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MINISTRY OF EDUCATION, YOUTH AND SPORTS

ATMOSPHERIC CHEMISTRY

Lecture No.: 6

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Organisation of study

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  building A, Dept. 216, door No.162
  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 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

- Main greenhouse gases – distribution and abbreviations:
  - H_2O (vapour)
  - CO_2
  - C_xH_y (especially CH_4)
  - N_2O
  - F-gases a ClF-gases:
    - CFCs (chlorofluorocarbons)
    - HFCs (hydrofluorocarbons)
    - PFCs (perfluorocarbons)
    - SF_6 (sulphur fluoride)
  - O_3

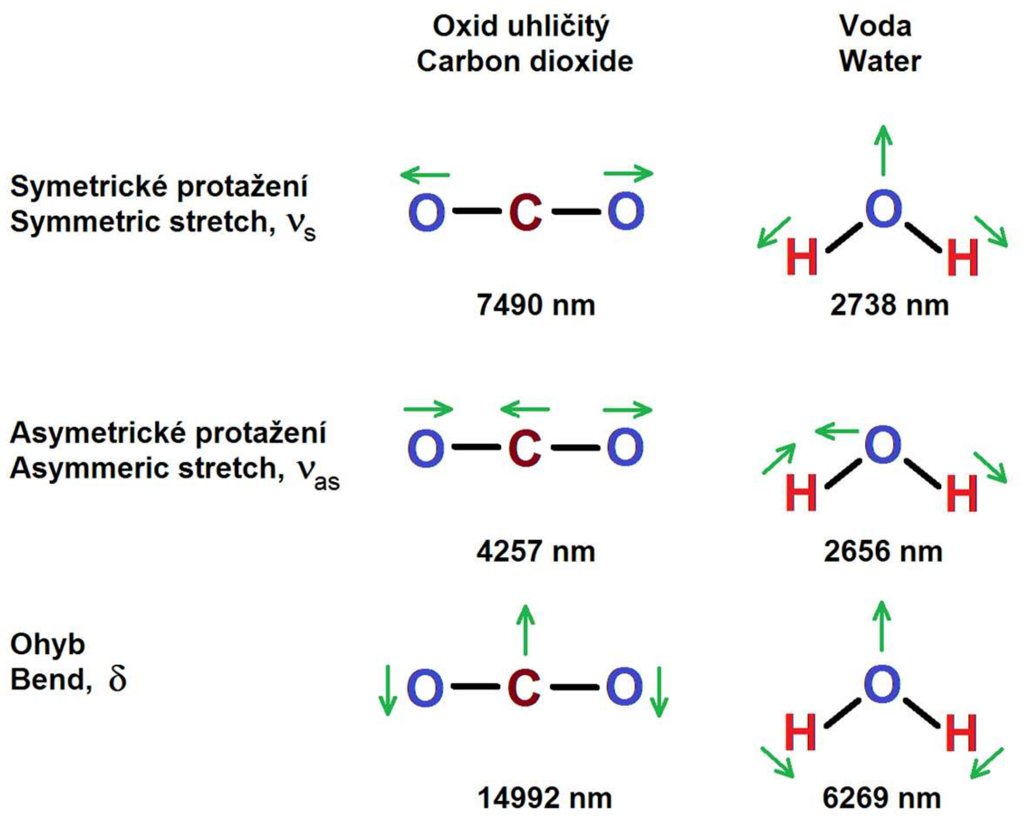
Effects of greenhouse gases

- Mechanism of GHG impact:
  - Greenhouse gases must absorb radiation in IR part of spectrum;
  - Quantum transition during IR absorption = values of molecular vibrations;
  - 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;
  - GHG molecules must have sufficient lifetime in the atmosphere and must be present at sufficient concentrations (e.g. average content of H_2O = 0.4 % vol., average content of CO_2 > 0.04 % vol.).

2018 highest CO_2 value = 412,6 ppm !

Effects of greenhouse gases

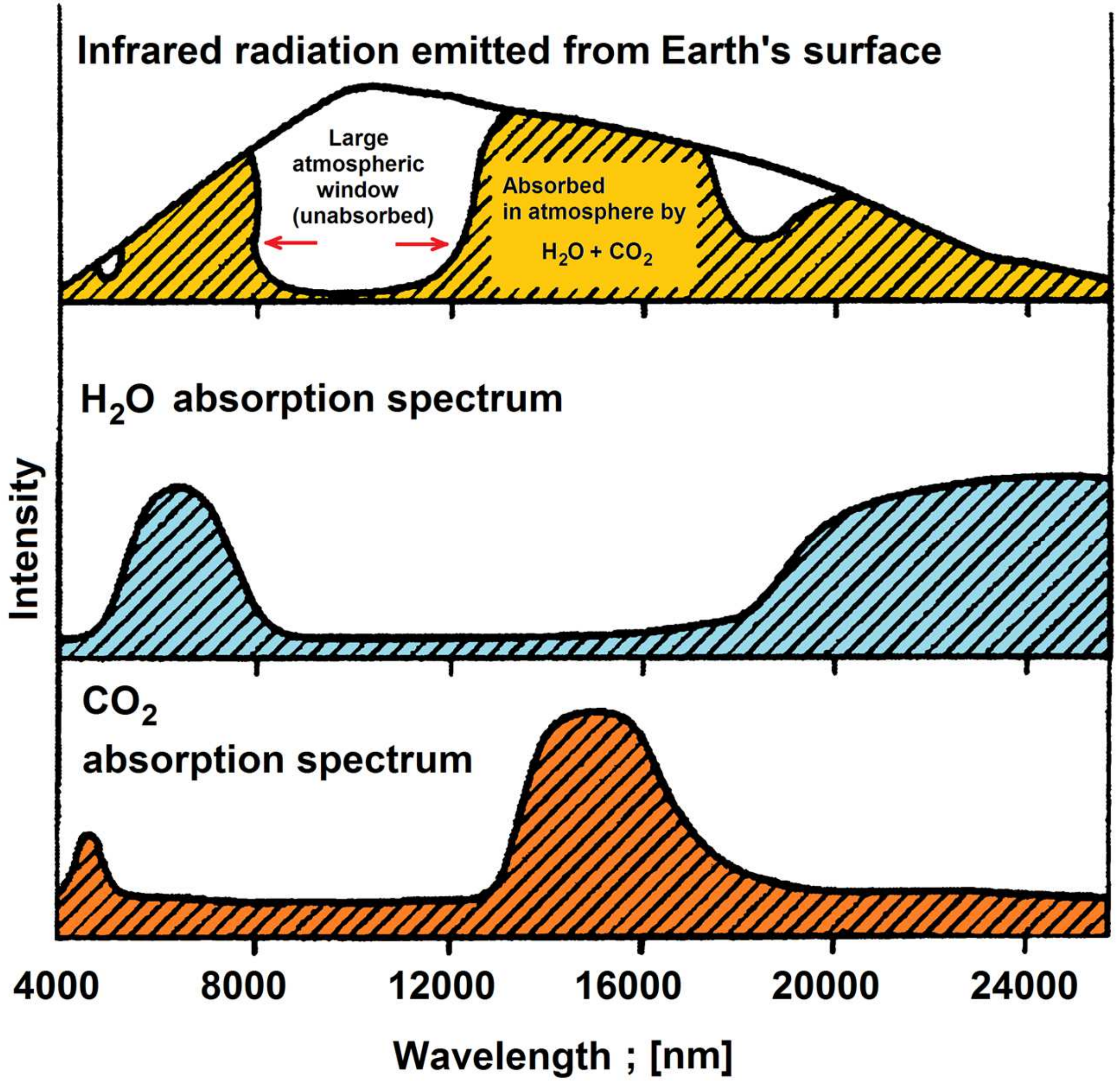
- Mechanism of GHG impact:
  - Each molecular vibration has its specific wavelength value, but 1 molecular vibration induces high number of various rotation levels ⇒ extension of absorption belt width.
  - Example – molecular vibrations of CO_2 and H_2O:



Effects of greenhouse gases

- Mechanism of GHG impact:

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



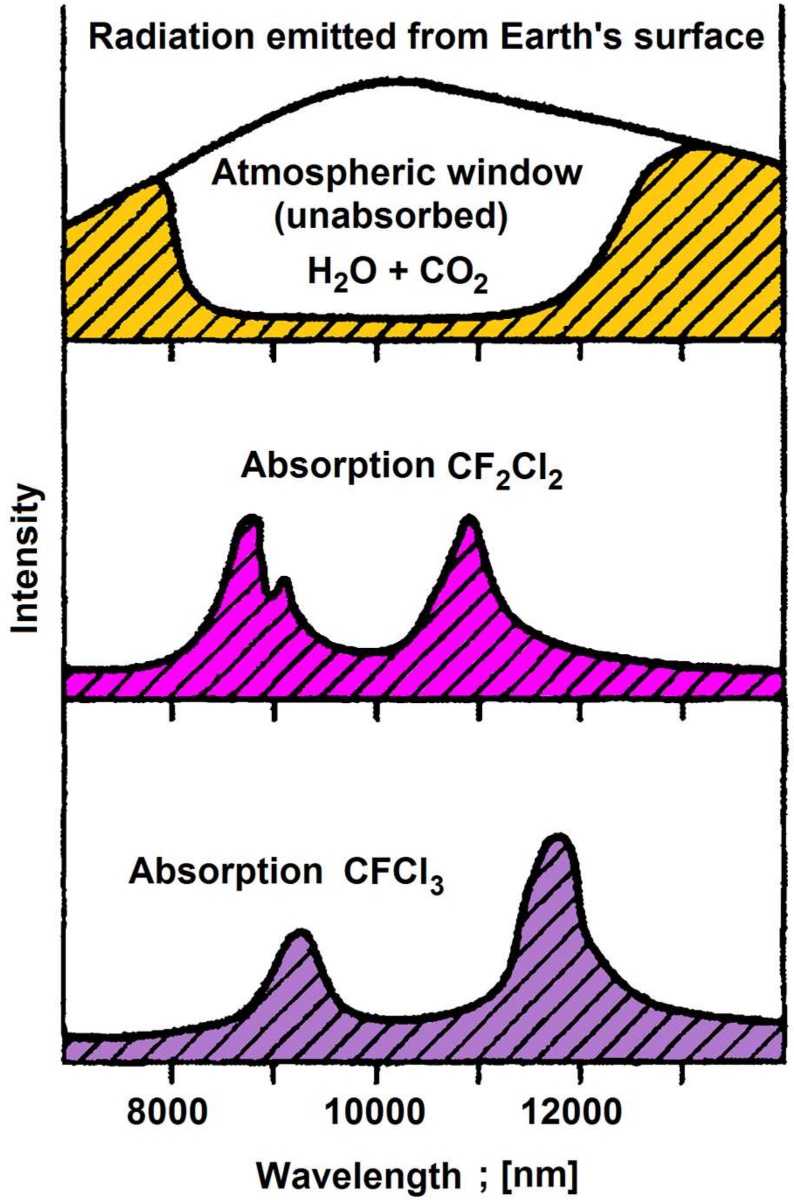
Effects of greenhouse gases

- 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.



Calculation of GHG impact

- Global warming potential, GWP
  - GWP is a relative measure of how much heat is retained in the atmosphere by a gas;
  - It compares the amount of heat, retained by the certain amount of the particular gas, relative to the same amount of CO_2;
  - It is expressed as a dimensionless factor related to CO_2, therefore $GWP(CO_2) = 1$;
  - GWP is calculated for specific time frames, usually 20, 100 or 500 years;
  - E.g. In the 5th IPCC report CH_4 had atmospheric lifetime 12.4 years and for a 20-years horizon GWP = 86, for a 100-year horizon GWP = 34 respectively (please, compare with the inventory);
  - Consequence: methodology for GWP calculation and choice of the time horizon significantly influence the numerical value.

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

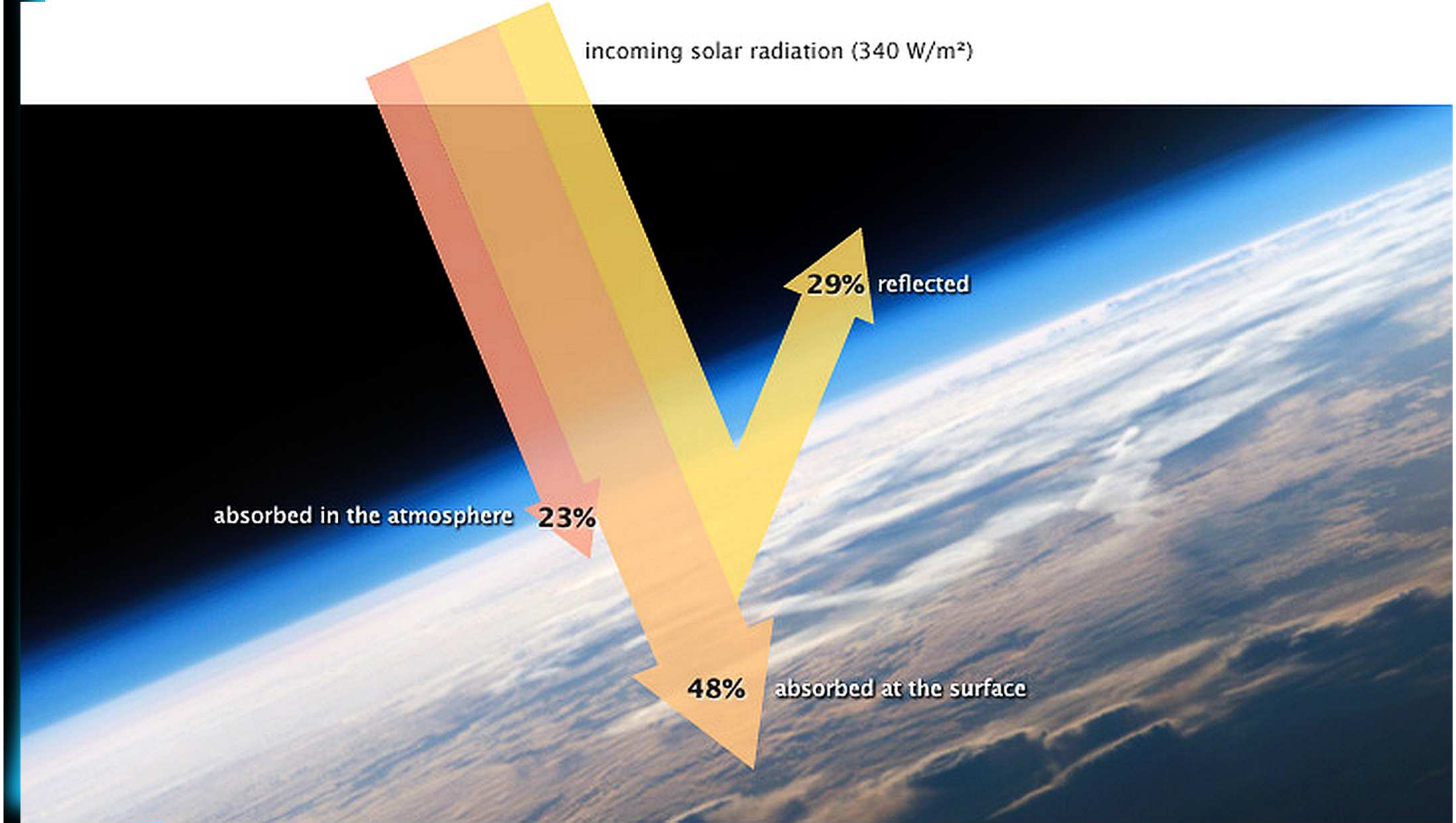
- Global warming potential, GWP
  - High GWP correlates with high absorption of IR part of the spectrum and with long lifetime of the substance in the atmosphere.
  - Dependence of GWP on the absorbed wavelength is more complicated. If the gas is absorbed at a particular wavelength, it does not have a large impact on its GWP, provided the atmosphere already absorbs most of the radiation with this wavelength in adifferent way.
  - A gas has the greatest effect when it absorbs in the window, where the atmosphere is transparent. Dependence of GWP as a function of wavelength has been determined empirically.
  - GWP of each greenhouse gas directly depends on its IR spectrum $\Rightarrow$ It is advantageous to use IR spectroscopy to study greenhouse gas emissions.

Calculation of GHG impact

- **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 $\Rightarrow$ warming of the system;
  - Negative radiative forcing = predominance of the emitted energy over absorbed energy $\Rightarrow$ cooling of the system.

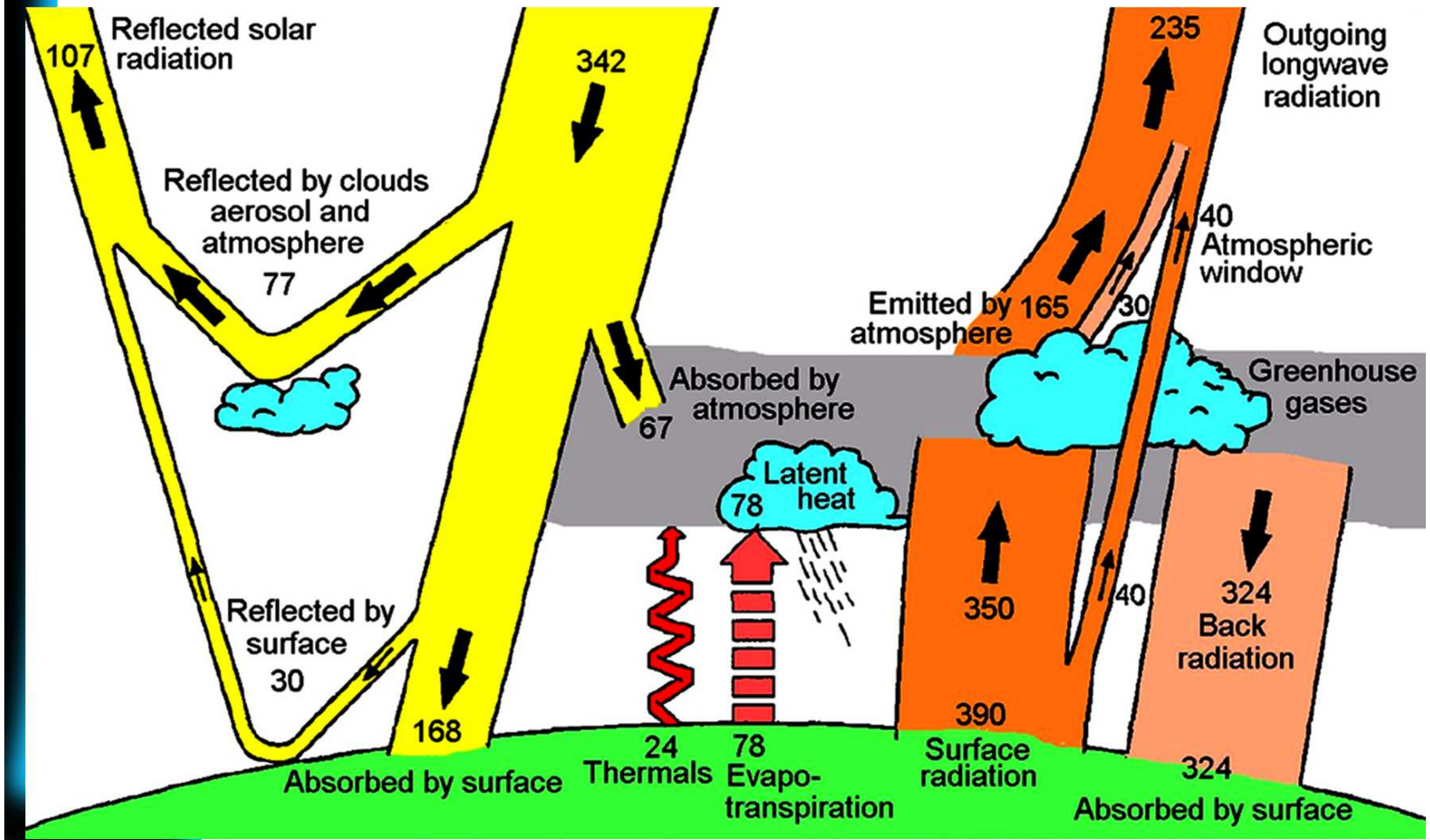
Calculation of GHG impact

- Balance of radiation (Source: IPCC)



Calculation of GHG impact

- 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

Calculation of GHG impact

- Radiative forcing and Radiative Forcing Capacity
  - Radiative forcing provides simplified means for comparing various factors that are supposed to influence the climate system.
  - Global Warming Potential (GWP) is a type of a simplified index, based on the radiative properties and usable to estimate the impact of gas emissions on the climate system.
  - GWP is based on a number of factors: radiation efficiency of the gas (absorption in the IR spectrum) relative to that of CO_2, the decay rate of the gas (gas quantity eliminated from the atmosphere per given time) relative to CO_2, etc.
  - **Radiative Forcing Capacity** (RF) is the amount of energy per unit area per unit time, absorbed by greenhouse gases, which would otherwise be radiated into space. RF can be expressed via equation, based on the Beer law:

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

Calculation of GHG impact

- Radiative forcing capacity

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

– Symbols in the figure above mean:

Subscript i = interval 10 cm^{-1};

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}]

– It follows therefrom that the RF value is determined instrumentally by measuring the absorbance of IR radiation by a gas within the scale of all wavelengths, which are absorbed by an analyte.

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)
  – Radiative efficiencies a_x; a_r are not always constant within the whole selected time horizon;
  – For the majority of gases IR absorbance increases linearly with their abundance in the atmosphere;
  – Several important GHGs show non-linear dependence, both for their current as well as (probably) for their future abundance in the air! These gases are particularly:

    CO_2, CH_4, N_2O
  – Problem: GWP calculations are based upon CO_2 ⇒ Carbon dioxide has non-linear dependence. Thus formerly calculated values of GWP for CH_4 and N_2O were undervalued.
  – It must be taken into account: Increase of CO_2 concentrations has lower impact on overall IR absorption (saturation of corresponding wavelengths) if compared with the gases with different IR absorption bands ⇒ This has been considered for new GWP values.

Calculation of GHG impact

- Global warming potential (GWP) – problem of its calculation for water
  - Unlike other GHGs water is not decomposed in the environment ⇒ the time scale of lifetime cannot be applied: Water vapour has the IR spectrum containing a higher number and wider absorption bands than CO_2;
  - Water vapour absorbs non-zero amounts of IR radiation even in its low absorbing spectral areas.
  - GWP of water is difficult to be calculated + its atmospheric concentration depends on temperature of air ⇒ cyclic calculation;
  - In addition the Earth's temperature is not equally distributed, continents differ from oceans as well as the northern hemisphere differs from the south.
  - Distribution of air humidity in Troposphere is unequal (average t = ca. 16 °C). Average water content ca. 0.4 % vol., but up to 1.8 % vol. near the sea level. CO_2 content more uniform (ca. 0.04 % vol.). Average concentration ratio H_2O/CO_2 = 10, maximum 45.

Monitoring of GHG

- National Greenhouse Gas Inventory:
  - Based on international agreement United Nations Framework Convention on Climate Change;
  - Realised according to IPCC methodology (Guidelines for National Greenhouse Gas Inventories + Good Practice Guidance and Uncertainty Management in National GHG Inventories);;
  - Elaboration of plan of control procedures QA/QC (Quality Assurance / Quality Control) is an inherent part of inventories planning.
  - QC = technical routine quality control of inventory; assessment whether: the data is complete, consistent in terms of time scales, data inputs are correctly inserted, calculations are without errors and omissions;
  - QA = independent assessment by a third party, which is not involved directly on the process of GHG inventory; + archivation of data and calculations for future checking by the international inspection team.

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 shows higher CO_2 capture than it emits ⇒ it means this sector shows negative CO_2 balance and diminishes overall emissions from other sectors;
    - Realisation of inventory according to methodology Good Practice Guidance for Land Use, Land-Use Change and Forestry, IPCC is based on the analysis of total quantity of wood in forests and its annual changes.

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

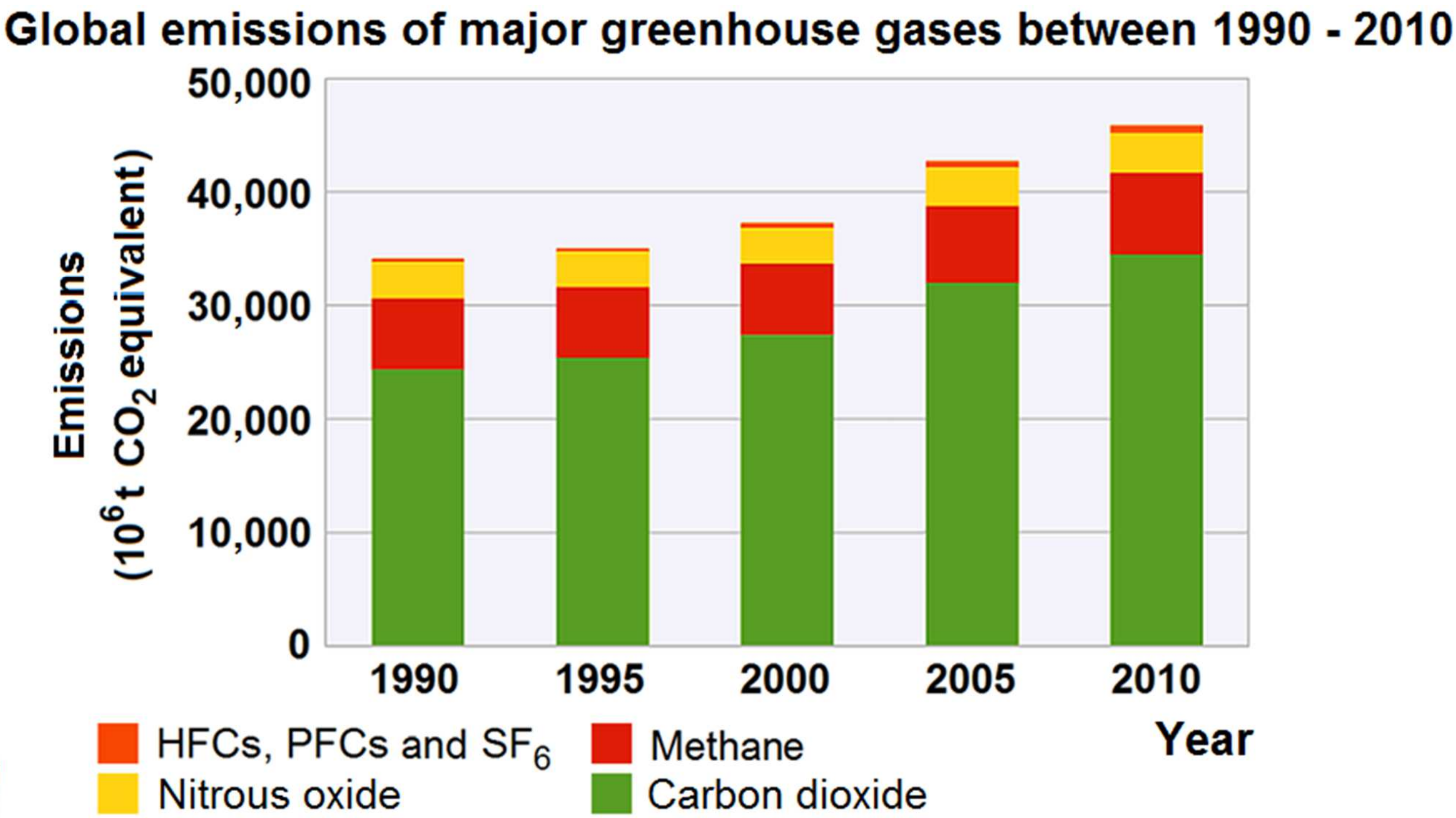
Monitoring of GHG

- **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

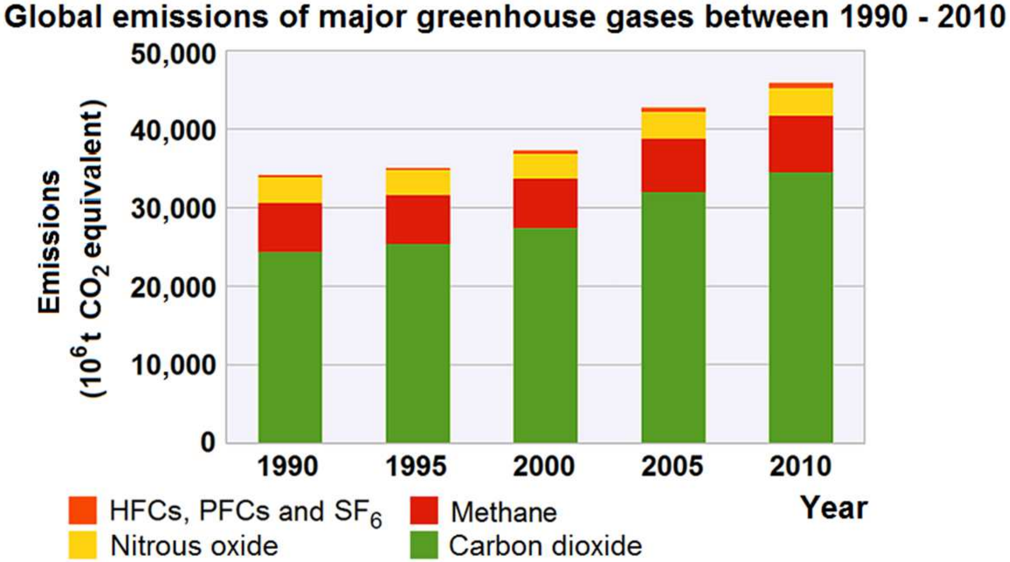
- **Production of greenhouse gases**
  (Sources: http://cait.wri.org, www.epa.gov/climatechange/indicators, http://faostat3.fao.org/faostat-gateway/go/to/download/G2/*/E))



Monitoring of GHG on global level

- Global emissions of greenhouse gases

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

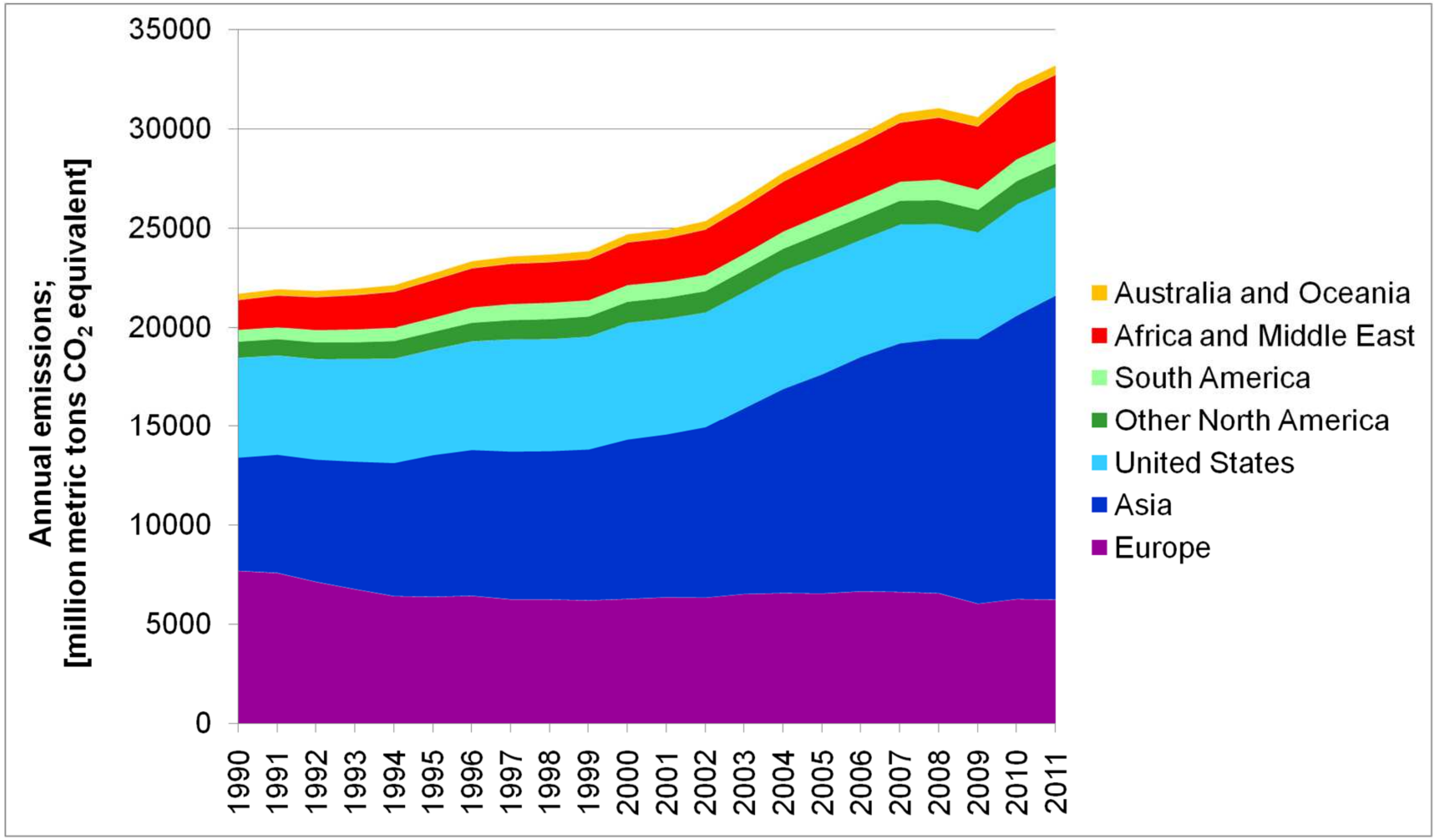


Annual emission; [million metric tons CO_2 equivalent]					
Year	Carbon dioxide	Methane	Nitrous oxide	HFCs + PFCs + SF_6	Total
1990	24 324	6 268	3 241	262	34 095
1995	25 345	6 205	3 193	291	35 033
2000	27 349	6 324	3 143	429	37 246
2005	31 949	6 816	3 367	598	42 730
2010	34 476	7 196	3 520	672	45 863

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)

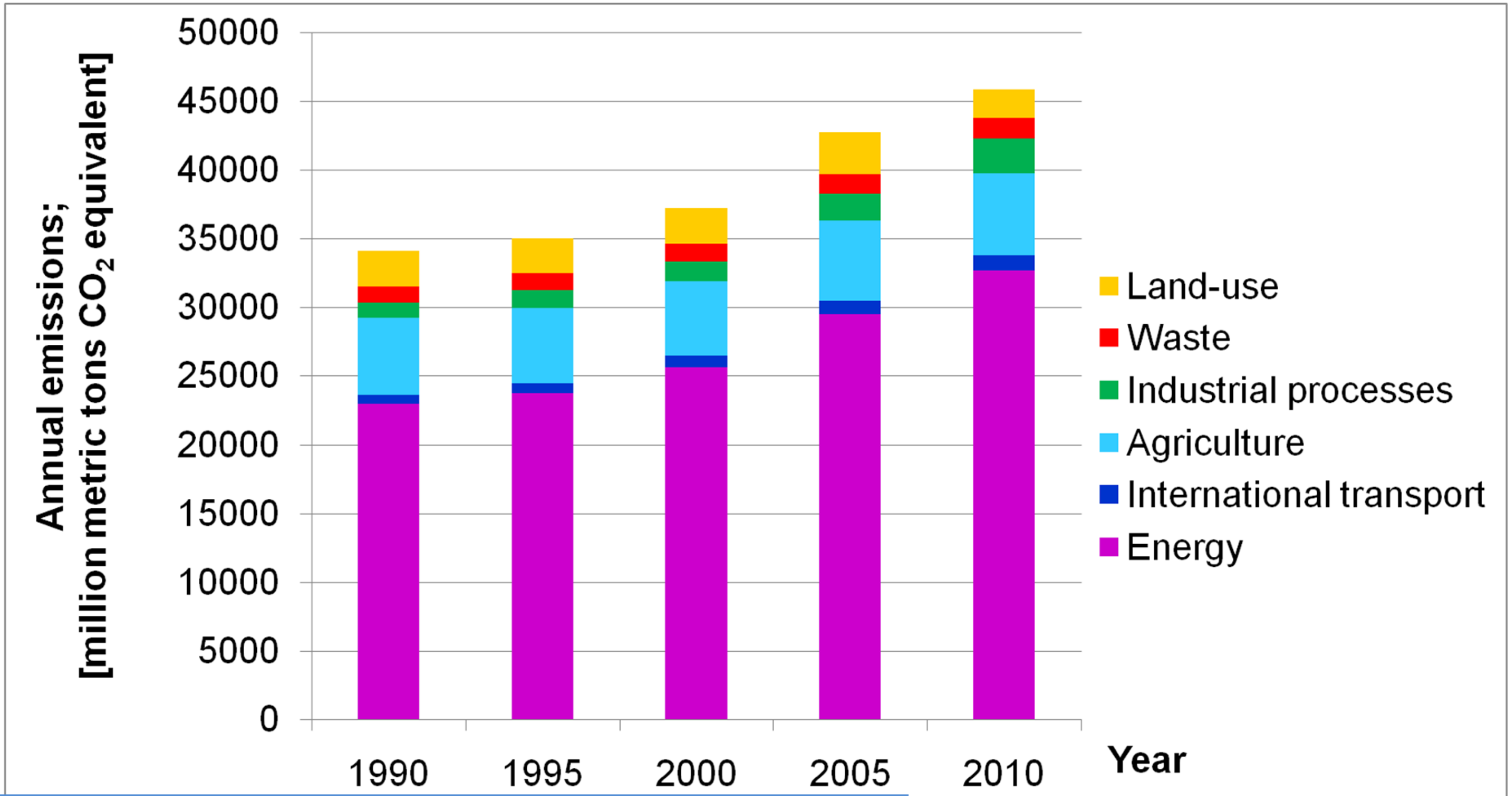


Region	Annual emission; [million metric tons CO_2 equivalent] 1990	1991	1992	1993	1994	1995	1996	1997	1998	1999	2000	2001	2002	2003	2004	2005	2006	2007	2008	2009	2010	2011
Europe	7 678	7 575	7 123	6 752	6 405	6 374	6 420	6 242	6 236	6 195	6 263	6 349	6 330	6 513	6 557	6 537	6 644	6 614	6 548	6 022	6 256	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