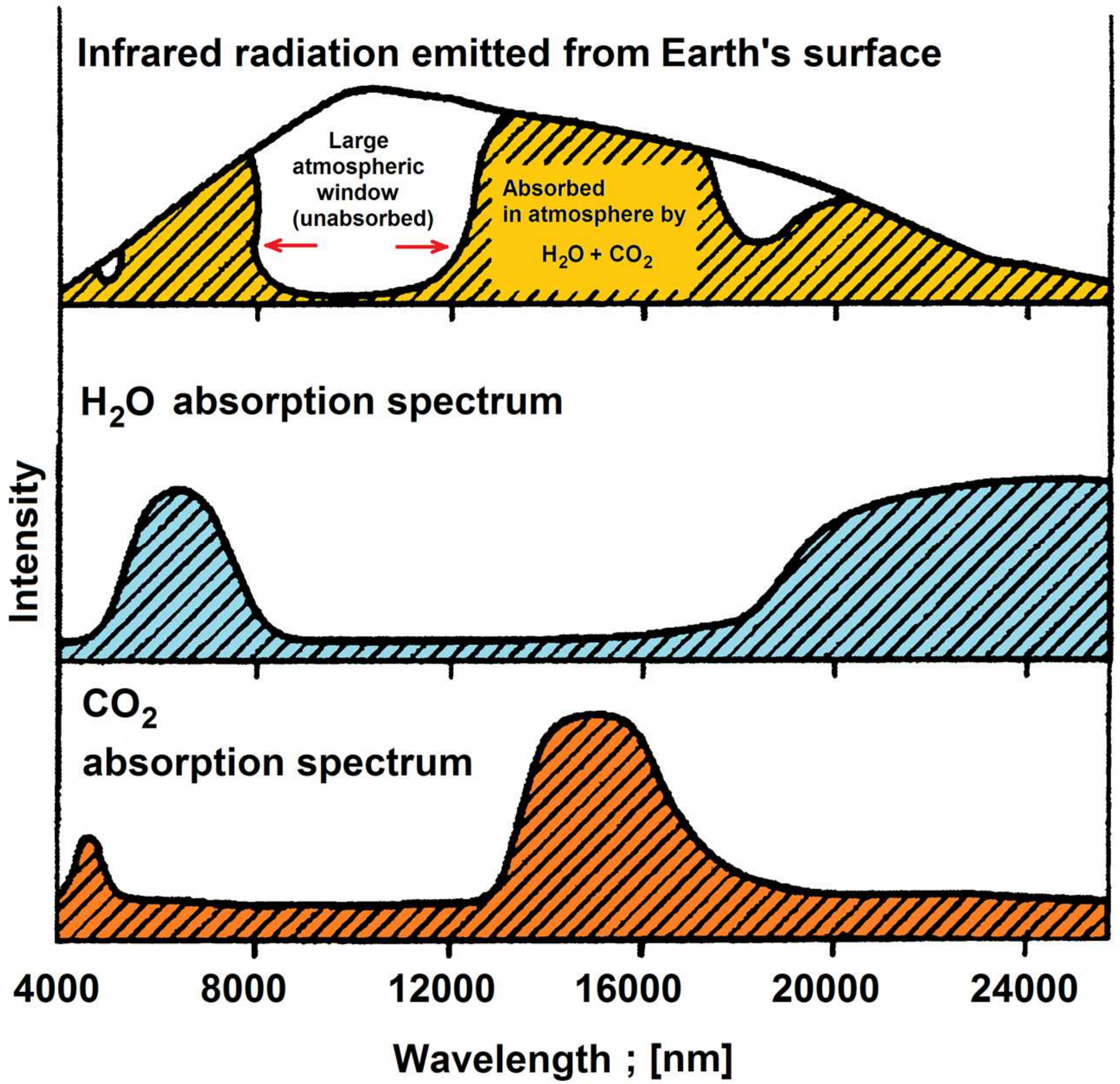


Effects of greenhouse gases

- Mechanism of GHG impact:

Due to extension of absorption belt width CO_2 and H_2O cover a dominant part of IR radiation emitted by the Earth’s surface back to the outer space



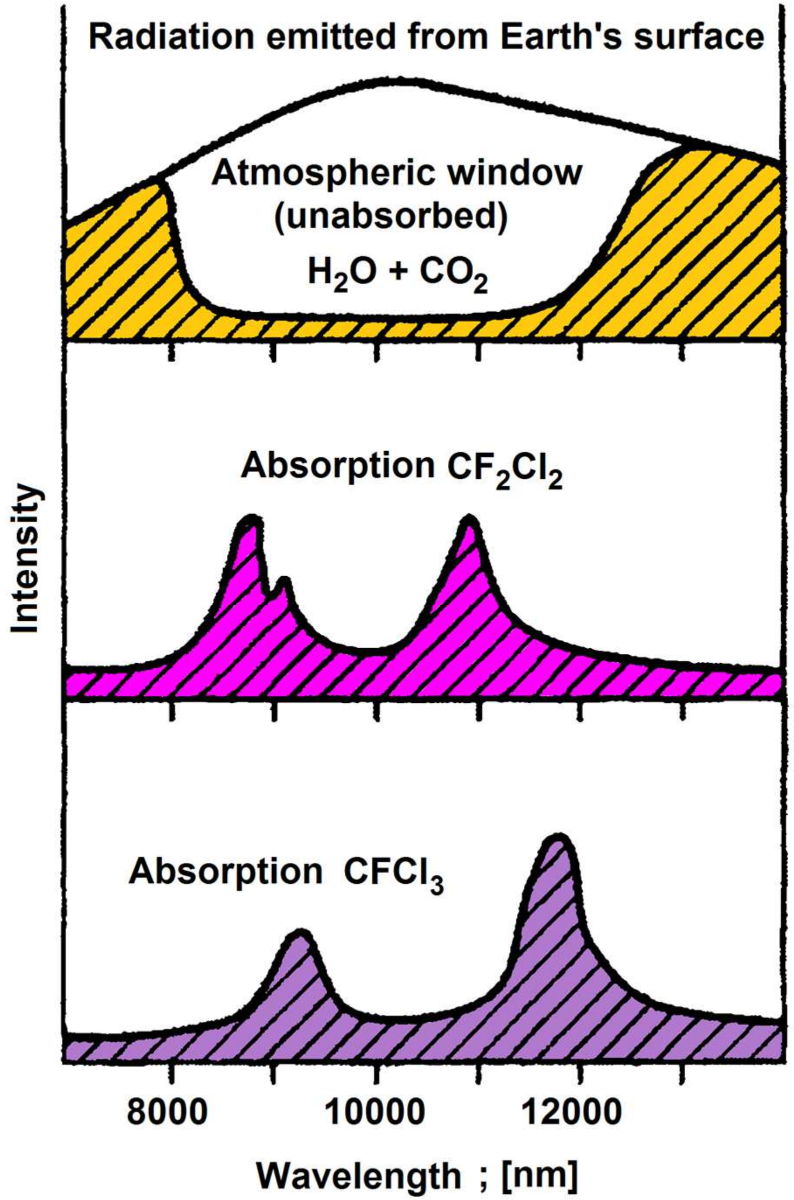
Effects of greenhouse gases

- Mechanism of impact:

Space of the large atmospheric window (possibility of free radiation of IR spectrum to outer space)
is eliminated by absorption caused by:

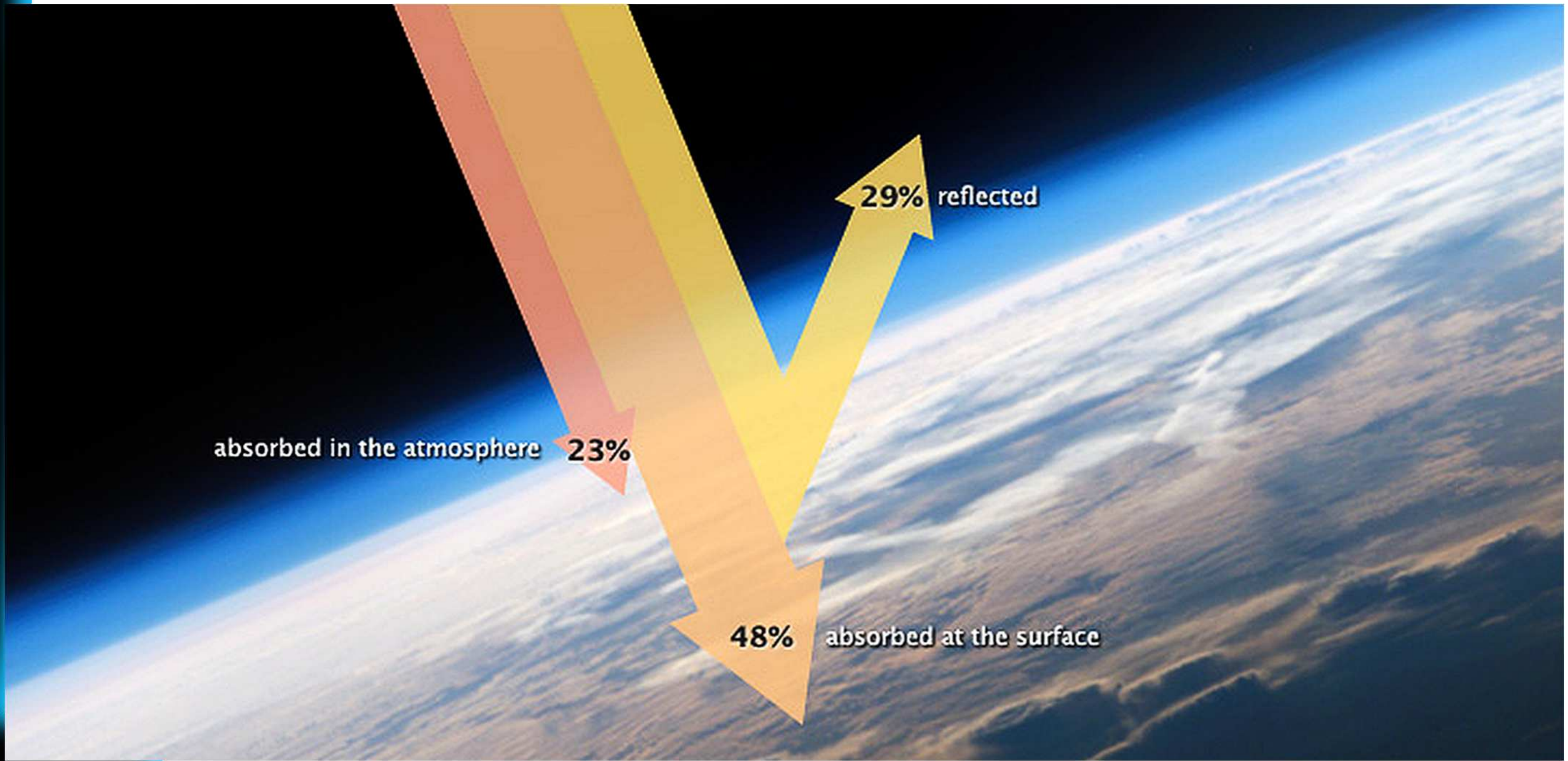
Methane
N_2O
CFC
HFC
PFC

Each compound absorbing within the atmospheric window is much mor dangerous than CO_2 and H_2O.



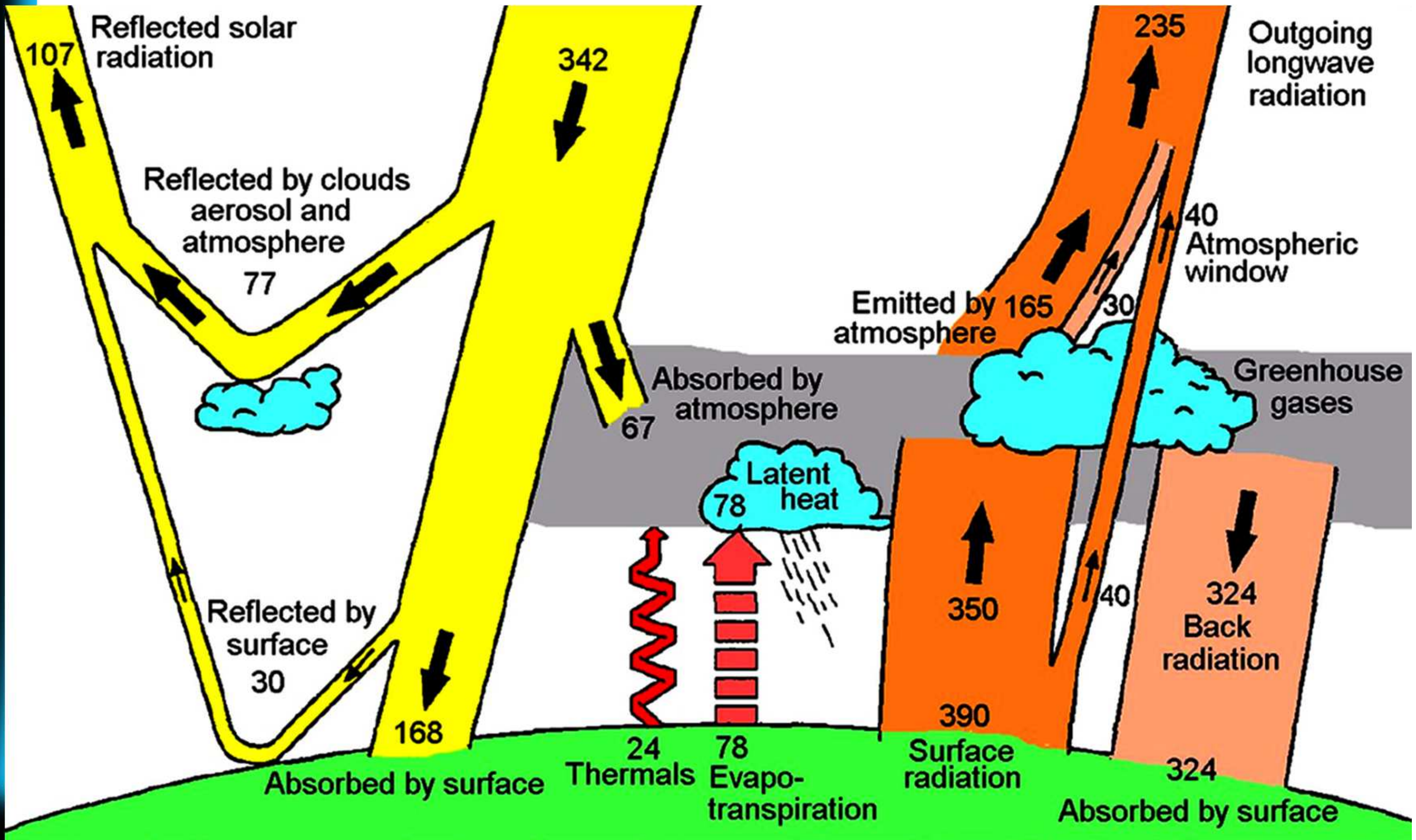
Energy balance of the atmosphere

- Balance of incoming solar radiation (UV + VIS)
  - Total incoming energy flux ≅ 340 W m^{-2} (defined in tropopause)
  - 29% reflected (98.6 W m^{-2}), 23% (78.2 W m^{-2}) absorbed in the atmosphere



Energy balance of the atmosphere

- Climatologic theory and energy balance: (Source: Kiehl and Trenberth, 1997)
  - Equilibrium between UV and visible radiation absorbed by the planet and reflection of IR radiation back to the space. Due to absorption of IR radiation, GHG gases change this ratio ⇒accumulation of energy.



Note 1:
Atmospheric window shown at 38% proportion of clear sky

Note 2:
30 W.m^{-2} = radiative energy of clouds in longwave area

Energy balance of the atmosphere

- **Radiative forcing**
  - Radiative forcing = climate forcing: It is defined as the difference between the solar energy absorbed by the Earth and the energy radiated back to outer space.
  - Standardly defined in Tropopause;
  - Unit: Watt per square meter of the Earth surface;
  - Positive radiative forcing = predominance of the absorbed energy over radiated energy ⇒ warming of the system;
  - Negative radiative forcing = predominance of the emitted energy over absorbed energy ⇒ cooling of the system.

What the Climatologic theory says

- There is the equilibrium between UV and visible radiation absorbed by the planet and reflection of IR radiation back to the space.
- Due to absorption of IR radiation, GHG gases change this ratio $\Rightarrow$ accumulation of energy
  – Since the beginning of the industrial era: Of all the investigated factors, only the concentration of GHGs changed along with the rise in temperature.

How we can express the GHG impact

- Several possible parameters, which the most widespread are:
  - Radiative Forcing Capacity (RFC)
  - Global Warming Potential (GWP)
- RFC = the amount of energy per unit area per unit time, absorbed by greenhouse gases, which would otherwise be radiated into space:
  - Do not confuse with „Radiative Forcing“ = difference between the solar energy absorbed by the Earth and the energy radiated back to outer space.
- GWP is a relative measure of how much heat is retained in the atmosphere by a gas.
  - GWP compares the amount of heat, retained by the certain amount of the gas, relative to the same amount of the reference gas
  - GWP is a dimensionless factor
  - GWP is related to CO_2, thus GWP(CO_2) = 1

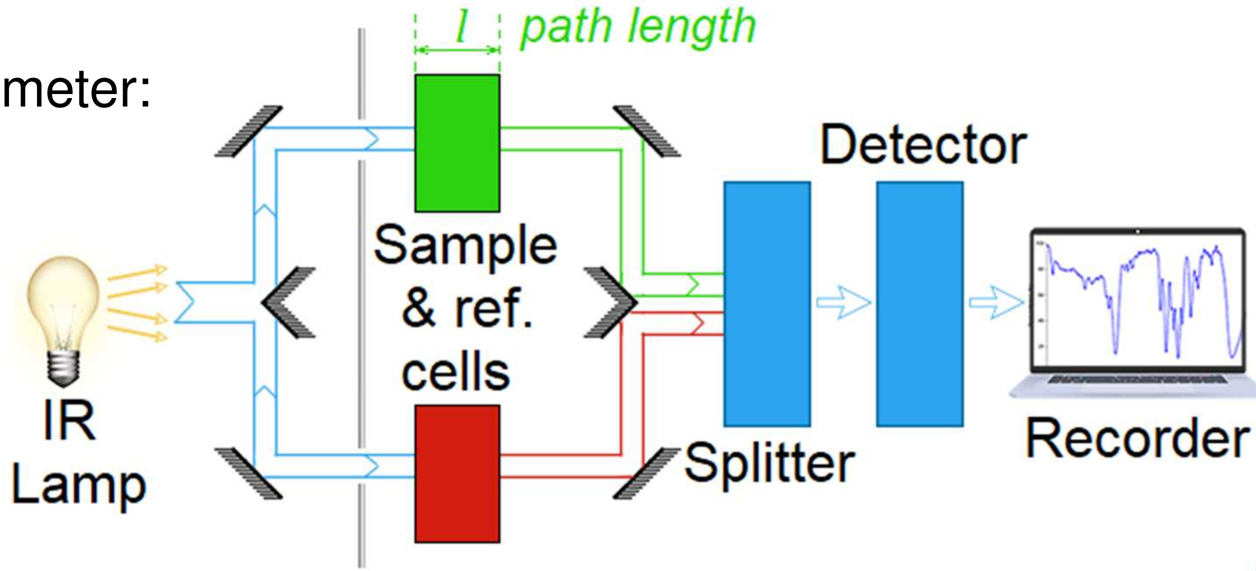
Radiative Forcing Capacity (RFC)

- RFC expressed by the formula (Beer's law):

$$RF = \sum_{n=1}^{100} \frac{Abs_i \cdot F_i}{l \cdot n}$$

  - Abs_i = integrated infrared absorbance in i^{th} interval
  - F_i = radiative forcing in i^{th} interval
  - l = path length of the IR measuring cell (cm)
  - n = number density of GHG molecules (cm^{-3})
  - Subscript i = interval 10 cm^{-1}

- RFC determined
  using the IR spectrometer:



Calculation of GHG impact

- Global warming potential (GWP)
  - GWP values, published by the Intergovernmental Panel on Climate Change (IPCC) were slightly changed several times between 1996 and 2001.
  - In 2001, the exact method for GWP calculation was published in the third IPCC report.
  - GWP is defined as a ratio of the **RF** of 1 kg of the trace gas, integrated according to time, and **RF** of 1 kg of the reference gas.
  - Equation for calculation of the GWP for a particular gas is following:

$$GWP(x) = \frac{\int_0^{TH} a_x \cdot [x(t)]dt}{\int_0^{TH} a_r \cdot [r(t)]dt}$$

Calculation of GHG impact

- Global warming potential (GWP)

$$GWP(x) = \frac{\int_0^{TH} a_x \cdot [x(t)]dt}{\int_0^{TH} a_r \cdot [r(t)]dt}$$

– The meaning of symbols in the equation is:

TH … Time horizon, for which the calculation is realized;

a_x … Radiative efficiency for unit increase of atmospheric abundance of the selected substance [$W.m^{-2}.kg^{-1}$]

[x(t)] … Time-dependent decay of the substance (decrease of its abundance from its release in the time t = 0 until t = TH)

Denominator of the fraction includes the same variables for the reference gas (e.g. CO_2).

Calculation of GHG impact

- Global warming potential, GWP
  - GWP depends on the following factors:
    - The rate of absorption of IR radiation by the substance;
    - Position of wavelengths, absorbed by the substance, in the solar spectrum;
    - Lifetime of the substance in the atmosphere.

Calculation of GHG impact

- GWP calculation meets problems:
  - Radiative efficiencies a_x, a_r not constant within the whole-time horizon
  - For the majority of gases IR absorbance increases linearly with their abundance in the atmosphere.
  - Several important GHGs show non-linear dependence, e.g. CO_2, CH_4, N_2O
  - Increase of CO_2 concentrations has lower impact on overall IR absorption (saturation of corresponding wavelengths) TOO HIGH CONCENTRATION
  - Calculation for H_2O almost impossible: Unequal H_2O distribution in troposphere (average ca. 0.4 % vol., but up to 1.8 % vol. near the sea level.

GHG from different economical sectors

- Statistical values given by the National Greenhouse Gas Inventory
- Based on international agreement United Nations Framework Convention on Climate Change (UNFCCC)
- Mandatory IPCC methodology (Guidelines for National Greenhouse Gas Inventories etc.)
- UNFCCC parties collect data from 5 sectors:
  - Energy
  - Industrial processes
  - Agriculture
  - Land-Use, Land-Use Change and Forestry (LULUCF)
  - Waste

Monitoring of GHG

- National Greenhouse Gas Inventory:
  - Emissions of all GHGs are assessed collectively (together) using overall = aggregated emissions;
  - Aggregated emission = sum of emissions of each gas, multiplied by GWP conversion coefficients;
  - For the purposes of the inventory GWPs are listed for 100-years horizon: $GWP(CO_2) = 1$, $GWP(CH_4) = 21$, $GWP(N_2O) = 310$
  - Overall aggregated emission, which is the fundament for obligation stated by Kyoto protocol, is expressed by:

    Equivalent amount of CO_2 causing the same impact as the sum of all gases included in an aggregated emission.

Monitoring of GHG

- National Greenhouse Gas Inventory – according to sectors:
  - Sector **Energy**; the most important category
  - Sector **Industrial processes**
  - Sector **Agriculture**
  - Sector **Land-Use, Land-Use Change and Forestry**, LULUCF
  - Sector **Waste**

For more detailed information about methodology, please see „National Inventory Report, NIR“, or visit page: http://unfccc.int/national_reports

Monitoring of GHG

- National Greenhouse Gas Inventory – according to sectors:
  - **Sector Energy** = the most important category
    - In central Europe > 85 % of the overall emissions of the greenhouse gases (mostly CO_2);
    - Combustion processes;
    - Processes joined with mining, conversion and manufacturing of fuels and energy(refineries, fugitive emissions of methane from coal mining and so on);
    - Emissions from local transport and other mobile sources;
    - Part of the fuel consumptions is reported in other categories, or it is not taken into account (non-energetic utilisation of fuels for production of industrial lubricants, asphalt etc.; usage of fuels for international and air transport, utilisation of coke as reducing agent for Fe production; non-energetic usage of fuels as raw materials in chemical production, e.g. of NH_3)

Monitoring of GHG

- National Greenhouse Gas Inventory – according to sectors:
  - **Sector Industrial processes**
    - Emissions from metallurgical and chemical processes (CO_2 from application of coke for reduction of iron ores to Fe, emissions of N_2O from production of HNO_3, CO_2 from production of ammonia etc.)
    - Processes of decomposition of carbonate minerals (thermal treatment of carbonates in production of cement and lime, during manufacture of glass and ceramics and during flue gas desulfurization using limestone);
    - Application of F-gases =HFC, PFC and SF_6 (particularly in cooling and chilling processes).

Monitoring of GHG

- National Greenhouse Gas Inventory – according to sectors:
  - **Sector Agriculture**
    - In central Europe mostly emissions of CH_4 and N_2O;
    - Breeding of animals (anaerobic decomposition of animal manure and CH_4 from enteric fermentation = digestion of vegetal aliment, especially breeding of bovine animals, less from swine breeding);
    - Bacterial denitrification in soil (N_2O).

Note: In Asia, the biggest methane emissions come from rice cultivation.

Monitoring of GHG

- National Greenhouse Gas Inventory – according to sectors:
  - **Sector Land-Use, Land-Use Change and Forestry**, LULUCF
    - Emissions of CO_2;
    - For example in the Czech Republic this sector showed higher CO_2 capture than it emits ⇒ showed negative CO_2 balance diminishing overall emissions from other sectors;
      - negative CO_2 balance only till 2018
      - forests damaged due to dry seasons ⇒ CO_2 emitted

Monitoring of GHG

- National Greenhouse Gas Inventory – according to sectors:
  - **Sector Waste**
    - In central Europe mostly emissions of CH_4, CO_2, N_2O;
    - Municipal waste dumps (CH_4); reported emissions of CH_4 are reduced by collected and energetically exploited volumes of methane (biogas);
    - Treatment of municipal and industrial wastewater (CH_4, N_2O); reported emissions of CH_4 are reduced by collected and energetically exploited volumes of methane (biogas);

Note. There are 2 methods for evaluation of CH_4 emissions from dumps:

1. It is supposed that a decomposable part of C, disposed in the dump in the one year is transformed into methane and biogenic CO_2
2. Application of mathematic model of slower, gradual decomposition of C into methane and carbon dioxide $\Rightarrow$ more precise, preferred model.

Anthropogenic influence on GHG

- Relationship between economic development and CO_2 production
  (Source: Gomes; Carbon Dioxide Capture and Sequestration)
  – Y. Kaya proposed the equation:

$$CO_2\uparrow_{total} = POP \times (GDP_{PC}) \times (BTU / GDP) \times (CO_2\uparrow / BTU) - CO_2\downarrow$$

$CO_2\uparrow$	total CO_2 released to atmosphere
$CO_2\downarrow$	total CO_2 captured by geosphere and biosphere
POP	worldwide population
GDP_{PC}	gross domestic product per capita
GDP	total gross domestic product
BTU/GDP	energy consumption per GDP
$CO_2\uparrow$/BTU	CO_2 released per consumed energy

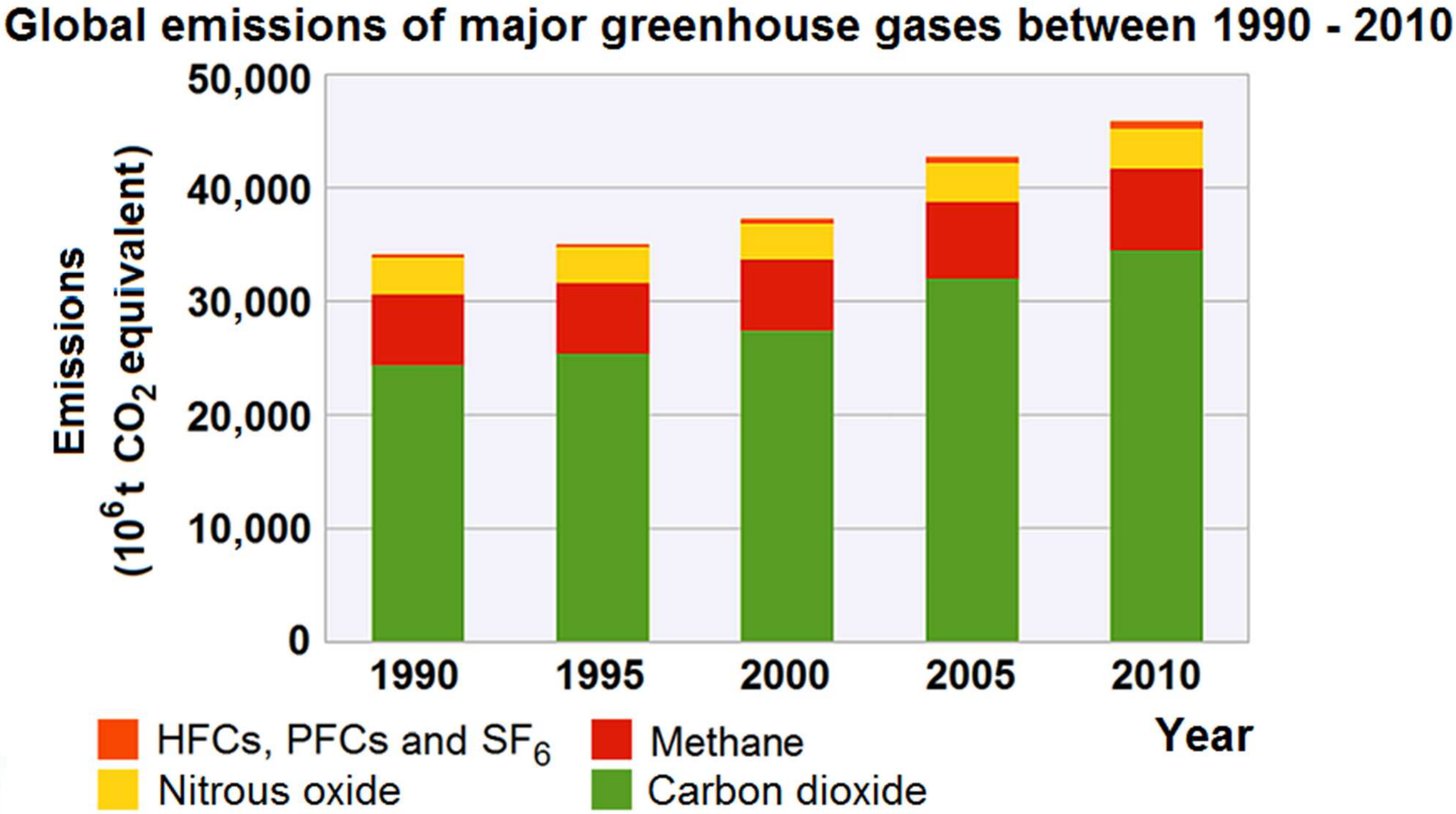
Monitoring of GHG

- **Production of greenhouse gases** (Source: Gomes; Carbon Dioxide Capture and Sequestration)
  - Values for preindustrial era have been obtained by ice core analysis;

Greenhouse gas (group)		Content in atmosphere		Lifetime in atmosphere	Main sources	GWP [CO_2 equ.]
		Preindustrial	1994			
Carbon dioxide	CO_2	280 $ppm_{vol.}$	358 ppm_{vol}	50 – 200 years	Fossil fuels combustion, change in soil usage	1
Methane	CH_4	700 $ppb_{vol.}$	1 720 $ppb_{vol.}$	12 – 17 years	Mining of fossil fuels, rice fields, waste dumps, animals breeding	21
Nitrous oxide	N_2O	275 ppb_{vol}	312 ppb_{vol}	120 – 150 years	Production of fertilizers, industrial processes, combustion	310
Chlorfluorinated hydrocarbons	CFC	0	503 $ppt_{vol.}$	102 years	Cooling fluids, production of foams	125 – 152
Hydrofluorinated hydrocarbons	HFC	0	105 $ppt_{vol.}$	13 years	Cooling fluids	140 – 11 700 (different types)
Perfluorinated hydrocarbons	PFC	0	110 $ppt_{vol.}$	50 000 years	Production of Aluminium	6 500 – 9 200 (different types)
Sulfur hexafluoride	SF_6	0.	72 $ppt_{vol.}$	1 000 years	Production of Magnesium	23 900

Monitoring of GHG on global level

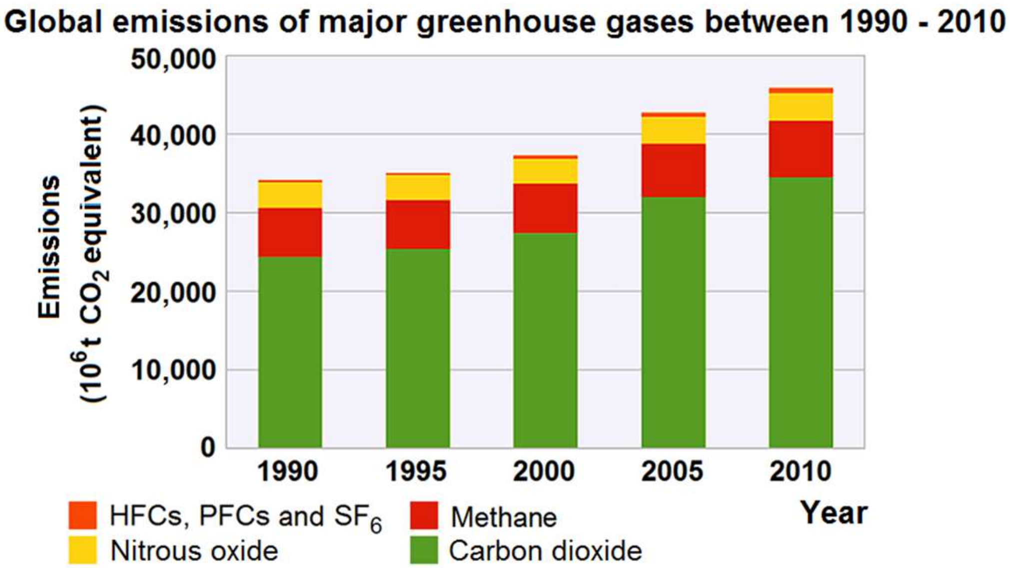
- **Production of greenhouse gases**
  (Sources: http://cait.wri.org, www.epa.gov/climatechange/indicators, http://faostat3.fao.org/faostat-gateway/go/to/download/G2/*/E))



Monitoring of GHG on global level

- Global emissions of greenhouse gases

  (Source: http://www3.epa.gov/climatechange/science/indicators/ghg/global-ghg-emissions.html)

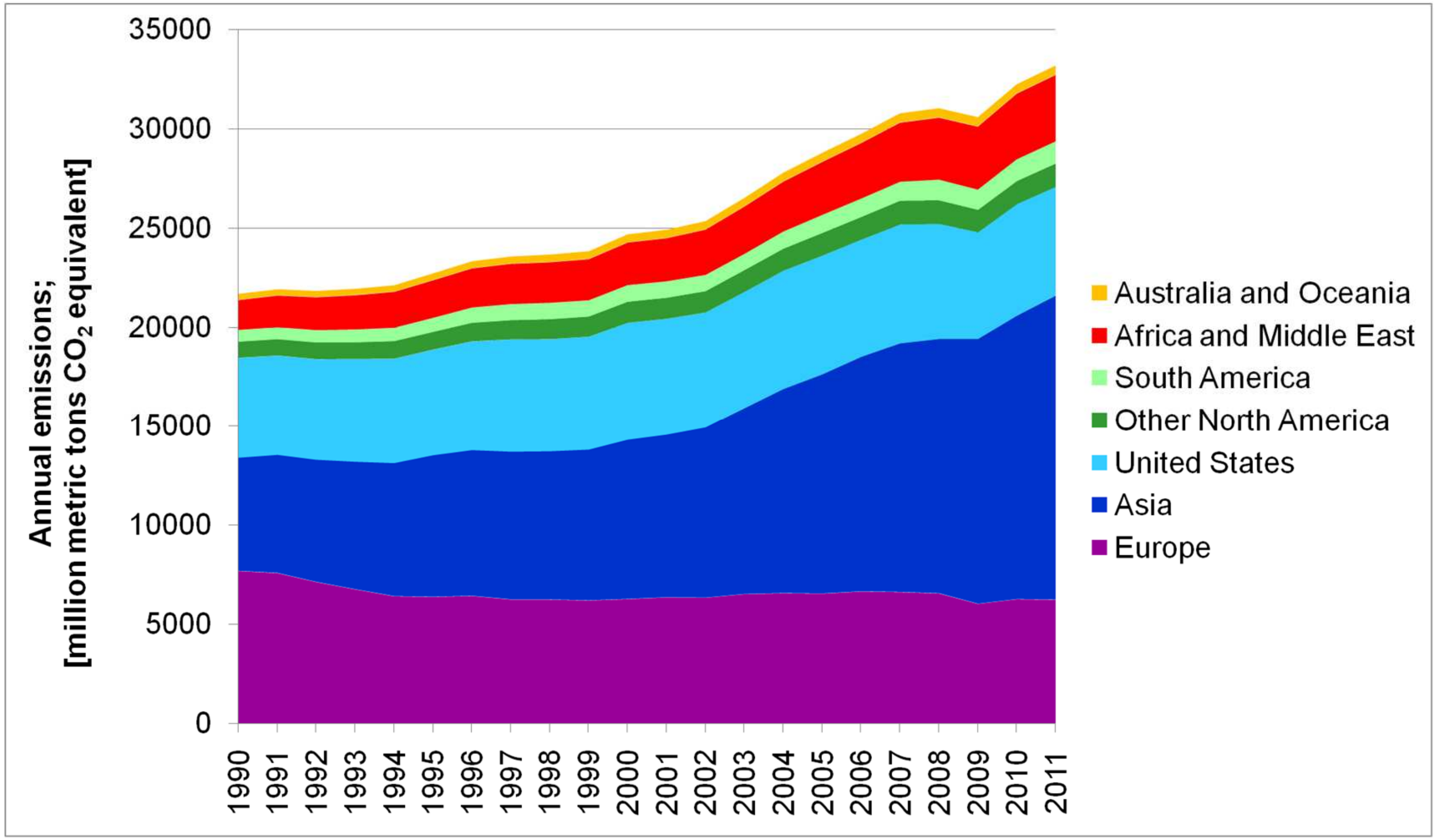


Annual emission; [million metric tons CO_2 equivalent]					
Year	Carbon dioxide	Methane	Nitrous oxide	HFCs + PFCs + SF_6	Total
1990	24 324	6 268	3 241	262	34 095
1995	25 345	6 205	3 193	291	35 033
2000	27 349	6 324	3 143	429	37 246
2005	31 949	6 816	3 367	598	42 730
2010	34 476	7 196	3 520	672	45 863

Monitoring of GHG on global level

- **Global emissions of greenhouse gases – according to regions**

(Source: http://www3.epa.gov/climatechange/science/indicators/ghg/global-ghg-emissions.html)

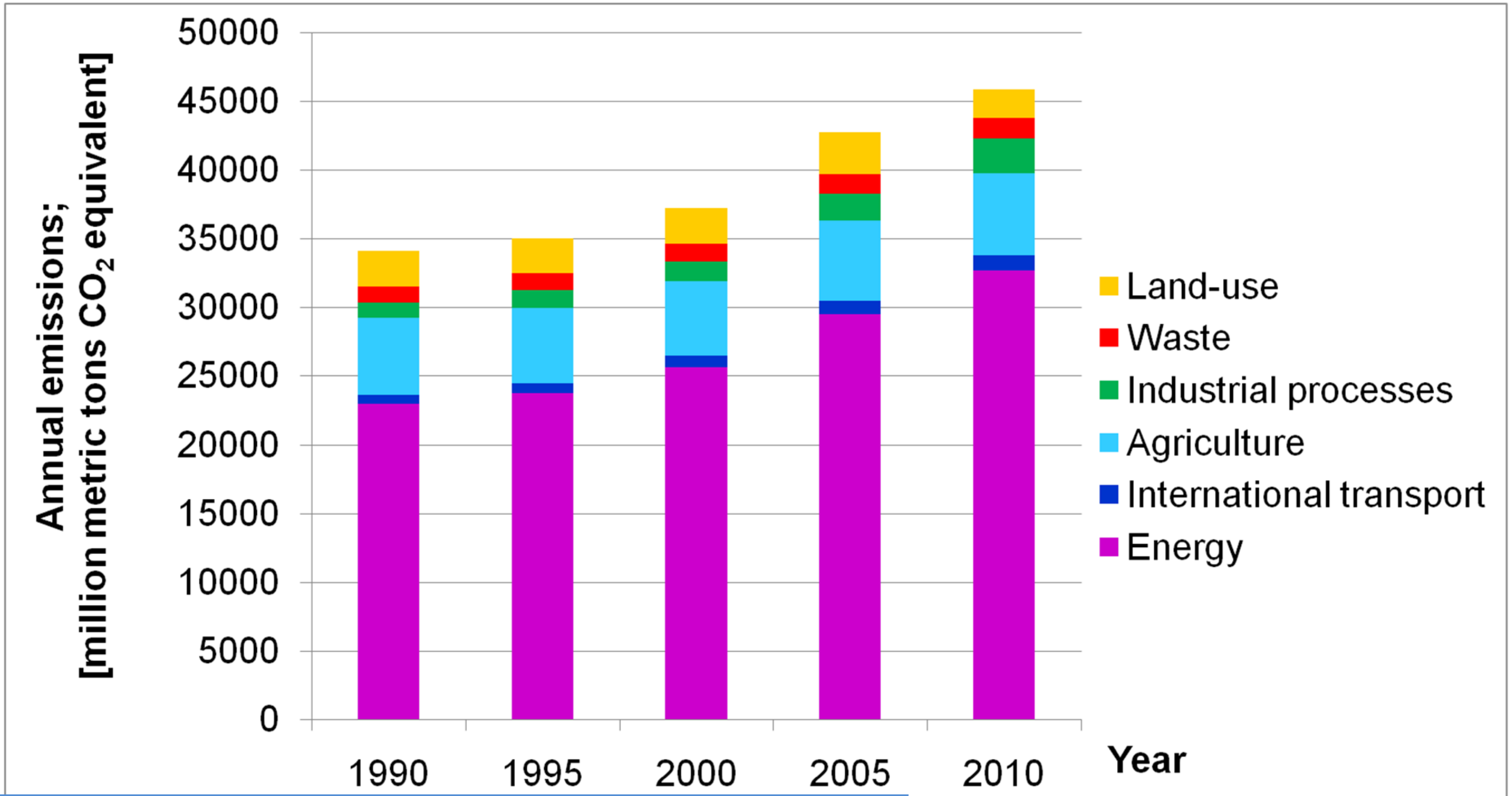


Region	Annual emission; [million metric tons CO_2 equivalent]																					
	1990	1991	1992	1993	1994	1995	1996	1997	1998	1999	2000	2001	2002	2003	2004	2005	2006	2007	2008	2009	2010	2011
Europe	7 678	7 575	7 123	6 752	6 405	6 374	6 420	6 242	6 236	6 195	6 263	6 349	6 330	6 513	6 557	6 537	6 644	6 614	6 548	6 022	6 256	6 231
Asia	5 733	5 979	6 187	6 456	6 734	7 164	7 375	7 474	7 500	7 627	8 059	8 229	8 613	9 402	10 327	11 083	11 859	12 569	12 855	13 380	14 316	15 352
United States	5 042	5 014	5 077	5 189	5 269	5 330	5 493	5 664	5 653	5 695	5 894	5 841	5 794	5 855	5 958	5 979	5 899	5 985	5 792	5 366	5 619	5 481
Other North America	825	836	851	851	899	902	940	981	1 018	1 026	1 071	1 066	1 080	1 109	1 113	1 146	1 150	1 203	1 194	1 145	1 169	1 180
South America	576	590	605	630	657	697	759	800	816	809	828	823	814	810	865	912	929	959	1 050	1 023	1 104	1 127
Africa and Middle East	1 507	1 596	1 660	1 727	1 810	1 896	1 972	2 029	2 044	2 074	2 153	2 173	2 282	2 392	2 515	2 674	2 799	2 978	3 123	3 172	3 311	3 347
Australia and Oceania	299	300	305	310	318	330	342	352	372	384	392	407	413	417	434	440	446	456	458	462	454	454

Monitoring of GHG on global level

- **Global emissions of greenhouse gases – according to sectors**

(Source: http://www3.epa.gov/climatechange/science/indicators/ghg/global-ghg-emissions.html)



Year	Annual emission; [million metric tons CO_2 equivalent]					
	Energy	International transport	Agriculture	Industrial processes	Waste	Land-use
1990	22 985	619	5 622	1 126	1 148	2 596
1995	23 727	709	5 502	1 300	1 226	2 569
2000	25 615	836	5 424	1 481	1 299	2 590
2005	29 538	973	5 798	1 982	1 379	3 060
2010	32 678	1 096	5 999	2 522	1 471	2 097