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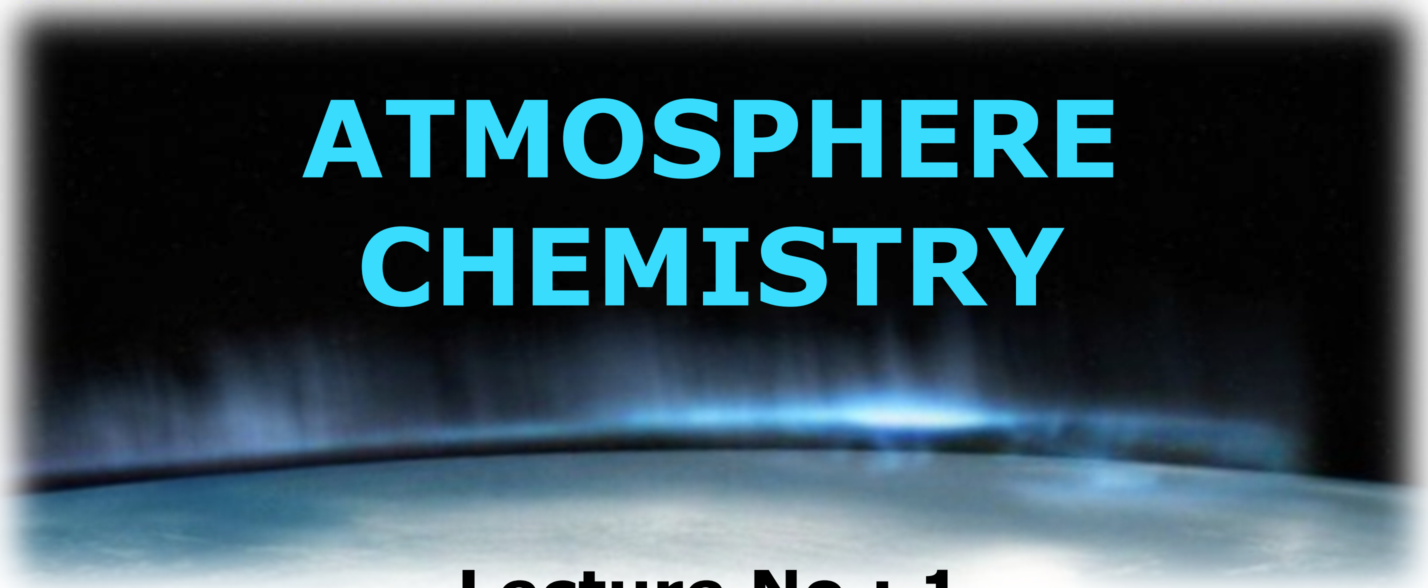

ATMOSPHERE CHEMISTRY

Lecture No.: 1

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 - oral form
- Note:

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Syllabus of subject

- Lecture 1. Atmosphere as basic component of natural environment
- Lecture 2. History of Earth’s atmosphere
- Lecture 3. Environmental information systems
- Lecture 4. Physical rules in atmospheric processes
- Lecture 5. Basic reactions in the atmosphere, homogeneous and heterogeneous reactions
- Lecture 6. Introduction to the problematics of greenhouse gases
- Lecture 7. Characterisation of the main greenhouse gases
- Lecture 8. Selected atmospheric pollutants – acidic substances
- Lecture 9. Selected atmospheric pollutants – toxic substances

Syllabus of subject

Lecture 10.	Reactions of oxygen and water, formation of clouds and precipitations
Lecture 11.	Reactions of ozone, chemistry of the background troposphere, hydroxyl radical, hydroperoxyl radical, stratospheric damaging of ozone layer
Lecture 12.	Worldwide evolution in the field of air protection and important international agreements
Lecture 13.	Power industry as the main contributor to air pollution – London-type smog
Lecture 14.	Road transport as a contributor to air pollution – photochemical smog

Scope of lecture 1

Atmosphere as basic component of natural environment

- Definition of atmosphere, its borders and distribution of weight
- Atmospheric stratification according to altitude
- Physical characterisation of atmosphere and its overall chemical composition
- Detailed description of the most important atmospheric layers
- How magnetic field influences the atmosphere
- Atmosphere as a filter for radiation

Basic properties of atmosphere

- Approximate height of measurable concentrations of atmosphere is 560 km (precise altitude is not available, however a part of thermosphere and whole exosphere are situated faraway)
- Overall weight of atmosphere is only estimated and the value is 5.15×10^{18} kg

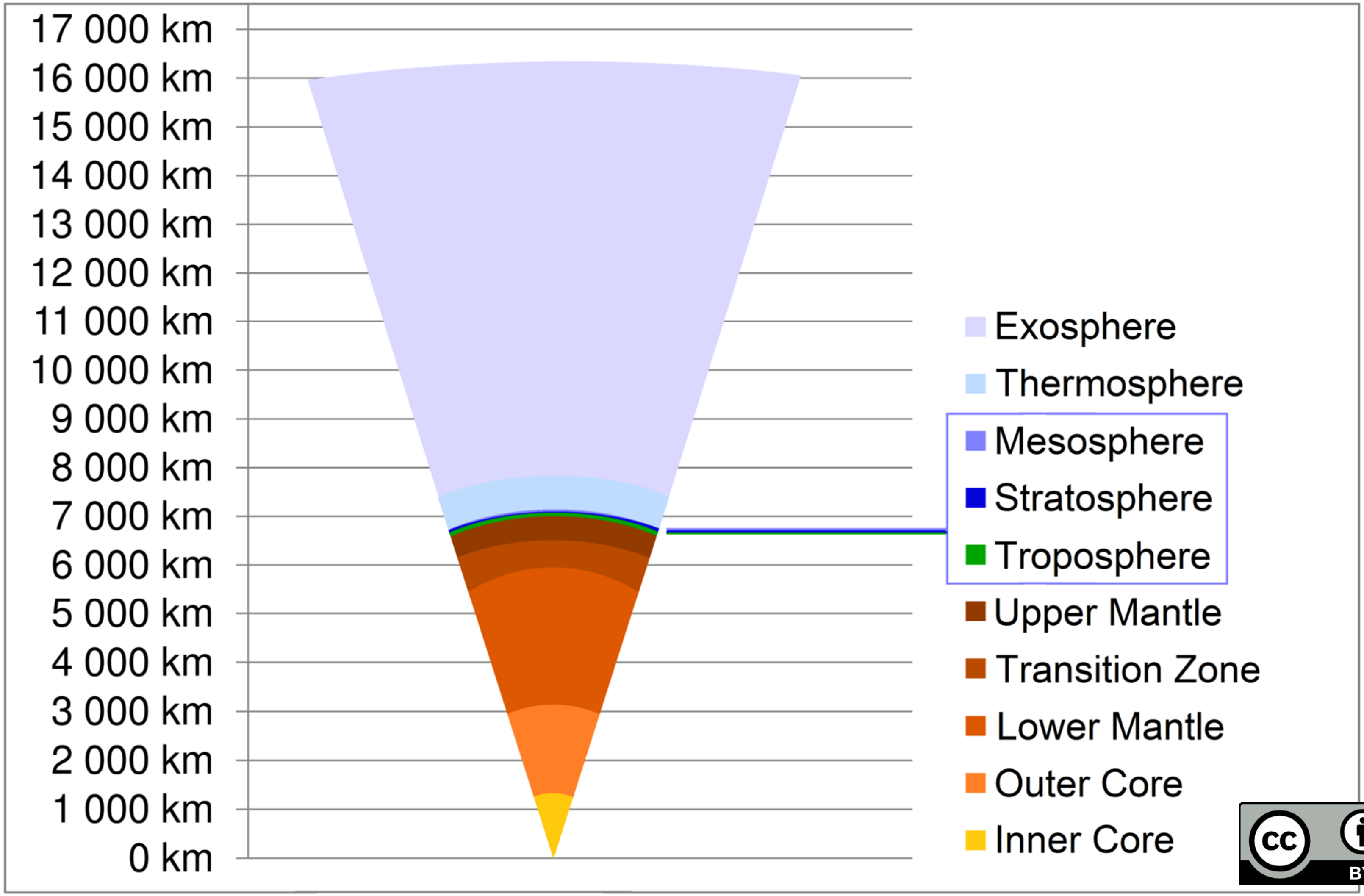
  (Source: American National Center for Atmospheric Research)
- Weight of the atmosphere distributed according to altitude is following:

ca. 50 %	height up to 5.6 km (above sea level)
ca. 75 %	height up to 11 km
ca. 90 %	height up to 16 km
99.99997 %	height up 100 km

- The border of the outer space is 100 km according to Féderátion Aéronautique Internationale (FAI) = International Aeronautical Federation – so called Kármán line (term pilot for flights under this line and astronaut for flights over the KL), but NASA’ border line 50 miles = 80 km.
- Up to KL we speak about altitude, over KL about distance from E

Basic properties of atmosphere

- Participation of atmosphere on the total weight of Earth, which is 8.62×10^{-5} % (it means < one millionth of the Earth's weight 5.972×10^{24} kg)



Stratification of atmosphere

- The atmosphere can be stratified according to various criteria: (Source: Kleczek, J. Toulky Vesmírem)

- According to temperature:
  - Troposphere
  - Stratosphere
  - Mesosphere
  - Thermosphere

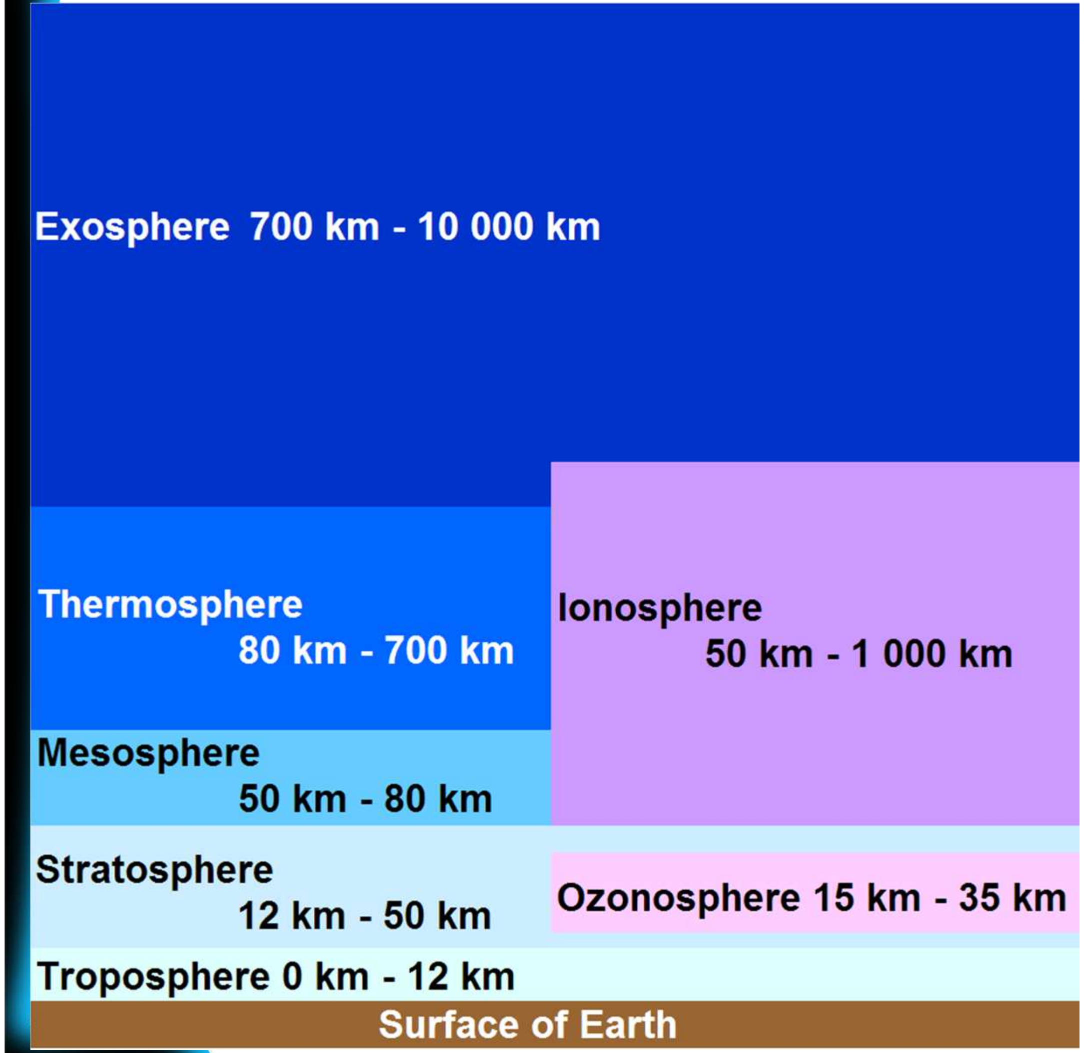
- According to chemical properties:
  - Ecosphere
  - Troposphere
  - Stratosphere
  - Chemosphere
  - Ozonosphere
  - Ionosphere
  - Mesosphere

Stratification of atmosphere

- The atmosphere can be stratified according to various criteria: (Source: Kleczek, J. Toulky Vesmírem)
- According to electrical properties
  - Neutrosphere
  - Ionosphere
- Accroding to movements
  - Troposphere
  - Stratosphere
- According to uniformity of composition
  - Homosphere
  - Heterosphere
- The most imoprtant and most frequently used stratification is according to the dependence of temperature and density upon altitude (seen on the next slide).

Stratification of atmosphere

Atmospheric layers and temperatures (by NASA and National Weather Service)



Exosphere 700 km - 10 000 km

Thermosphere 80 km - 700 km

Ionosphere 50 km - 1 000 km

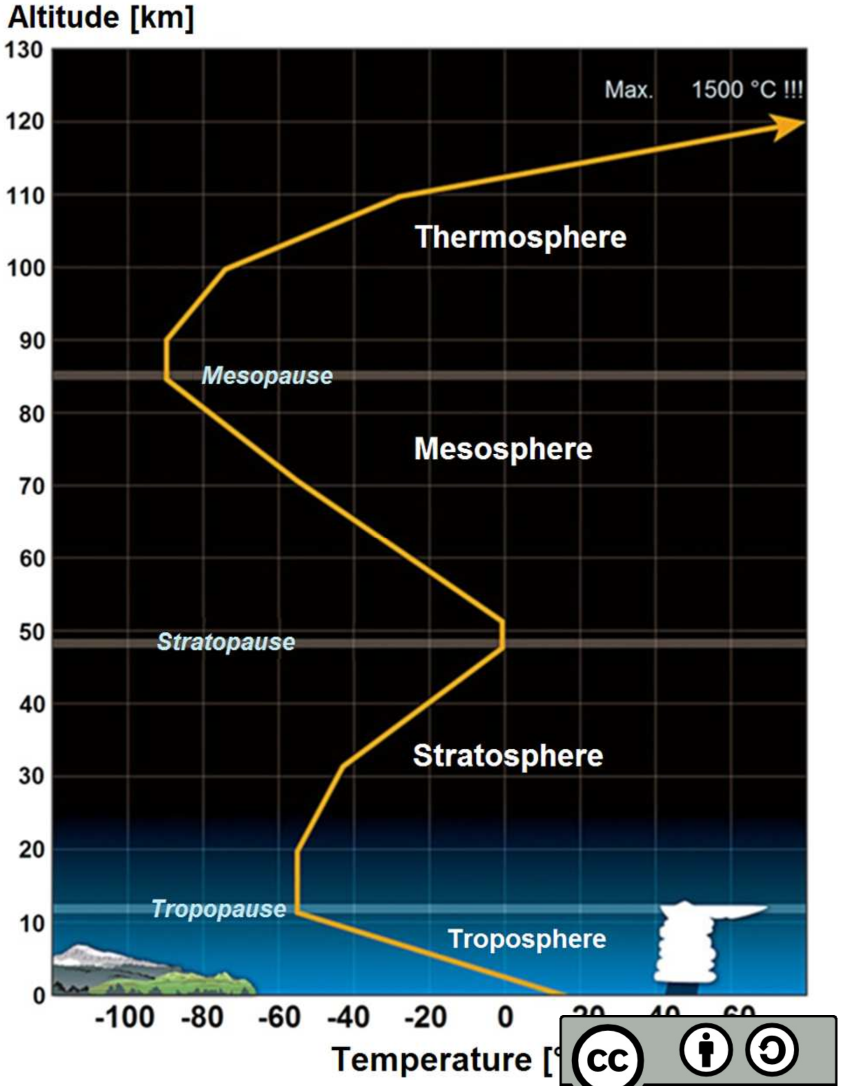
Mesosphere 50 km - 80 km

Stratosphere 12 km - 50 km

Ozonosphere 15 km - 35 km

Troposphere 0 km - 12 km

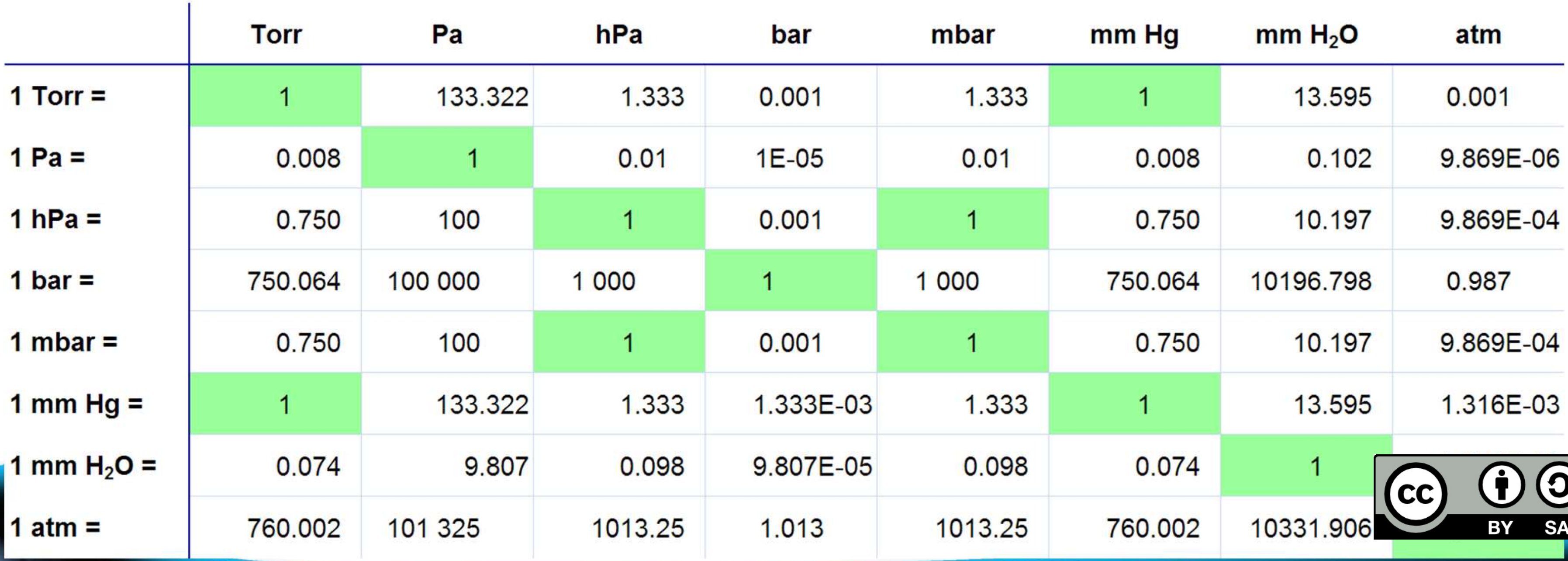
Surface of Earth



Relation altitude - parameters

- Expression of pressure in meteorology:

By SI permitted only:	Pascal	[Pa] = $[N.m^{-2}]$
Traditionally used also:	Torr	[Torr]
	Bar	[bar]
	Conventional mm of Mercury	[mm Hg]
	Conventional mm of water	[mm H_2O]
	Physical atmosphere	[atm]
Multiples in meteorology:	Milibar	[mbar]
	Hektopascal	[hPa]



	Torr	Pa	hPa	bar	mbar	mm Hg	mm H_2O	atm
1 Torr =	1	133.322	1.333	0.001	1.333	1	13.595	0.001
1 Pa =	0.008	1	0.01	1E-05	0.01	0.008	0.102	9.869E-06
1 hPa =	0.750	100	1	0.001	1	0.750	10.197	9.869E-04
1 bar =	750.064	100 000	1 000	1	1 000	750.064	10196.798	0.987
1 mbar =	0.750	100	1	0.001	1	0.750	10.197	9.869E-04
1 mm Hg =	1	133.322	1.333	1.333E-03	1.333	1	13.595	1.316E-03
1 mm H_2O =	0.074	9.807	0.098	9.807E-05	0.098	0.074	1	
1 atm =	760.002	101 325	1013.25	1.013	1013.25	760.002	10331.906	

Relation altitude - parameters

- Calculation of pressure dependence on the height above sea level (Source: The Engineering ToolBox)

  Simple empirical model used: $p = 101\,325 \cdot (1 – 2.25577 \cdot 10^{-5} \cdot h)^{5,25588}$

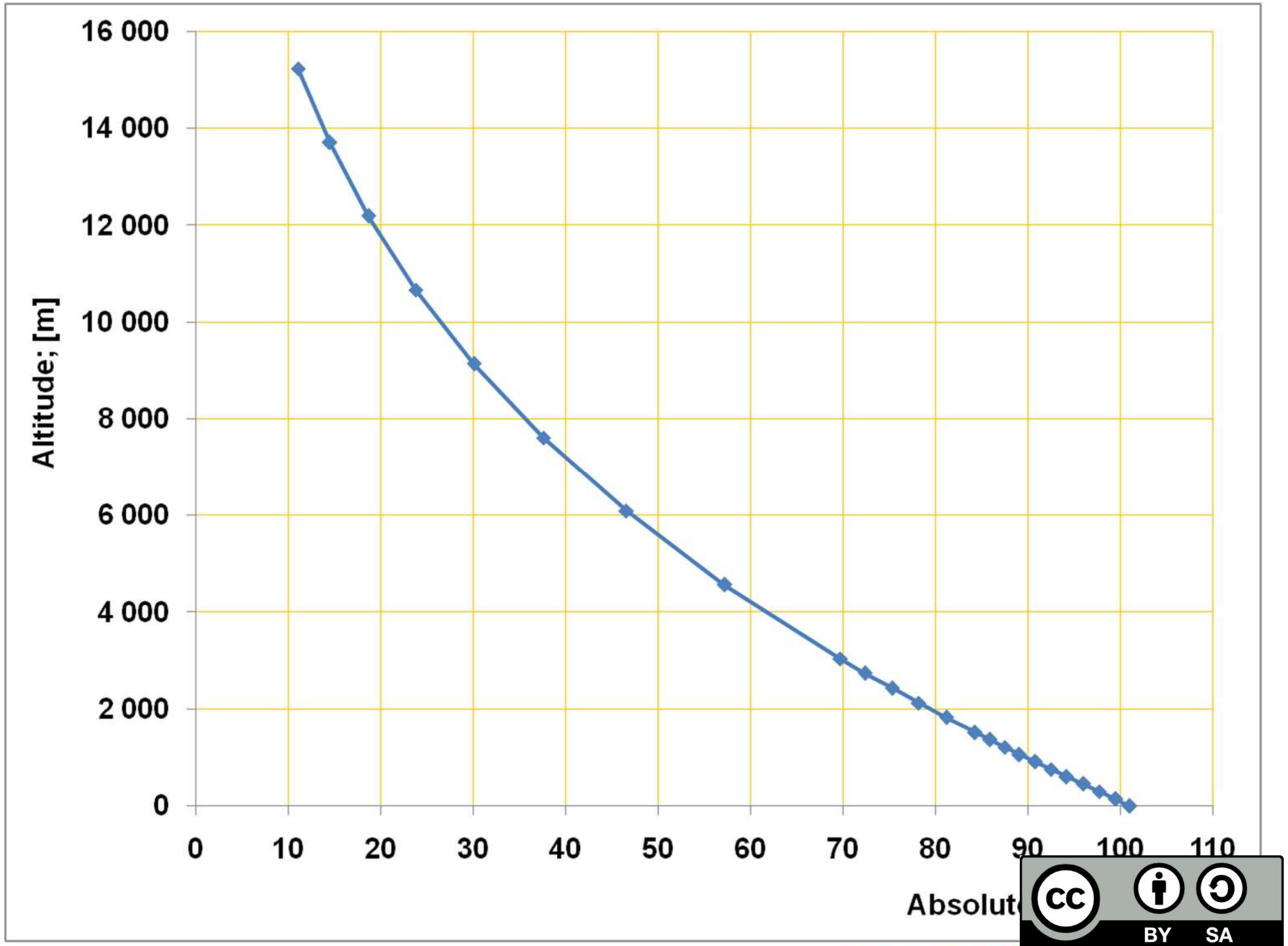
Where is:

p … pressure [Pa]

h … altitude [m]

(Applicable only

up to 20 km)



Relation altitude - parameters

- Common dependence of p a T on altitude (Source: Engineering Smart Technology Products)

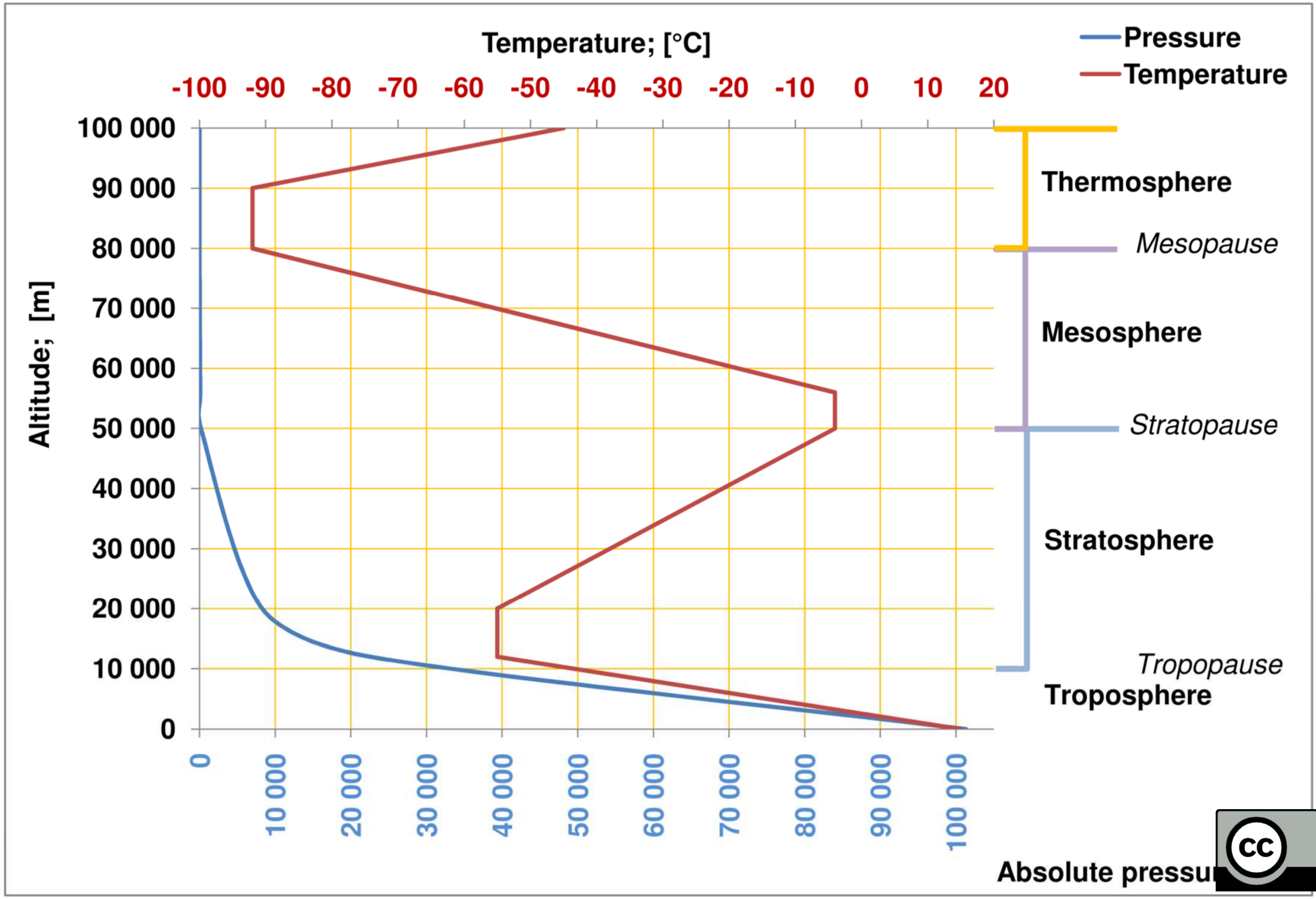
Alternative equation for air pressure with wider range applicability

$$p = p_s \cdot e^{\left[\frac{g \cdot M \cdot (h - h_s)}{R \cdot T_s}\right]}$$

Where is:	p	… pressure in the given altitude		[Pa]
	p_s	… pressure on the sea level		[Pa]
	g	… gravity acceleration	9.80665	$m.s^{-2}$
	M	… average molar weight of air	0.0289644	$kg.mol^{-1}$
	R	… molar gas constant	8.31432	$N.m.mol^{-1}.K^{-1}$
	T_s	… average temperature on the sea level		[K]
	h	… altitude (height above sea level)		[m]
	h_s	… reference height	0	m

Relation altitude - parameters

- Using the equation $p = p_s \cdot e^{\left[\frac{g \cdot M \cdot (h-h_s)}{R \cdot T_s}\right]}$ following graph obtained:



Basic chemical composition

- Chemical composition of dry atmosphere (volumic percentage):

N_2	78.08 %;	O_2	20.95 %;	Ar	0.93 %
CO_2	0.03 %;	Ne	18.18×10^{-4} %;	He	5.25×10^{-4} %
CH_4	2×10^{-4} %;	Kr	1.14×10^{-4} %;	N_2O	0.5×10^{-4} %;
H_2	0.5×10^{-4} %;	Xe	0.087×10-4 %;	O_3	$0\text{-}0.07\times10^{-4}$ %
SO_2	$0\text{-}1\times10^{-4}$ %;	NO_2	$0\text{-}0.02\times10^{-4}$ %		

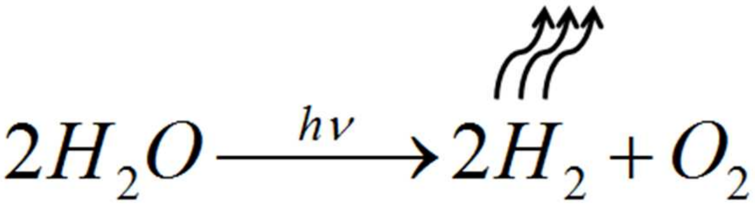
H_2O overall content represents 0.25 % of the total weight of atmosphere.

Characterisation of layers

- Troposphere
  - average scale12 km
  - thickness depends on latitude as well as on season of the year
  - thickness near poles is 8 – 9 km, over the equator up to 17 km
  - represents 85 % of the overall weight of atmosphere
  - has 2 sub -layers:
    Planetary Border Layer (PBL)
    Open Troposphere (OT)
  - PBL has thickness ca. 1 km; it is significantly turbulent due to contact with relief ⇒ mixing of gases incl. pollutants and aerosols
  - OT has temperature decreasing with altitude (negative temperature gradient) down to -55 °C in moderate latitudes; gas composition homogeneous, mixing independent on the relief (determined by pressure gradients and Coriolis force); OT accumulates majority of water (layer where rains are ge

Characterisation of layers

- Tropopause
  - Cold, thin layer between troposphere and stratosphere;
  - Temperature ca. -55 °C, altitude ca. 12 km;
  - Significant barrier blocking raising of water vapors to higher atmospheric layers;
  - In case of absence of tropopause water would ascend to the layer with high-energetic irradiation, subsequent photodissociation and leakage of Hydrogen to outer space:

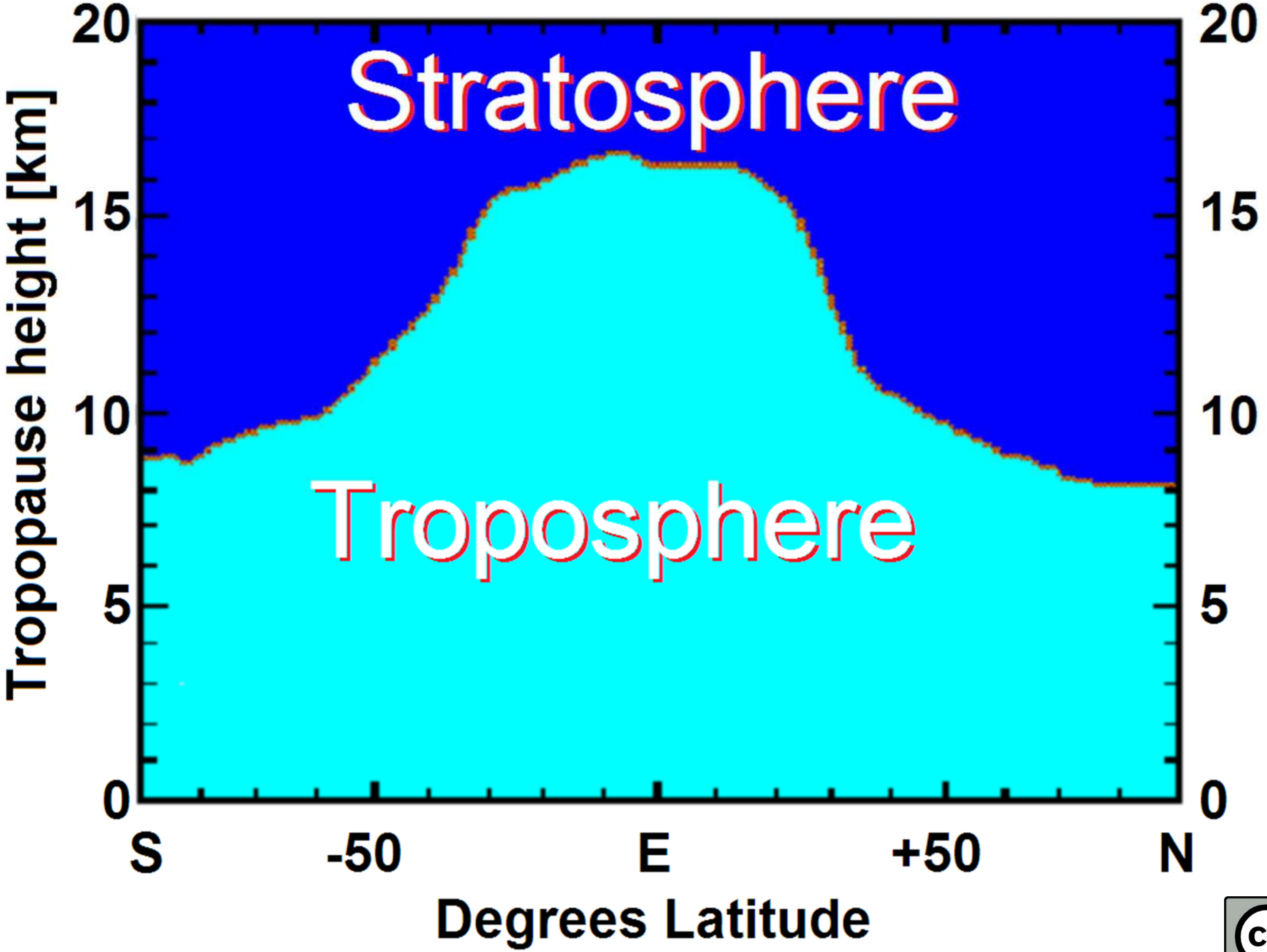


$$2H_2O \xrightarrow{h\nu} 2H_2 + O_2$$

  - it happened in geological history of the planet; Earth lost irreversibly majority of Hydrogen and Helium by this chemical mechanism.

Characterisation of layers

- Variable thickness of troposphere according to lattitude (E = Equator)



Characterisation of layers

- Stratosphere
  - Layer above tropopause, limited by area, where temperature ceases to decrease according to altitude, and area where temperature starts to decrease again;
  - Temperature -55 up to – 4°C, altitude 12 – 50 km;
  - Ozonosphere is a part of stratosphere (15 – 35 km);
  - Content of Ozone in the ozonosphere is 10 ppm ⇒ absorption of UV irradiation causes simultaneous emission of heat (therefore positive temperature gradient in stratosphere);
- Mesosphere
  - Layer with typical rapid decrease of temperature with altitude;
  - The reason is absence of molecules capable to absorb irradiation from Sun;
  - Temperature between -4 and -90 °C, altitude 50 – 80

Characterisation of layers

- Thermosphere
    - Layer above mesosphere, which has remarkable positive temperature gradient;
    - Thickness of the layer is bigger than count of all the layers situated underneath; Thermosphere occupies altitudes between 80 and 700 km; temperature raises from -90 up to +1200 °C;
    - Atmosphere in this layer has very low density (pressure drops from ca. 7 kPa practically to zero);
    - Temperature in its upper part (500 – 700 km) reaches 1200 °C due to absorption of irradiation having wavelength < 200 nm;
    - Note: Above mentioned high temperatures are not measurable using conventional method, due to extremely low particle concentrations – the method only available is measurement of mean kinetic energy of molecules.

Characterisation of layers

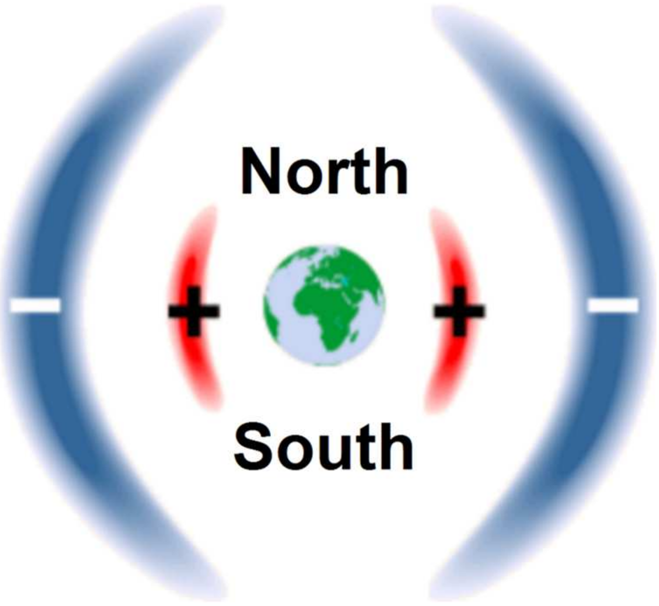
- Exosphere
  - Transition zone, which residues can be measured by sensitive analyzers up to the distance of 10 000 km from the Earth’s surface;
  - Temperature changes are not significant;
  - Atoms, molecules and ions are irreversibly released to interplanetary space;
  - Exosphere has very low density; almost containing only light gases H_2 and He;
  - Note. Decreasing of concentrations of heavier gases is gradual, it means their concentrations change with distance from Earth ⇒ alternative denomination of whole exosphere and thermosphere above ca. 85 km is heterosphere.

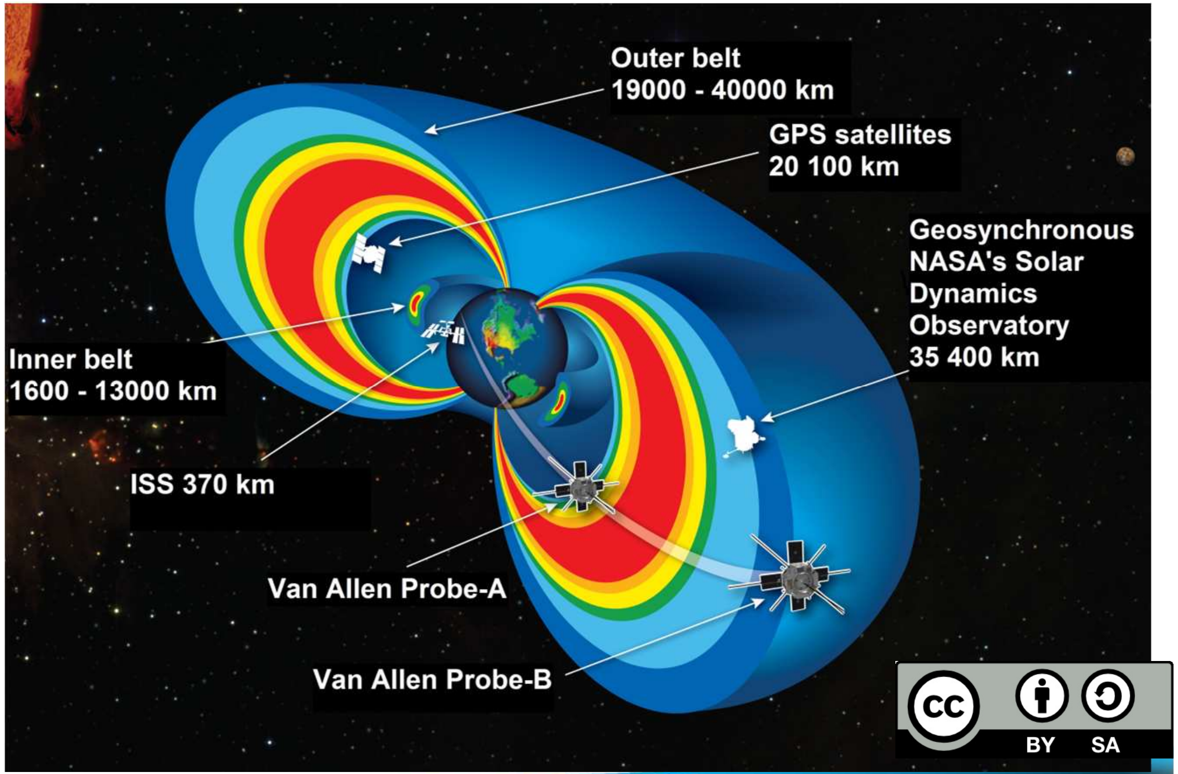
Characterisation of layers

- Ionosphere
  - Layer discovered in 1901 and defined on the basis of electrical criteria instead of of altitude dependence of pressure etc.;
  - It occupies whole mesosphere, whole thermosphere and lower part of exosphere;
  - Generation of ions inducted by electromagnetic irradiation in the range of UV wavelengths;
  - On the night side of the planet slow recombination of cations occurs with free electrons (disappearing of ions faster in lower layers, where higher concentration of particles is achieved) ⇒ therefore it causes night shift of lower border of ionosphere to higher altitudes;
  - Big practical importance of ionosphere for communication = reflection of electromagnetic waves back to the surface ⇒ transmission of radio waves.

Characterisation of layers

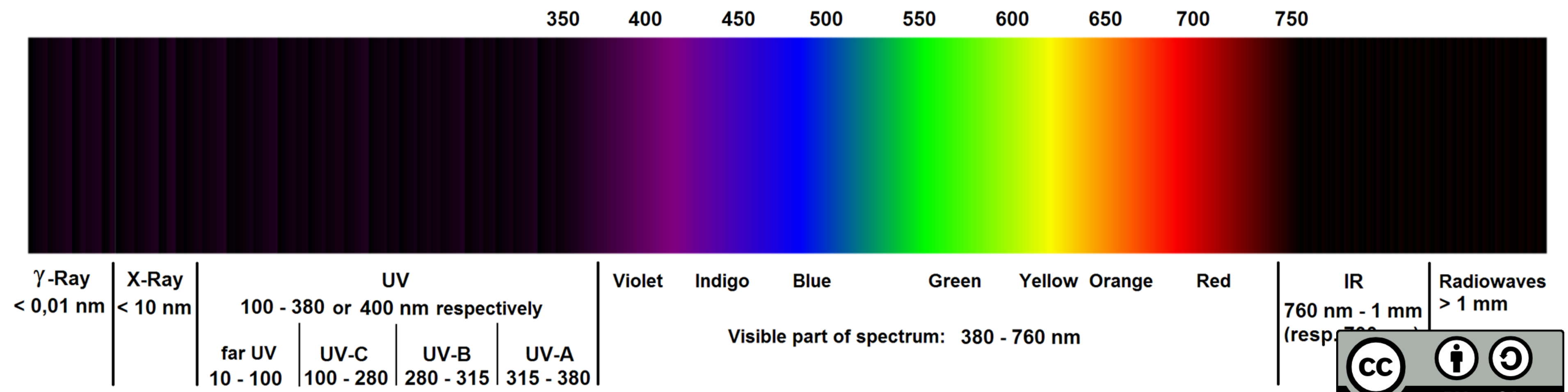
- Influence of magnetic field – capture of charged particles, so called solar wind
  - Van Allen belts of ionized particles (discovered in 1958);
  - Inner belt with positive and outer belt with negative charge (range 400 - 50 000 km);
  - Alert! High energy p^+ a e^- in the belts dangerous for astronauts.





Atmosphere as irradiation filter

- Irradiation with wavelength > 330 nm (i.e. part of UV, visible and IR)
  - breakthrough to the surface
- Irradiation with wavelength 200 – 330 nm (i.e. part of UV)
  - breakthrough 50 km above the surface
- Irradiation with wavelength 100 – 200 nm (i.e. part of UV)
  - breakthrough 200 km above the surface
- Note: So called cosmic irradiation is in fact particles (99 % cores of elements, 1 % electrons, regarding cores: 90 % isolated protons, 9 % alpha particles and 1 % heavier cores) ⇒ interaction with magnetic field.



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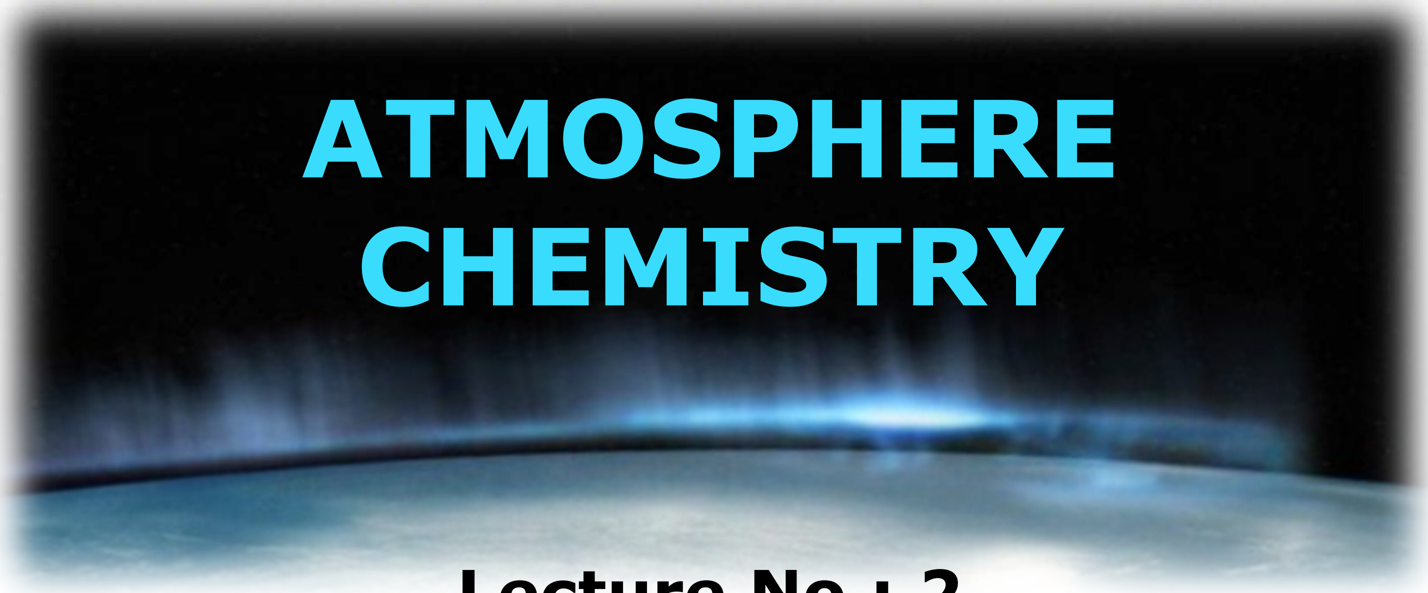

ATMOSPHERE CHEMISTRY

Lecture No.: 2

Organisation of study

- Lecturer: Marek Staf, MSc., Ph.D., phone: +420 220 444 458
  e-mail: marek.staf@vscht.cz,
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Scope of lecture 2

History of Earth’s atmosphere

- Chronostratigraphic history of Earth
- Evolution of Earth’s atmosphere
- Fluctuations in oxygen concentration
- Fluctuations in planetary temperature

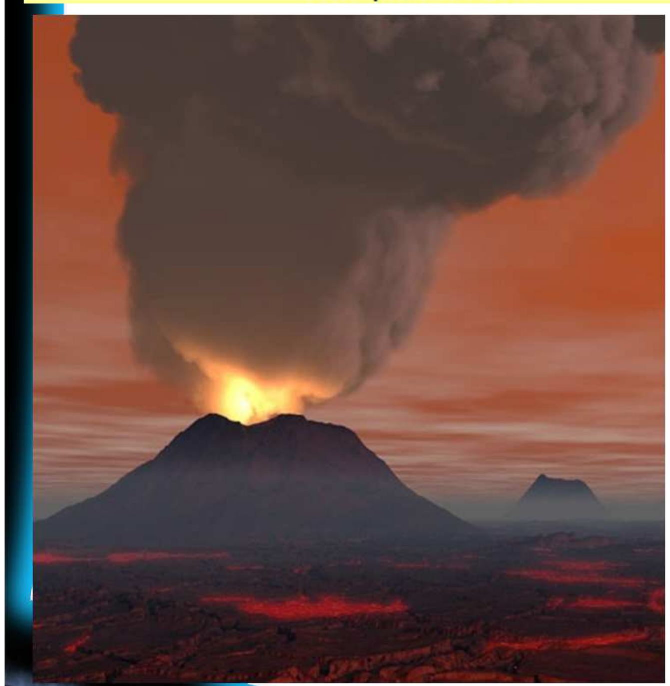
How does environmental information system work

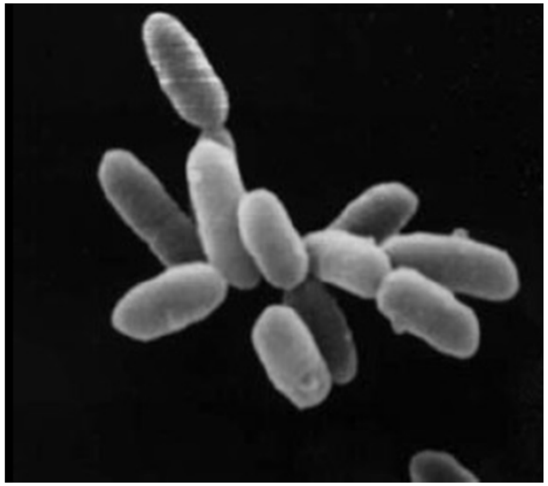
- Description of essential conditions for operation of environmental information systems
- Main automated analytical techniques
- Development of computers and network
- Life cycle of information within the EIS

Chronostratigraphic history of Earth

- The age of Earth is ca. 4.54 billion ± 70 mil. years (Source: Wilde, S. A., Valley, J. A., Peck, W. H., Graham, C. M. (2001))

Eon	Era	Period	Epoch	Time [mil. years]	Organisms
Hadean				4 540 - 3 800	
Archean	Eoarchean			3 800 - 3 600	
	Paleoarchean			3 600 - 3 200	Genesis of archebacteria
	Mesoarchean			3 200 - 2 800	
	Neoarchean			2 800 - 2 500	
Proterozoic	Paleoproterozoic			2 500 - 1 600	First eucaryotic cells
	Mesoproterozoic			1 600 - 1 000	
	Neoproterozoic			1 000 - 541	Genesis of multicellular organisms, worms





Chronostratigraphic history of Earth

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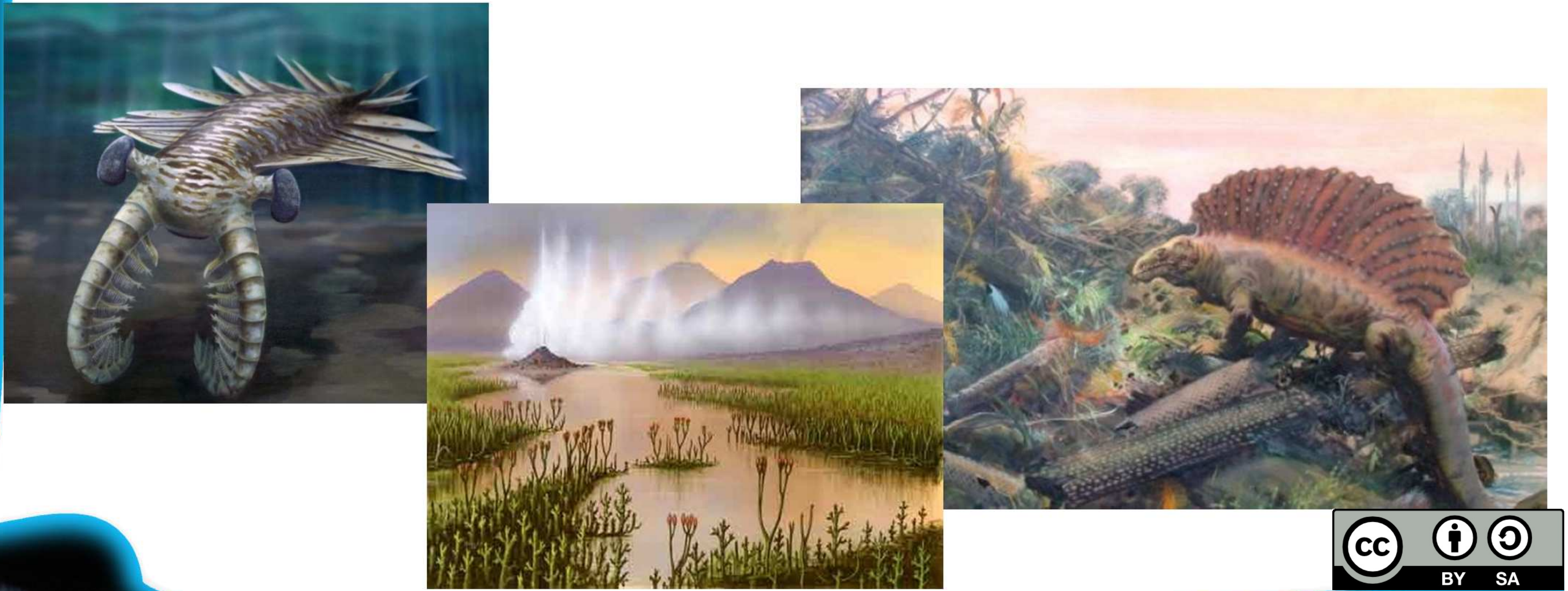
Eon	Era	Period	Epoch	Time [mil. years]	Organisms
Phanerozoic	Paleozoic	Cambrian		541 - 485	Cambrian explosion, genesis of trilobites
		Ordovician		485 - 443	Growth of invertebrates
		Silurian		443 - 419	First terrestrial plants
		Devonian		419 - 359	Genesis of amphibians (salamanders etc.)
		Carboniferous		359 - 299	Growth of insect, genesis of reptiles
		Permian		299 - 252	Growth of reptiles



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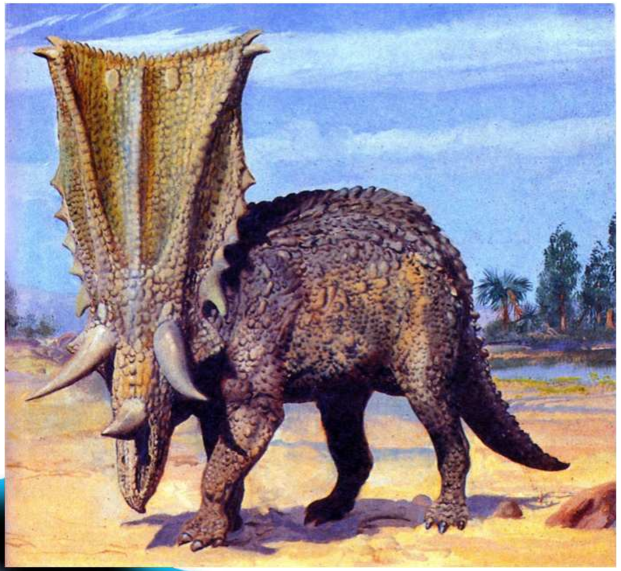
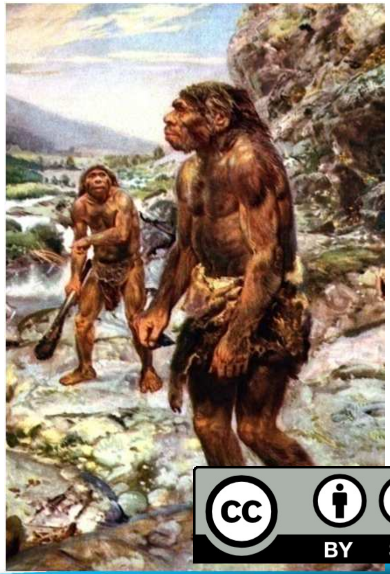
Eon	Era	Period	Epoch	Time [mil. years]		Organisms
Phanerozoic	Mesozoic	Triassic		252 -	201	Genesis of dinosaurs, oviparous mammals
		Jurassic		201 -	145	Genesis of birds and marsupial mammals
		Cretaceous		145 -	66	Genesis of placentals, extinction of dinosaurs
	Kenozoic	Paleogene	Paleocene	66,0 -	56,0	
			Eocene	56,0 -	33,9	
			Oligocene	33,9 -	23,0	
		Neogene	Miocene	23,0 -	5,33	
			Pliocene	5,33 -	2,59	
		Quaternary	Pleistocene	2,59 -	0,0117	Evolution of modern human
			Holocene	0,0117 -	0	





Chronostratigraphic history of Earth

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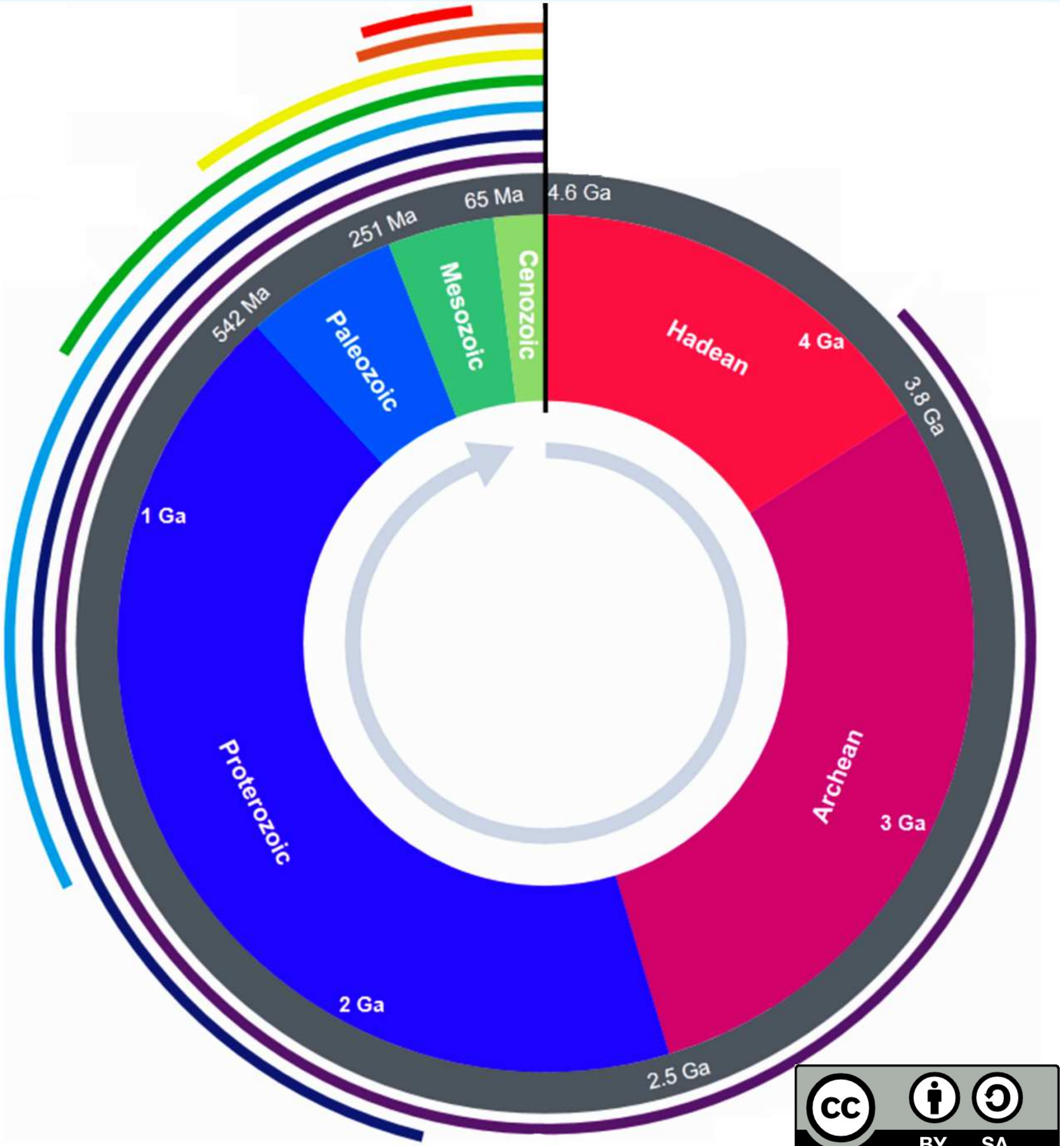
Legend (in million years):

⬛	2	first hominids
🟧		mammals
🟥	230–65	dinosaurs
🟨		land plants
🟩		animals
🟦		multicellular life
🟦		eukaryotes
🟪		prokaryotes
	ca. 2300	first oxygen rich atmosphere
	ca. 3500	photosynthesis starts
	ca 4000	first life
	4527	Moon created



Evolution of Earth's atmosphere

- Primary atmosphere
  - Formation before 4.0 – 3.8 billion years
  - Absence of heavier molecules – atmosphere mostly consisting of H_2 + He
  - Big leakage to the outer space

- Secondary atmosphere

  - Formed due to volcanic processes and from the planet surface during cooling of the Earth's Crust; it initially contained: CO_2, CH_4, higher C_xH_y, NH_3, H_2O and small quantity of N_2;

  - Maximum greenhouse effect reached ca. 800 mil. years after creation of Earth (t = ca. 44 °C, p = 1.4 times higher than present);

  - Subsequent condensation of water leading to first seas and rivers;

  - In the consequence of absorption of CO_2 in H_2O and following reactions in solution formation of carbonate sediments and parallel decrease of CO_2 concentration in atmosphere → suppression of greenhouse effect.

Evolution of Earth’s atmosphere

- First organisms
  - Heterotroph organisms, getting energy by the anaerobic process:
    $NH_4^+ + 2H_2O \rightarrow NO_2^- + 8H^+ + 6e^-$
    $NO_2^- + H_2O \rightarrow NO_3^- + 2H^+ + 2e^-$
  - Alternative mechanism of cleavage of the simple organic molecules:

    $CH_3COOH \rightarrow CH_4 + CO_2$
  - Genesis of cyanobacterias - the first life form capable to synthetize saccharides via photosynthesis (i.e. photoautotroph):

    $CO_2 + H_2O + h\nu \rightarrow [CH_2O]n + O_2$
  - Majority of oxygen bonded by reaction with bivalent iron in ancient ocean (big initial content of Fe^{2+})

    $4Fe^{2+} + O_2 + 4H_2O \rightarrow 2\,Fe_2O_3 + 8H^+$

    production of $Fe(OH)_3 + Fe_2O_3$

Evolution of Earth’s atmosphere

- First organisms
  - Another part of oxygen (after consuming Fe^{2+} ions) was bonded due to reaction with pyrite

    $$FeS_2 + 15/4\ O_2 + 7/2\ H_2O \rightarrow Fe(OH)_3 + 2H_2SO_4$$
  - 2,5 billion years after the formation of Earth Oxygen, produced by photosynthesis, removed methane, ammonia and higher hydrocarbons from the atmosphere:

    $$2CH_4 + 4O_2 \rightarrow 2CO_2 + 4H_2O$$

    $$4NH_3 + 3O_2 \rightarrow 2N_2 + 6H_2O$$
  - Above mentioned processes further reduced greenhouse effect ⇒ 2 billion years ago low temperature period began (temperature 6 °C, pressure 0.6 of current value), then gradual stabilization ca. 400 million years ago.
  - In geological history Oxygen concentration fluctuated.

Evolution of Earth’s atmosphere

- Content of O_2 in atmosphere
  - O_2 concentration probably has not been constant since Paleozoic till present.
  - There is not conformity among scientists upon the concrete values.
  - Oxygen concentrations obtained by measurement of ratio of C isotopes in the samples taken from drillings in deep sea rocks and subsequent calculation using bio-geochemical models

    (Source: Falkowski, P.; Science 309: 2202-2204 (2007));
  - Fluctuation as a result of various factors:

    changes in photosynthesis intensity and changes in Sun activity

    course of erosion of rocks and minerals

    movement of continents (e.g. Break up of Pangea resulting in flat seas with huge concentration of photosynthesizing organisms, algae)

    putrefaction in large swamps during declination of dry lands

Evolution of Earth’s atmosphere

- Content of O_2 in atmosphere (Source: Falkowski, P.; Science 309: 2202-2204 (2007));
  - Acquired values:

300 – 350 million years ago	35 %
205 million years ago	10 %
55 million years ago	23 %

  - Possible consequences:

    Influencing of biotopes (decrease of Oxygen content below 13 – 16 % suppression of spontaneous growth of forest fires)

    Influencing of evolution

    genesis of large forms of terrestrial arthropods

    transition of primitive amphibians and amphibious fish to dry land

    possibility of growth of the big mammals (indricoth
    mastodon etc.) due to higher O_2 concentration

Evolution of Earth’s atmosphere

- Oxygen content (Source: Falkowski, P.; Science 309: 2202-2204 (2007));
  - Example – gigantic insect: insect generally don’t have lungs, but less efficient tracheas ⇒ functional only in small bodies (large species may live only in higher concentration of Oxygen)

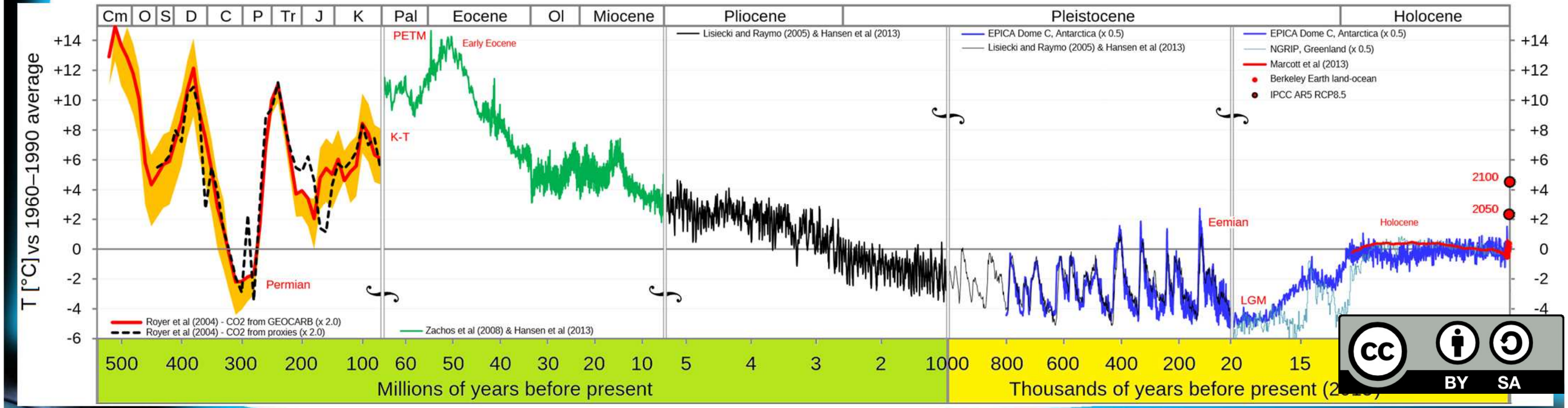
Arachnid: Megarachne servinei (50 cm)

Dragonfly: Meganeura 75 cm)

Arthropleura (200 cm) – the biggest millipede ever

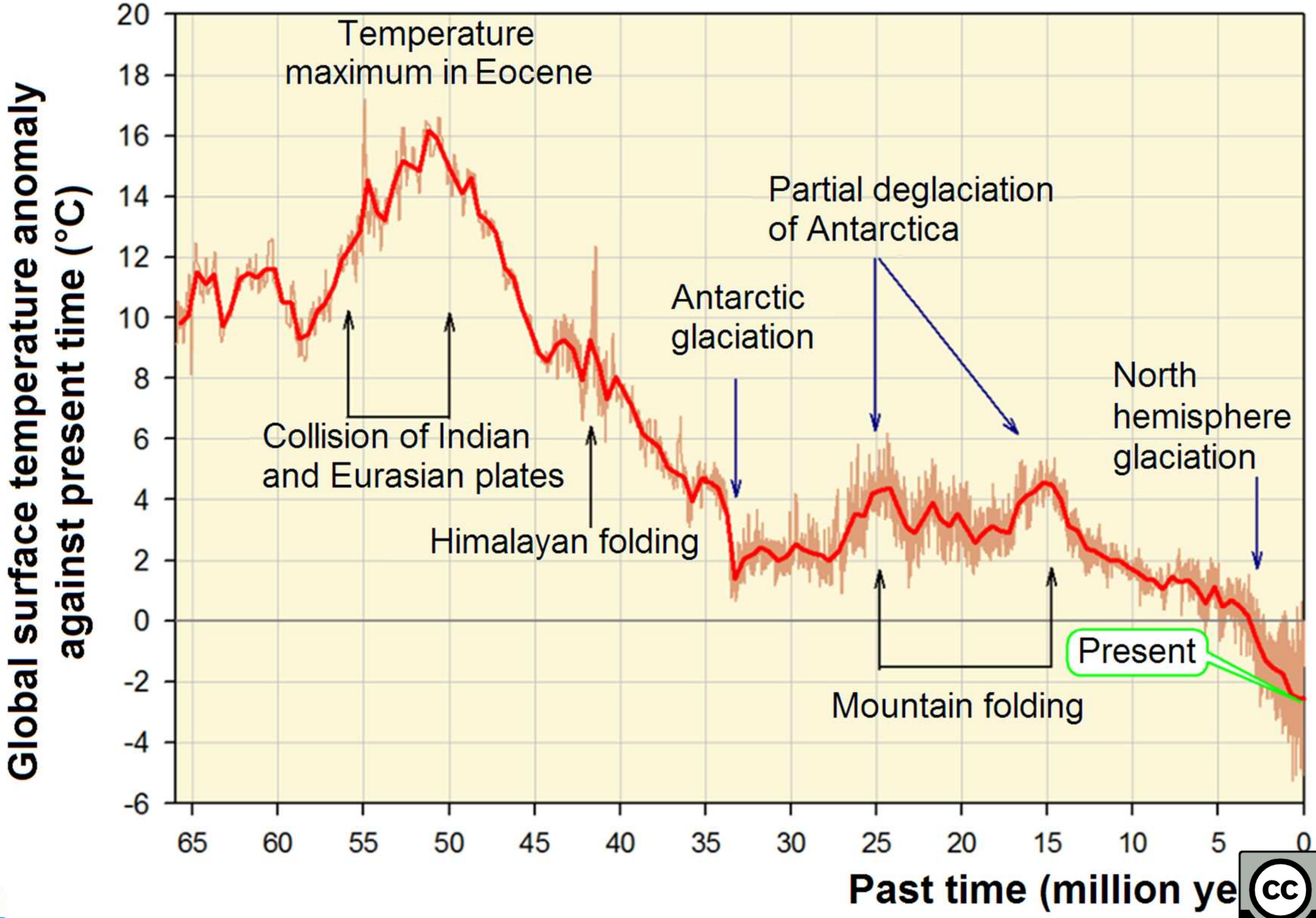
Evolution of global temperatures

- Changes of global average temperatures between Cambrian and present (Source: Fergus, G.; Royer et al (2004), Zachos et al (2008), Hansen et al (2013))
- 30 years average between 1960 and 1990 taken as zero line;
- Temperatures till 0,8 mil. years ago calculated using EPICA model EPICA (European Project for Ice Coring in Antarctica) –core drilling has proceeded in the Dome C area in East Antarctica since 1996; projects realised on the iceberg with 3270 m thickness;
- EPICA data summarizes calculated temperatures and measured concentrations of atmospheric CO_2 a CH_4 (back to -0.65 mil. years)
- Due to EPICA climatological data known for 8 glacials (ice ages).



Evolution of global temperatures

- Changes of global temperatures in range paleocene - present (Source: Open Science Conference of the World Climate Research Program, 2011, Denver CO, USA)



Factors allowing build up the IS

- 1. Public demand of national and international authorities for collecting and sharing of environmental data
- 2. Availability of methods for environmental analysis (automated instrumental analysis)
- 3. Availability of electronics for build up and storage of databases = computers
- 4. Availability of systems for sharing of created database = network

Public demand – 1st condition

- Acceptation of necessary legislation, based on political consensus, adoption of international agreements and so on.
- Example – legal background for stations of imission monitoring system:

Nationwide system of Automatic Imission Monitoring (AIM) and Manual Imission Monitoring (MIM);

Budget (in CZ) ensured by Regulation of Government No.: 596/2006 of the Legal Code, Annex No.: 4 (allowable level of public support);

Operation of IM is supervised, according to the law No.: 201/2012 (on the air protection), by Ministry of the Environment and it is technically operated by Czech Hydrometeorological Institute (CHMI).

Building up the AIM stations done by Regulation No.: 330/2012, on the assessment and evaluation of the level of pollution, scale of public information about level of pollution and during smog situations

System AIM launched in Prague in 1986 and in nationwide since 1992.

Analytics– 2nd condition for IS

- Example – AIM stations in Prague
- 206 stationary stations nationwide 206 (126 CHMI, ca. 39 Public Health Institutes, the rest other organisations, e.g. Energetic Corporation CEZ)

Prague city:

15 stations AIM

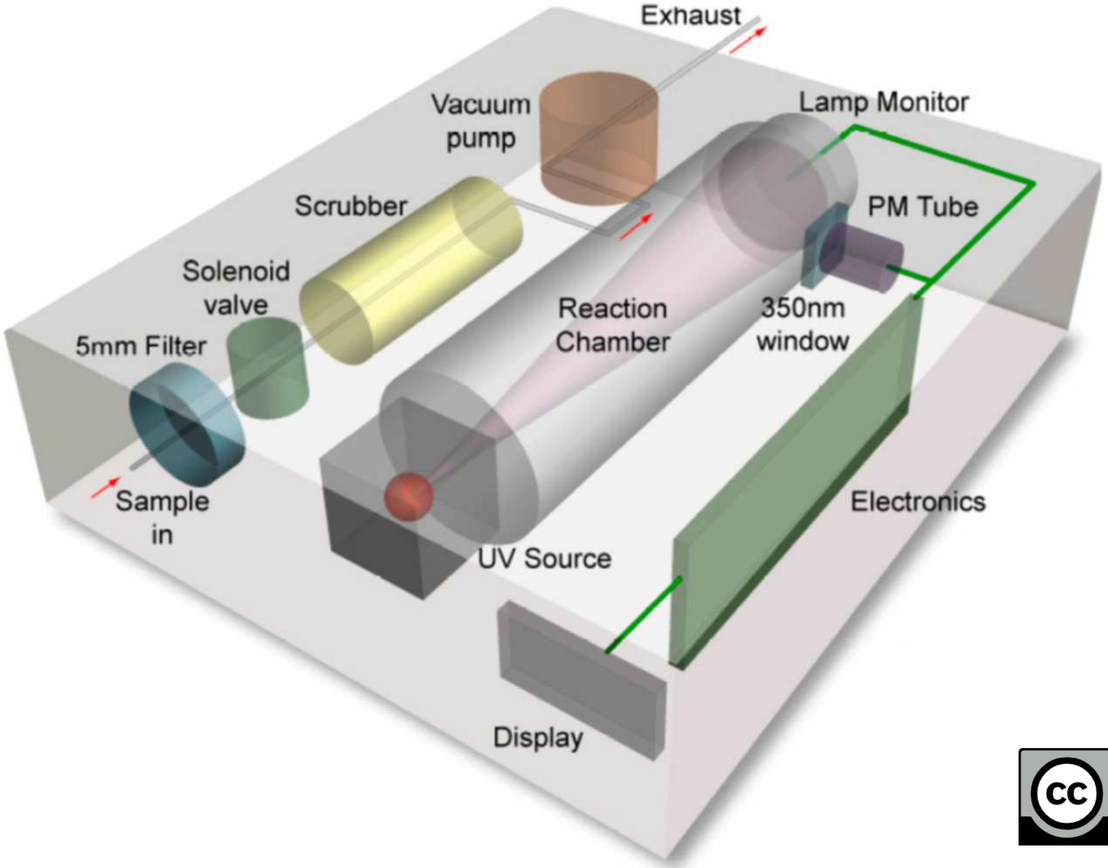
Analytics– 2nd condition for IS

- Example – AIM stations
- 206 stationary stations nationwide 206 (126 CHMI, ca. 39 Public Health Institutes, the rest other organizations, e.g. Energetic Corporation CEZ);
- Prague city: 15 stations AIM + 1 station countryside in Ondrejov
- Standard on-line measurement of: SO_2, NO_x, PM_{10} (Particulate Matter fraction < 10 µm), furthermore following substances measured at selected stations: CO, O_3, BTX fraction (benzene, toluene, ethylbenzene, xylenes)
- Applied on-line methods:

– SO_2	ultra violet fluorescence spectrometry
– NO_x ($NO + NO_2$)	chemiluminiscence spectrometry
– PM_{10}	radiometric method
– CO	IR spectrophotometry
– BTX fraction	gas chromatography

Analytics– 2nd condition for IS

- Example – AIM station, method overview (examples only)
- SO_2 Molecules absorb UV irradiation with wavelength in the range of 200 – 240 nm, which makes the atoms excited. During return to the energetic base level the particles emitt the UV irradiation with another wavelength. Its intensity corresponds to the SO_2 concentration and is measured in the right angle to the trajectory.



Analytics– 2nd condition for IS

- Example – AIM station, method overview (examples only)
- NO_x ($NO + NO_2$) chemiluminiscence method

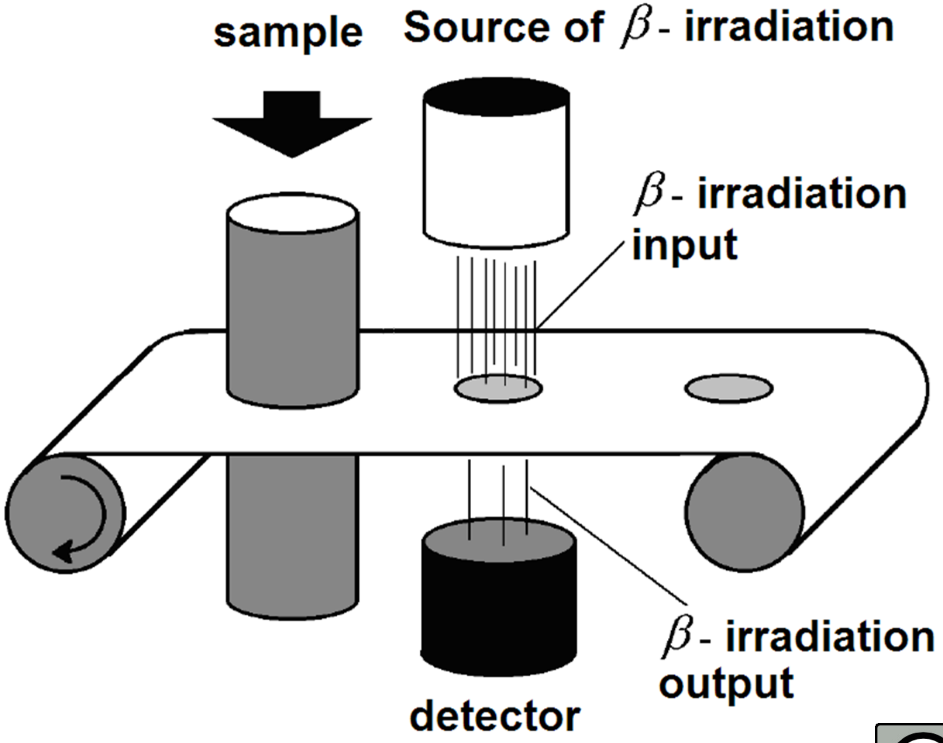
NO measurement: The device generates the ozone, which reacts with NO and oxides it to form NO_2. Ca. 10 % of the generated NO_2 is obtained in excited state. During its transition back to the initial state the particles produce the irradiation, which corresponds to the NO_2 concentration. This secondary irradiation is detected by the photodiode.

Measurement of NO_2: In the first step molecules of NO2 are reduced to NO, which is measured by the same mechanism as described above. Then the sum of NO_x is done by count $NO + NO_2$.

Analytics– 2nd condition for IS

- Example – AIM station, method overview (examples only)
- PM_{10} radiometric method
  Absorption of β-irradiation in the sample captured by the flat filtering material. Difference in absorbanies between exposed and unexposed filter corresponds to the concentration of particulate matter in the air.

Sampling head



Method principle

Analytics– 2nd condition for IS

- Example – AIM station (Source: Ekologické centrum Most)
- Conventions and possibilities of AIM distribution according to the purposes:
  - traffic AIM stations – installed within 50 m from the road with high traffic intensity (it should represent the line with maximum length);
  - industrial AIM stations – installed inside the industrial company premises or in the area with supposed impact by the smoke (due to predominant wind direction);
  - background AIM stations – installed in the localities with no direct influence of industry or traffic; it measures the tropospheric background in the cities, countryside or industrial districts:
    - representative radius for downtown and suburban AIM: more than 1 – 1,5 km,
    - representative radius fro countryside AIM: more than 5 – 60 km (usually 10 – 20 km).

Computers – 3rd condition for IS

- Development of computers

  (Source: http://www.fi.muni.cz/usr/pelikan/ARCHIT/TEXTY/HISTOR.HTML)

- Division into the generations, which each generation has characteristic configuration, performance and basic construction element:

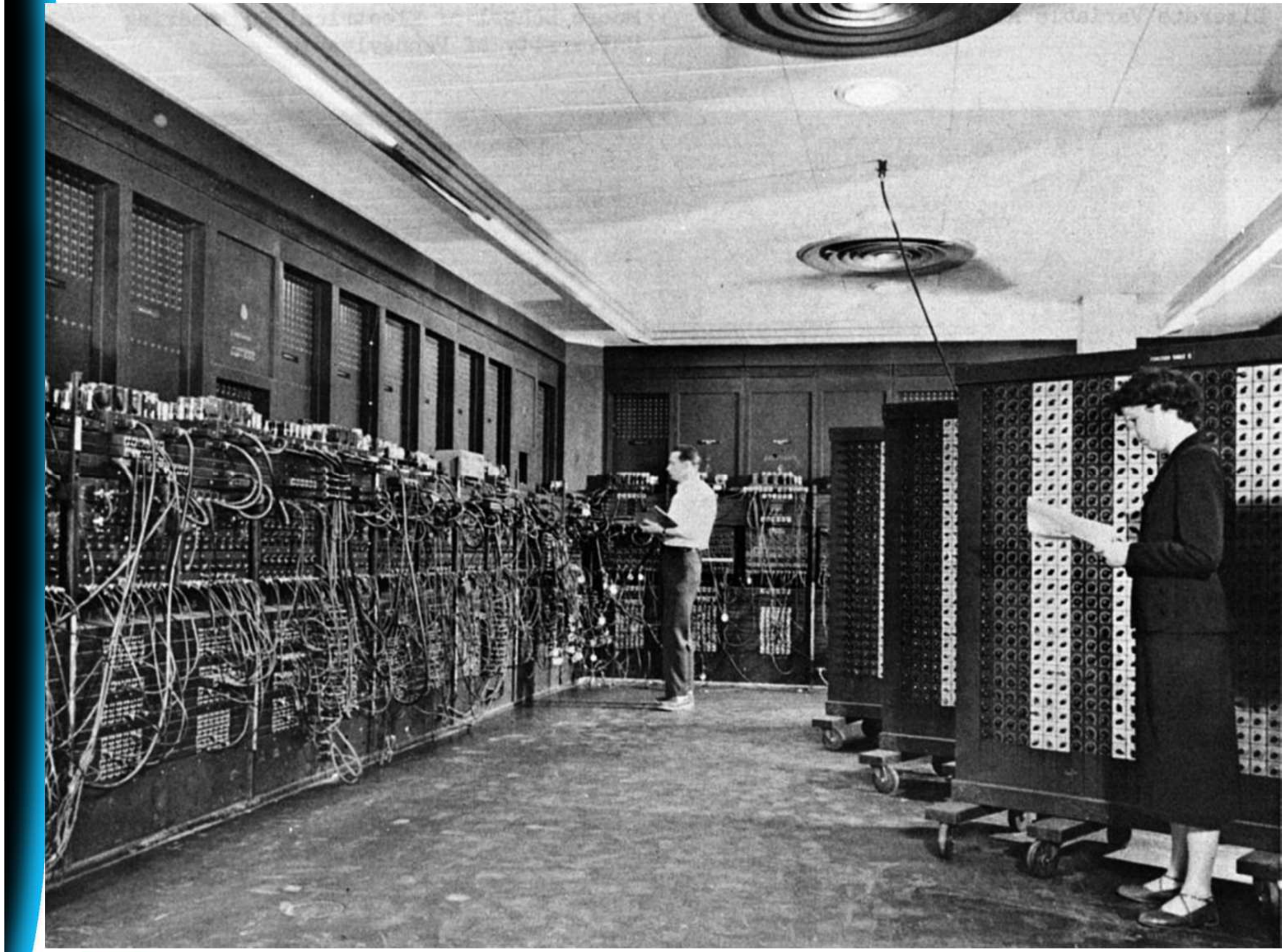
Generation	Beginning	Cases	Configuration	Operations
0.	1940	many	relays	units/s
1.	1945-52	tenths	tubes	100 – 1 000
2.	1958	< 10	transistors	10^3
3.	1964	< 5	circuits SSI, MSI	10^4
3½.	1972	1	circuits LSI	10^5
4.	1981	1	circuits VLSI	10^7 and more

4 th generation remains till present, only miniaturization and increase of performance.
5th generation = artificial intelligence; not available

Note . Circuits according to logical members: SSI = Small Scale Integration, MSI = Middle Scale Integration, LSI Large Scale Integration, VLSI Very Large Scale Integration

Computers – 3rd condition for IS

- Development of computers – ENIAC 1946 (1st generation) – military purposes



Computers – 3rd condition for IS

- Development of computers

IBM 7090 – 2nd generation

IBM 360 – 3rd gen

Computers – 3rd condition for IS

- Development of computers – beginning of 4th generation
- One of the very first laptops:

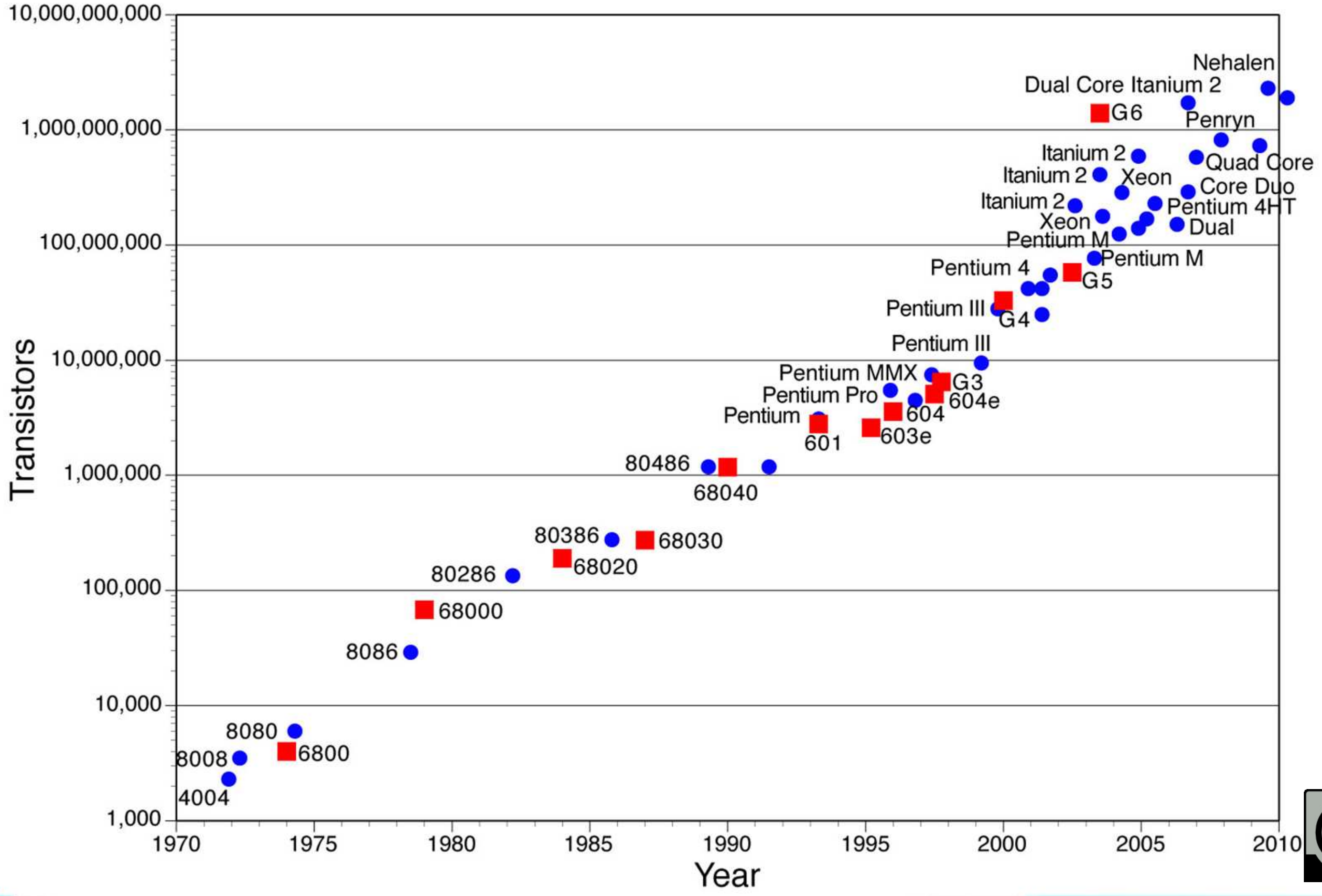
Osborne 1	
Introduced	1981
Contemporary price	1795 $
CPU frequency	4 MHz
RAM	64 kB
HDD	none

HP Spectre Pro x360 G1 ultrabook
1490 $ in the year 2014

CPU frequency (dual core)	2.7 GHz
RAM DDR3	4 GB
HDD SSD	128 GB

Computers – 3rd condition for IS

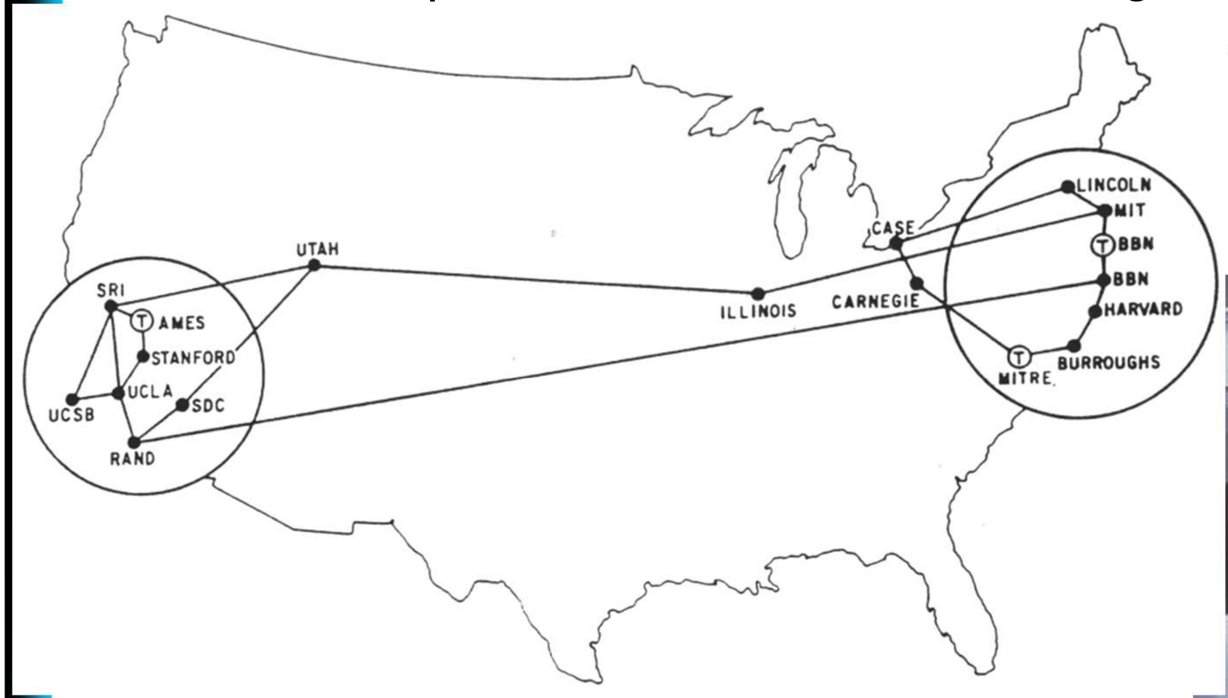
- Progress in computers – increase of performance, so called Moore’s law (from 1965: number of transistors in integrated circuit is doubled each 18 months). However actually the multiplication of transistors occurs each 2 years and validity of the law is estimated for next ca. 20 years.



Network – 4th condition for IS

- Development of networks
  - The oldest network using data packs and having decentralized conception and possibility to be accessed by various types of computers was enclosed for U.S. government computers:

ARPANET
solution published in1964
commissioned in 1969



State of ARPANET in 1971

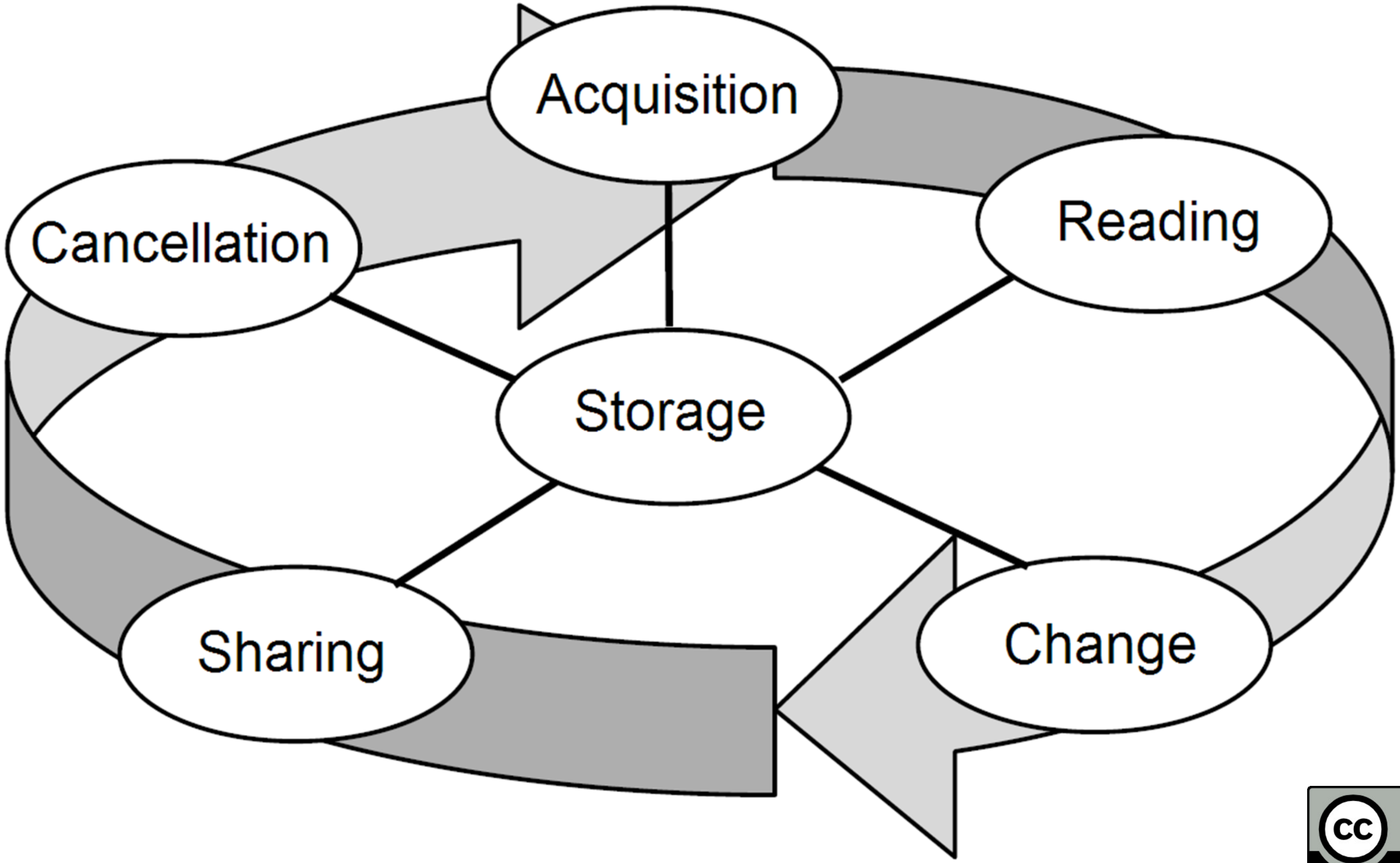
Network terminal
(end of sixties)

Network – 4th condition for IS

- Development of network, milestones
  - 1969 ARPANET – Note: stopped in 1990
  - 1971 introduced email
  - 1972 introduced Telnet – terminal program, which allows remote working on the selected servers
  - 1973 widely used FTP – File Transfer Protocol (first version published in 1971)
  - 1977 introduced mailing list
  - 1979 Usenet, uucp – fundamentals of chat groups, based on architecture Unix-To-Unix Copy
  - 1982 TCP/IP expansion – Transmission Control Protocol/Internet Protocol, primary protocols for internet
  - 1984 DNS – Domain Name System
  - 1986 NSFNET – National Science Foundation Network, fundaments of internet between 1986–1995
  - 1991 WWW, Gopher – Gopher service had similar purpose as www, (later overcame commercially by www)
  - 1992 Veronica – search engine for Gopher servers .

Life cycle of information

- Level of permissions for working with database according to authorization: the basic user should not have full access ⇒ he downloads available data only through the online application – better for data safety (Source: Hřebíček J.: Environmentální informační systémy)



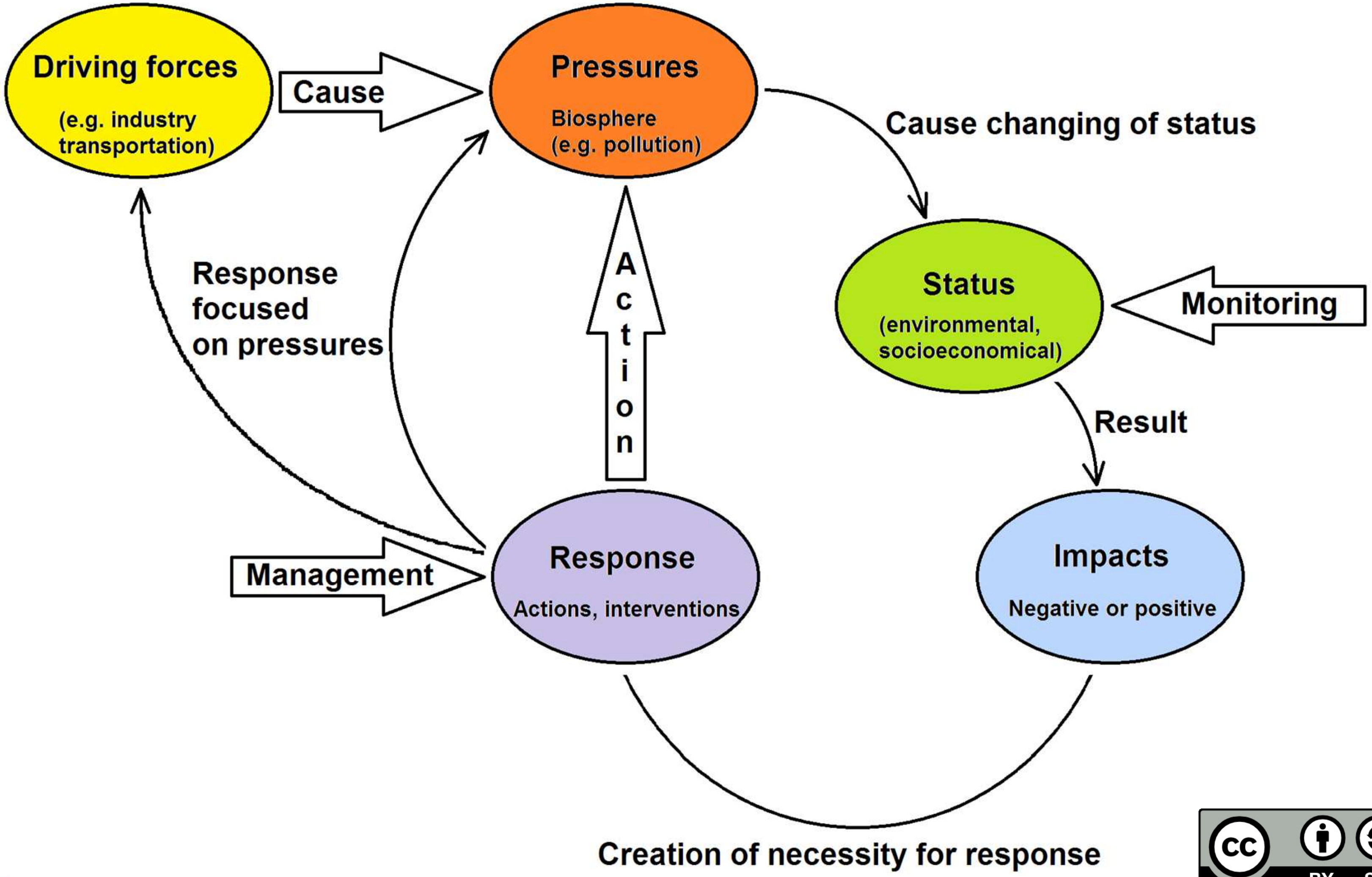
Purpose of environmental IS

- European model for influencing the environmental pollution by the state authority (Source: Hřebíček J.: Environmentální informační systémy)
- In the EU model DPSIR was proposed (Driving force-Pressure-State-Impact-Response)
- Model DPSIR is actually applied for handling of the environmental data by European Environment Agency – EEA.
- Model DPSIR depicts relationships among those factors, which influence the environment, and the tools available for their regulation.

Purpose of environmental IS

- Model DPSIR (Driving force-Pressure-State-Impact-Response)

  (Source: Hřebíček J.: Environmentální informační systémy)



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European Structural and Investing Funds
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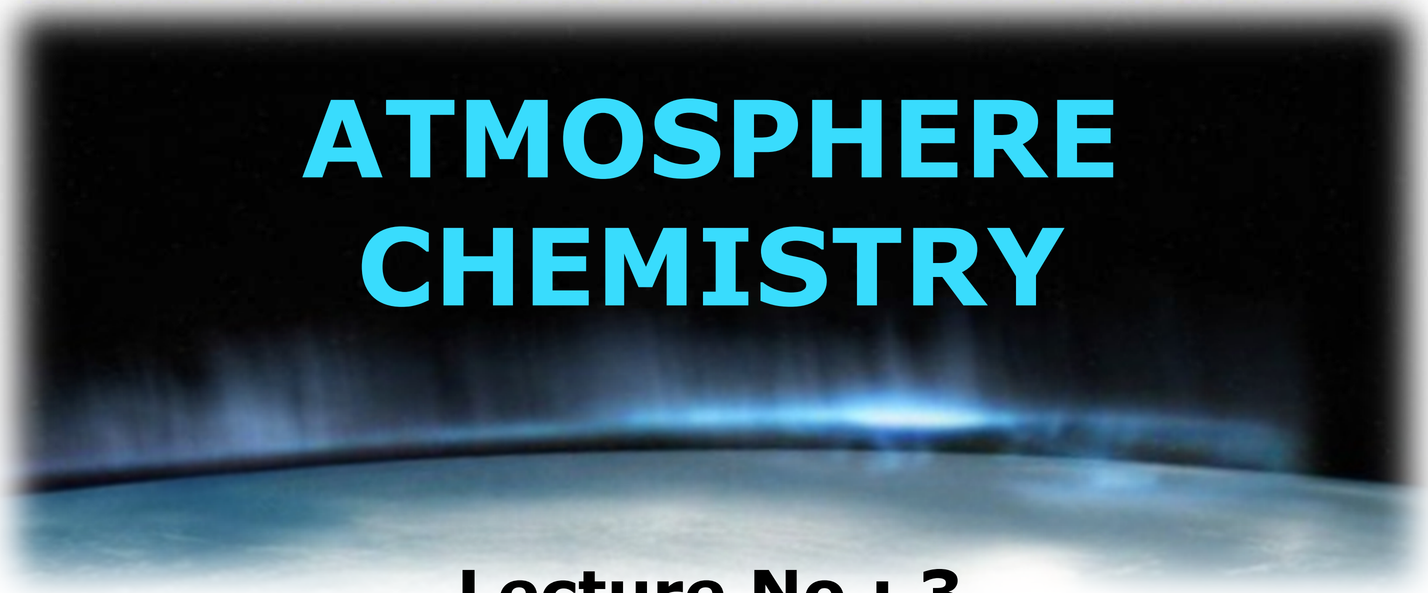
MINISTRY OF EDUCATION,
YOUTH AND SPORTS



ATMOSPHERE CHEMISTRY

Lecture No.: 3

Organisation of study

- Lecturer: Marek Staf, MSc., Ph.D., phone: +420 220 444 458
  e-mail: marek.staf@vscht.cz,
  web: http://web.vscht.cz/~stafm/
  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 - oral form
- Note:

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Uveřejněné materiály jsou určeny studentům Vysoké školy chemicko-technologické v Praze jako studijní materiál. Některá textová i obrazová data v nich obsažená jsou převzata z veřejných zdrojů. V případě nedostatečných citací nebylo cílem autora/ů záměrně poškodit event. autora/y původního díla. S eventuálními výhradami se prosím obracejte na autora/y konkrétního výukového materiálu, aby bylo možné zjednat nápravu.

Scope of lecture 3

Examples of the most important environmental information systems

- History of information systems in the Czech Republic
- Examples of basic IS in Europe
- List of fundamental IS in the Czech Republic
- System of data collection for IS
- Example of user interface of IRZ
- Example of special database – sources of GHG within EU ETS

Examples of IS and databases

- Some of the IS are only informative, other serves as platform for restrictions, other for dragging the public into the decision process etc.
- Some of the IS have public access, some have limited access only for authorized persons and organizations;
- Some of the IS are local, other are international.
- Examples of Environmental Information Systems (EIS):
    - EIS provide processing, searching and presentation of environmental data and information;
    - Example of national system: Unitary Information System of Environment (JISŽP) in the Czech republic;
    - Examples of international systems: Shared Environmental Information System – SEIS);
    - EnviroWindows;
    - European Environment Information and Observation Net Eionet.

Examples of IS and databases

- Globally active Environmental information systems (EIS):
  - Global Monitoring for Environment and Security – GMES,
  - Global Earth Observation System of Systems – GEOSS.
    - It covers particular national as well as international observation systems
    - National observation systems are operated by countries, which are the members of Group on Earth Observations – GEO.

Examples of IS and databases

- eEnvironment (in the EU)
  - White book of eEnvironment introduced in plenary session of CAHDE (Council of Europe activities in the field of e-democracy) in 2007.
  - Legal fundament for eEnvironment is so called Aarhus agreement (according to regulation nr. 2003/4/ES, on access of public to information about environment etc.)
  - Basic principles of eEnvironment:

    Principle of control = legal security of citizens requires access to resolutions of the state authorities (access for the people allows them notifying about faults).

    Principle of participation = Right to have the access to the information enhances transparency and allows public to participate on the decisions of the state authorities.

Examples of IS and databases

- eEnvironment (in the EU)

- Basic principles of eEnvironment:

  Principle of education: Knowledge about environment leads to enhancement of the public participation on adopting the measures for the environment protection.

  Principle of prevention: Right to publish all environmental information should discourage the potential polluters.

  Principle of standardization: International agreements and European regulations and activities to approach to environmental information give wide rules regarding environment protection and data sharing (e.g. systems INSPIRE, GMES, SEIS)

- eEnvironment is a part of extensive project of electronic democracy (eDemocracy).

Historical situation in Czechoslovakia

- **After WW2, 1950s**
  Intensive transformation from light and consumer industry to heavy industry, metallurgy, brown and black coal mining and so on;
  Start of massive building up the brown coal-fired power plants;
  Monitoring of imission strain (stress) only in few isolated points by hygienic service organization;
  At the end of 1950s involvement of Hydrometeorological Institute (particularly monitoring of scattering of pollutants);

- **1960s**
  Hike increase of imission strain due to growth of brown coal power plants;
  First enforced sawing down the forests damaged by acid rains.

1966	Foundation of Tušimice observatory for air monitoring;
1966	Law nr. 20/1966, on public health care incl. environment;
1967	Law nr. 35/1967, on measures against air pollution (so called chimney law); HMI entrusted by problematics of air protection
1967	Established Ministry of forest and water administration (incl. Management of air protection)

Information systems in Czech republic

- Historical situation in Czechoslovakia – 1950s – heavy industry

(coal miner & founder)

Information systems in Czech republic

- Historical situation in Czechoslovakia – 1960s

  1968 Laboratory of air protection established by HMI

- **1970s**
  Beginning of suppression of particulate matter emissions in the power plant blocks (2-stage precipitators);
  Significant damage of forests (especially spruces and pines) in the Northwest mountains by acidic deposition;
  Increase of rate of chronic respiratory diseases and allergies;
  1970 Laboratory of air protection completed with research of systems for air monitoring;
  1971 HMI commissioned internal computer information system; establishing of local Imission Information System – IIS;
  1978 Czechoslovakia assessed by the UN as third worst country in Europe as regards SO_2 imission strain (1st east Germany, 2nd Belgium);
  1979 Commissioning of nationwide information system Register of Emissions and Sources of Air Pollution (Czech abbre REZZO);

Information systems in Czech republic

- **1980s**
  Culmination of pollution level;
  Situation deteriorating due to contribution of brown coal power plants + long range transboundary transport of pollutants + pollution from local heating + growth of car traffic;
  Preparation of the first complex of regulation measures (precautions made based on prognosis of meteorological situation and data from Imission Monitoring)
  1988 Establishing of laboratory/observatory Košetice for air monitoring;

- **1990s**
  New Ministry of Environment established; CHMI transferred under competence of this ministry;
  Increasing of popular interest in air protection;
  Building up the AIM network in the nationwide scale;
  Continuous monitoring of PM_{10} and $PM_{2,5}$, tropospheric O_3 a VOCs.
  1992 Start up the Information System of Air Quality (Czech abbreviation ISKO; IIS incorporated into ISKO);

Information systems in Czech republic

- Actual situation in Czech republic – examples of systems:

- **JISŽP** Unified information system on environment

  Target: Preparation of one complex system, which covers water, air, waste management, sources of pollution and so on.

  Admin: Czech ecological institute

  Status: Currently under construction, actual co-existence of 37 various particular IS, managed by different institutions.

- **ISOP** Information system of nature protection

  Admin: Nature Protection Agency

  Purpose: Data about protected areas, natural biotopes, natural heritage and so on

- **ÚSOP** Central list of nature protection

  Purpose: Overview of reservations, national parks, protected areas and so on (some data additional to ISOP, some du

Information systems in Czech republic

- Present situation in Czech republic
- **HEIS** Hydroecological Information System

  Admin: T. G. Masaryk Water Research Institute

  Purpose: Composition of surface and underground water incl. wastewater;
- **ISKO** Information system of air quality

  Admin: responsible Ministry of environment, assigned CHMI;

  Purpose: common system containing sub-registers (e.g. REZZO)

  It includes results of assessment and evaluation of pollution.

  It includes also register of emissions and register of stationary sources of pollution.

Note: Ministry report on air and prediction for next 2 years published yearly;

The report includes also ratio PM_{10} a $PM_{2,5}$ against overall

Information systems in Czech republic

- **REZZO** Register of Emissions and Sources of Air Pollution

Admin: Ministry of environment, assigned CHMI

Purpose: part of ISKO, contains list of pollutants (excl. local heating), information about concentrations in air and composition of rains

Divided into sub-registers:

- **REZZO 1**– big stationary sources > 5 MW of heat performance and very serious technologies;
- **REZZO 2**– medium stationary sources 0,2 – 5 MW and serious technologies;
- **REZZO 3**– small stationary sources < 0,2 MW;
- **REZZO 4**– mobile sources of pollution;

Data about big and medium sources submitted by the polluters under supervision of Czech Inspection of Environment. Data about small sources received from municipal authorities;

Data about: PM, SO_2, NO_x, CO, C_xH_y.

Information systems in Czech republic

- **IRZ** Integrated Register of Pollution

Admin: Formerly Czech ecological institute (Agency of integrated prevention) ⇒ actually Czech Environmental Information Agency CENIA; supervised by EEA (European Environment Agency)

Purpose: in the future it will replace following registers: REZZO, HEIS and ISOH (Information system of waste management)

Data for the database obligatory submitted by the polluters, based on Integrated system of accomplishing of the report duties

Laws: Nr. 25/2008 on integrated register of environmental pollution and system of accomplishing of the report duties in the area of environmental pollution
updated by Nr. 77/2011 of the Legal Code

Above mentioned laws created on the basis of Directive 96/61/EC including (among other things) rules for IPPC

(Integrated Pollution Prevention and Control)

Information systems in Czech republic

- **IRZ** Integrated Register of Pollution

  Scope: totally 88 substances, which require obligatory reporting (inorganic and organic)

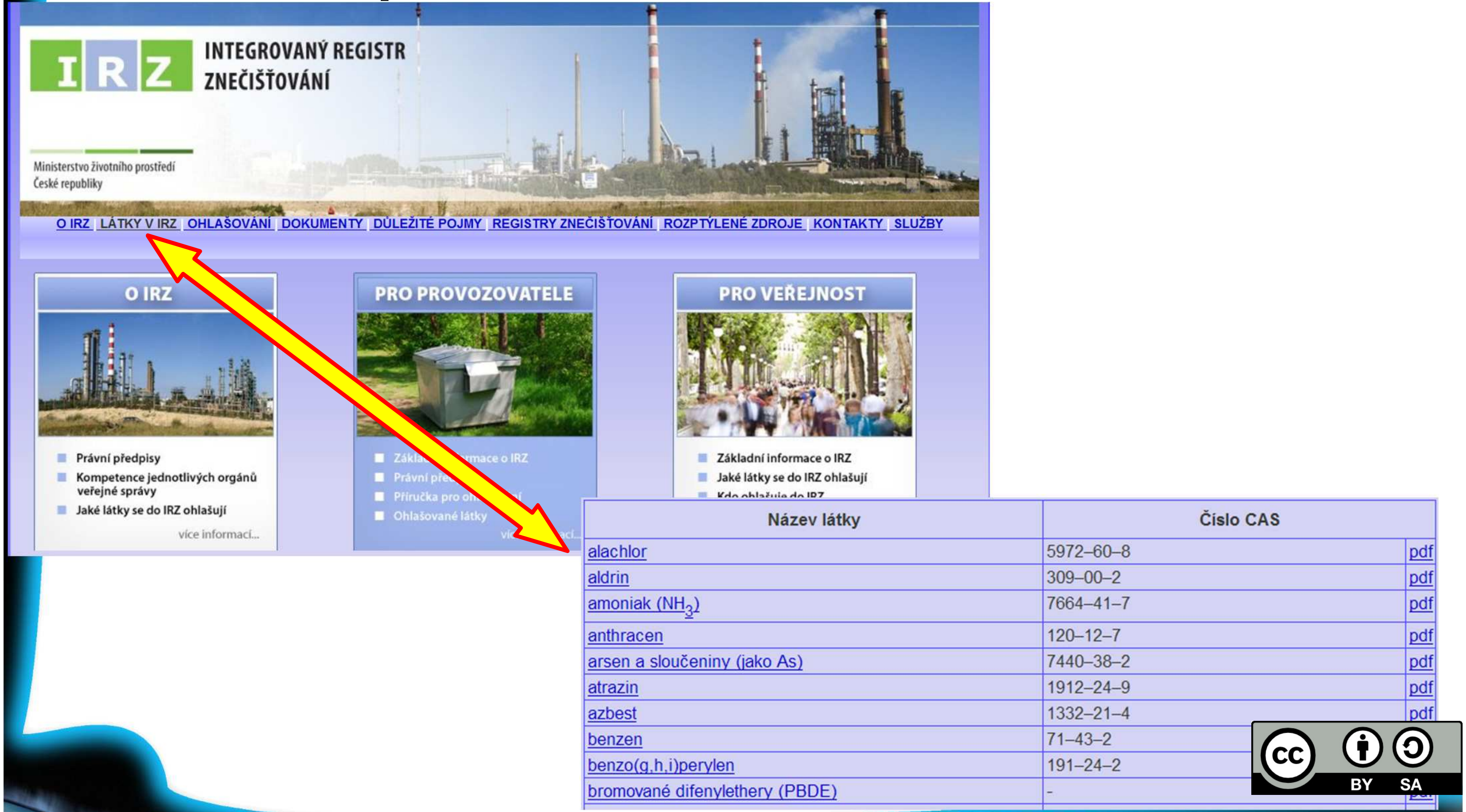
IRZ constructed on the basis of European Directive 96/61/EC, containing (besides all) IPPC and rules for other activities:

- European Pollutant Emission Register (EPER)
- Commission releases the outcomes in three-years intervals
- Register EPER is completed by PRTR (Pollutant Release and Transfer Register), concerning especially wastes
- Czech agency for Integrated Pollution Prevention and Control – (IPPC) incorporated into CENIA in 2002.

Information systems in Czech republic

- **IRZ** Integrated Register of Pollution – example of searching:

Initial page: **http://www.irz.cz**



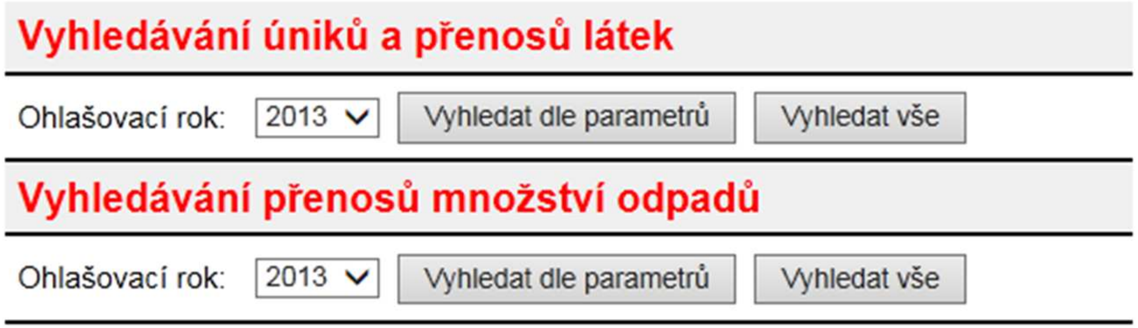
Název látky	Číslo CAS	
alachlor	5972–60–8	pdf
aldrin	309–00–2	pdf
amoniak (NH_3)	7664–41–7	pdf
anthracen	120–12–7	pdf
arsen a sloučeniny (jako As)	7440–38–2	pdf
atrazin	1912–24–9	pdf
azbest	1332–21–4	pdf
benzen	71–43–2	
benzo(g,h,i)perylen	191–24–2	
bromované difenylethery (PBDE)	-	

Information systems in Czech republic

- **IRZ** Integrated Register of Pollution – example of searching:

http://www.irz.cz

http://portal.cenia.cz/irz/



Vyhledávání úniků a přenosů látek

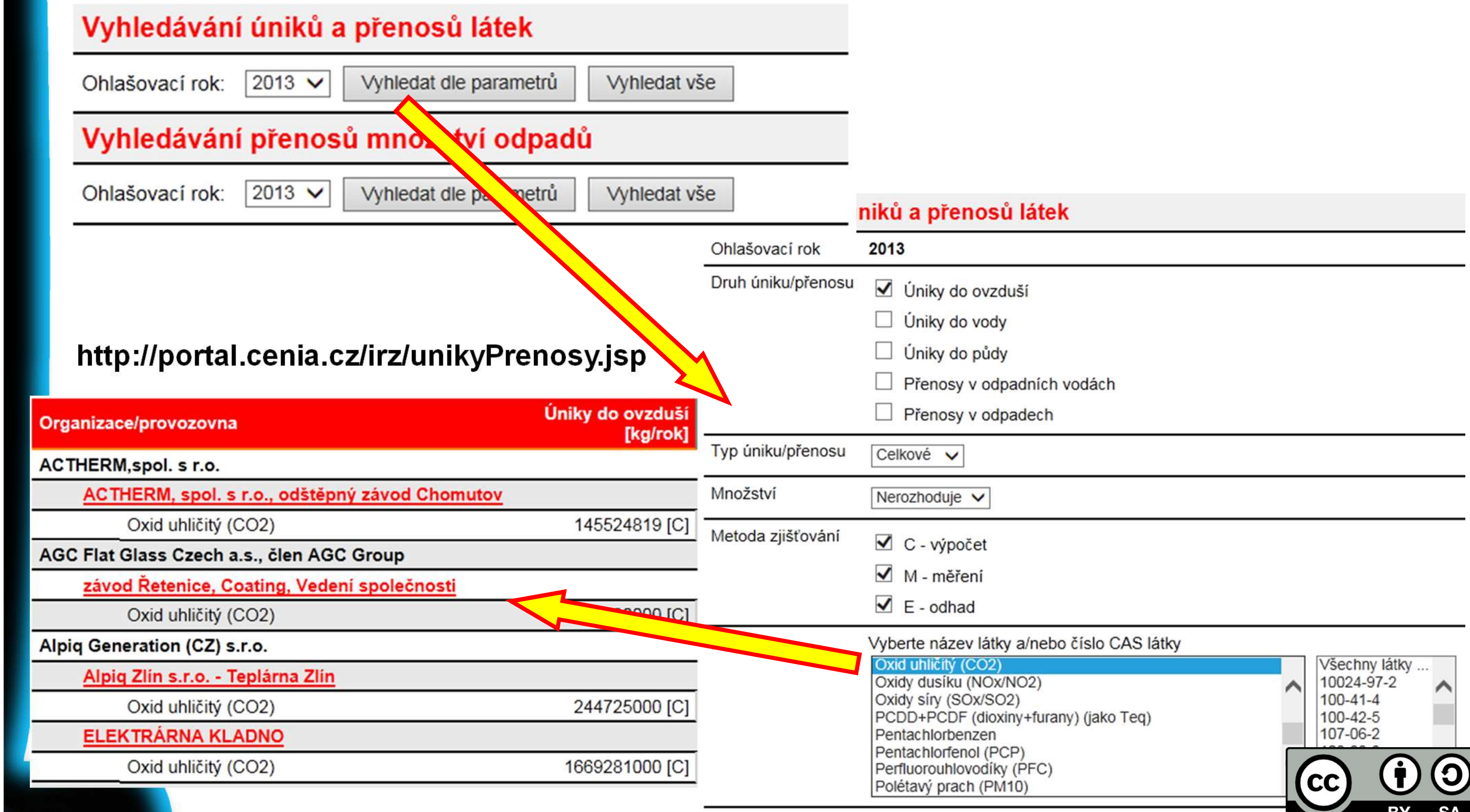
Ohlašovací rok: 2013

Vyhledávání přenosů množství odpadů

Ohlašovací rok: 2013

Information systems in Czech republic

- **IRZ** Integrated Register of Pollution – example of searching: http://portal.cenia.cz/irz/



Vyhledávání úniků a přenosů látek

Ohlašovací rok: 2013

Vyhledávání přenosů množství odpadů

Ohlašovací rok: 2013

http://portal.cenia.cz/irz/unikyPrenosy.jsp

niků a přenosů látek

Ohlašovací rok: 2013

Druh úniku/přenosu:
☑ Úniky do ovzduší
☐ Úniky do vody
☐ Úniky do půdy
☐ Přenosy v odpadních vodách
☐ Přenosy v odpadech

Typ úniku/přenosu: Celkové

Množství: Nerozhoduje

Metoda zjišťování:
☑ C - výpočet
☑ M - měření
☑ E - odhad

Vyberte název látky a/nebo číslo CAS látky

Organizace/provozovna	Úniky do ovzduší [kg/rok]
ACTHERM,spol. s r.o.	
ACTHERM, spol. s r.o., odštěpný závod Chomutov	
Oxid uhličitý (CO2)	145524819 [C]
AGC Flat Glass Czech a.s., člen AGC Group	
závod Řetenice, Coating, Vedení společnosti	
Oxid uhličitý (CO2)	[illegible]0000 [C]
Alpiq Generation (CZ) s.r.o.	
Alpiq Zlín s.r.o. - Teplárna Zlín	
Oxid uhličitý (CO2)	244725000 [C]
ELEKTRÁRNA KLADNO	
Oxid uhličitý (CO2)	1669281000 [C]

Database of GHG sources EU ETS

- Information sources: mandatory reports about emissions from polluters
- Purpose: preparation of background for trading with emissions allowances
- Principle: ETS = Emission Trading System

  System works on the principle „cap and trade“, where the limit values are decreased step by step.
- ETS targets: In 2020 the emissions within the ETS should be reduced by 21 % compared to the year 2005 (benchmark)

  Beginning 2013 yearly decrease of emissions ⇒ it means allocated allowances from stationary sources by 1,74 %

  Commission proposes reduction by 43 % in the year 2030 (compared to 2005).

Database of GHG sources EU ETS

- Trade process:

  Polluters obtain or purchase emission allowances.

  The allowances may be sold to another subject.

  Polluters may also purchase international credits of the projects aimed at emission sequestration.

  At the end of calendar year the company must write of the exact number of allowances, which covers its own emissions.

- Legislation:

  Introduced in 2005 by Directive 2003/87/EC, and for Czech rep. transposed by:

  Law Nr. 695/2004 on conditions for trading with emission allowances for greenhouse gases

  updated by law Nr. 212/2006 and Nr. 315/2008.

  Instructions for monitoring and declaration of GHGs emissions (Greenhouse Gases) done by Commission regulation 2007/589/ES

Database of GHG sources EU ETS

- Data acquisition: regular reporting from polluters
- Scope: Only big pollution source involved into the EU ETS database.
- ETS includes: CO_2 from production of heat and electric energy, from energetically important industrial productions (refineries, production of steel, iron, aluminium and other metals, cement, ceramics, treatment of cellulose, acids and other chemicals) as well as CO_2 from commercial aeronautics

  N_2O from production of nitric acid, adipic acid, glyoxal (ethanedial) and glyoxalic acid (oxoacetic acid).

  perfluorinated hydrocarbons (PFCs) aluminum production
- EU ETS is currently the biggest carbon market in the world
- Involved more than 11000 facilities and power plants within 31 countries worldwide + air transportation (since 2013); it covers ca. 45% overall GHGs emissions in the EU.

Database of GHG sources EU ETS

- Data verification - Correctness of values verified in following levels:
  - Big company has its own ecologist, responsible for reporting in ETS;
  - Ecologist is checked by independent verificator, having appropriate certificate (e.g. from Czech Accreditation Institute);
  - Company has a monitoring plan elaborated – verificator controls conformity of real data wit this plan; audit once per 3 years (checking if the emission list is complete and data are correct);
  - Verificator assesses validity of training of authorized personnel;
  - Verificator checks conformity of the relevant parameters (consumption of natural gas, coal, invoicing data about fuels etc.);
  - Activity of verificator is secondary checked by so called expert, assigned by the accreditation institute.

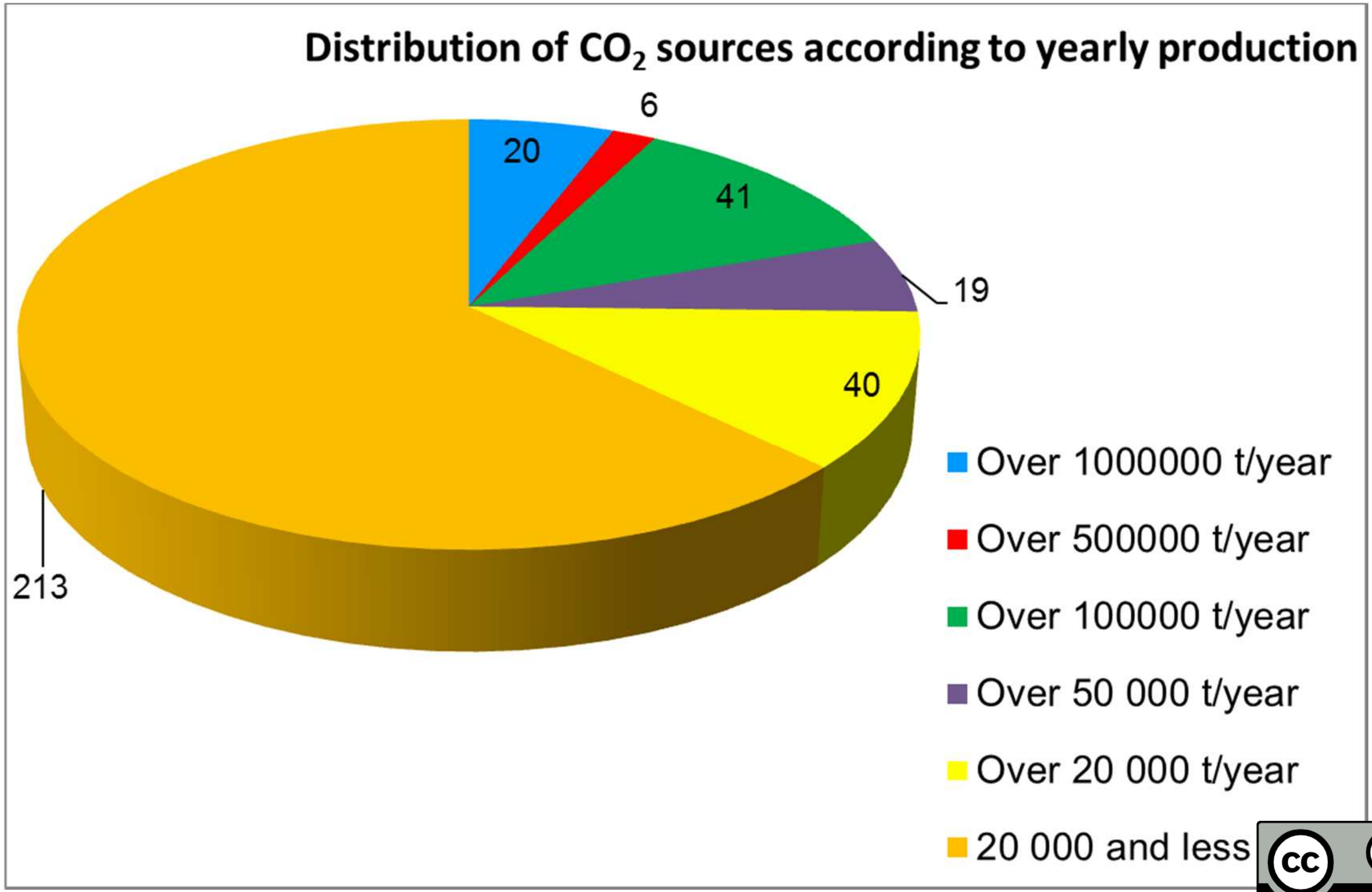
Data example: Year 2014 Czech republic – 339 polluters identified

Overall reported weight of emitted CO_2

66,435,610 metric t/year

Database of GHG sources EU ETS

- User data editing: E.g. outcomes for various projects, aimed at sequestration of GHG emissions; example of aggregated data = divided into groups according to criteria (Czech republic 2014):



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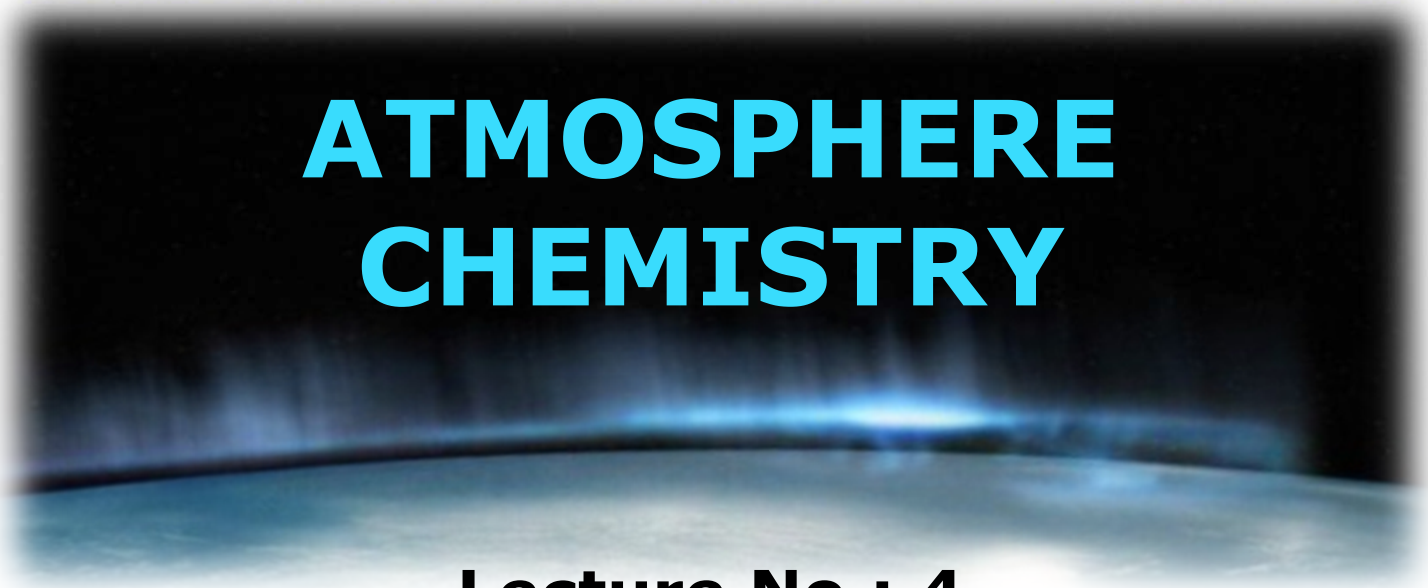

ATMOSPHERE CHEMISTRY

Lecture No.: 4

Organisation of study

- Lecturer: Marek Staf, MSc., Ph.D., phone: +420 220 444 458

  e-mail: marek.staf@vscht.cz,

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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 - oral form
- Note:

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Uveřejněné materiály jsou určeny studentům Vysoké školy chemicko-technologické v Praze jako studijní materiál. Některá textová i obrazová data v nich obsažená jsou převzata z veřejných zdrojů. V případě nedostatečných citací nebylo cílem autora/ů záměrně poškodit event. autora/y původního díla. S eventuálními výhradami se prosím obracejte na autora/y konkrétního výukového materiálu, aby bylo možné zjednat nápravu.

Scope of lecture 4

Physical rules in atmospheric processes

- Main forces contributing on movements of atmospheric masses
- Atmospheric circulation cells
- Tropospheric and stratospheric jet streams
- Wind speed and method of its subjective evaluation (wind scale)
- Local air flows – long range and short range winds
- Introduction to synoptic meteorology
- Preparation and evaluation of the synoptic maps
- Methods of data acquisition for weather forecasts
- Distribution of weather forecast according to time scale and available methods for their elaboration

Stratification of atmosphere (review)

Atmospheric layers and temperatures (by NASA and National Weather Service)

Exosphere 700 km - 10 000 km

Thermosphere 80 km - 700 km

Ionosphere 50 km - 1 000 km

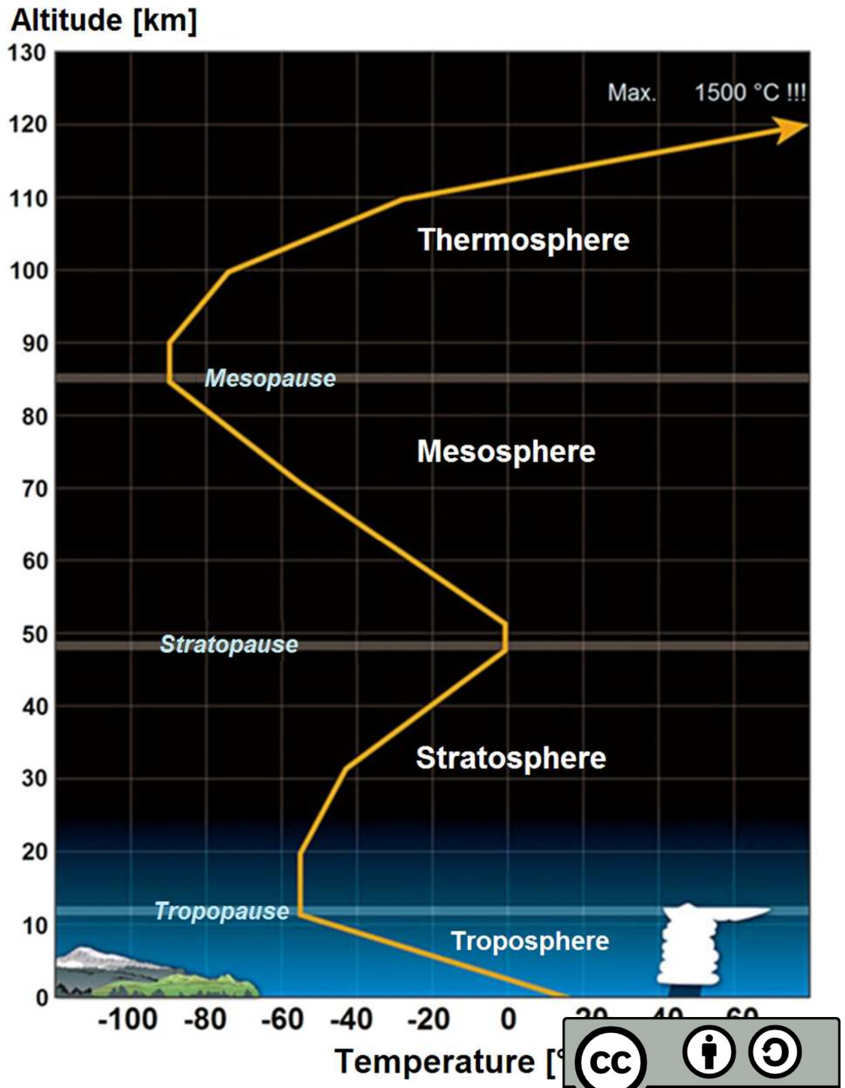
Mesosphere 50 km - 80 km

Stratosphere 12 km - 50 km

Ozonosphere 15 km - 35 km

Troposphere 0 km - 12 km

Surface of Earth

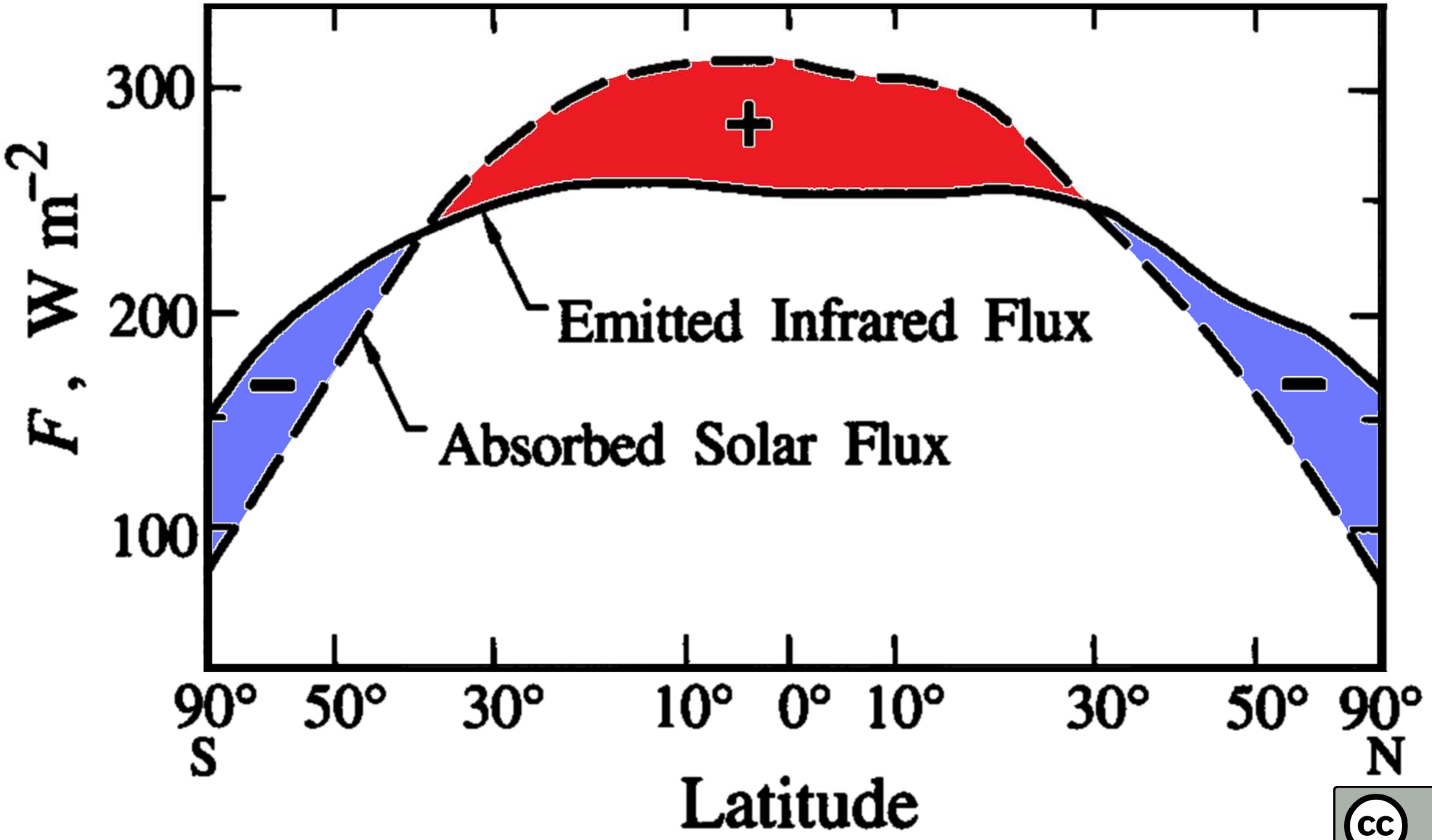


General rules for air circulation

- Driving forces for air movement
  - Basic force = uneven heating of different parts of the planet by sunlight;
  - Tropical regions receive more energy than is reflected back;
  - Polar regions receive significantly less energy than is reflected;
  - Surplus energy (absorption – radiation) between 40° north and 40° south latitude;
  - Approximately 60% of the circulation is realised due to the aforementioned mechanism;
  - Approximately 40% of the circulation is due to ocean mechanism;
  - Movement in Hadley cell (described in 1735) is given by the principle of rising warm air with lower density and descending of the air, which density is higher.
  - Another significant force - the Coriolis force is caused b of the Earth (see below).

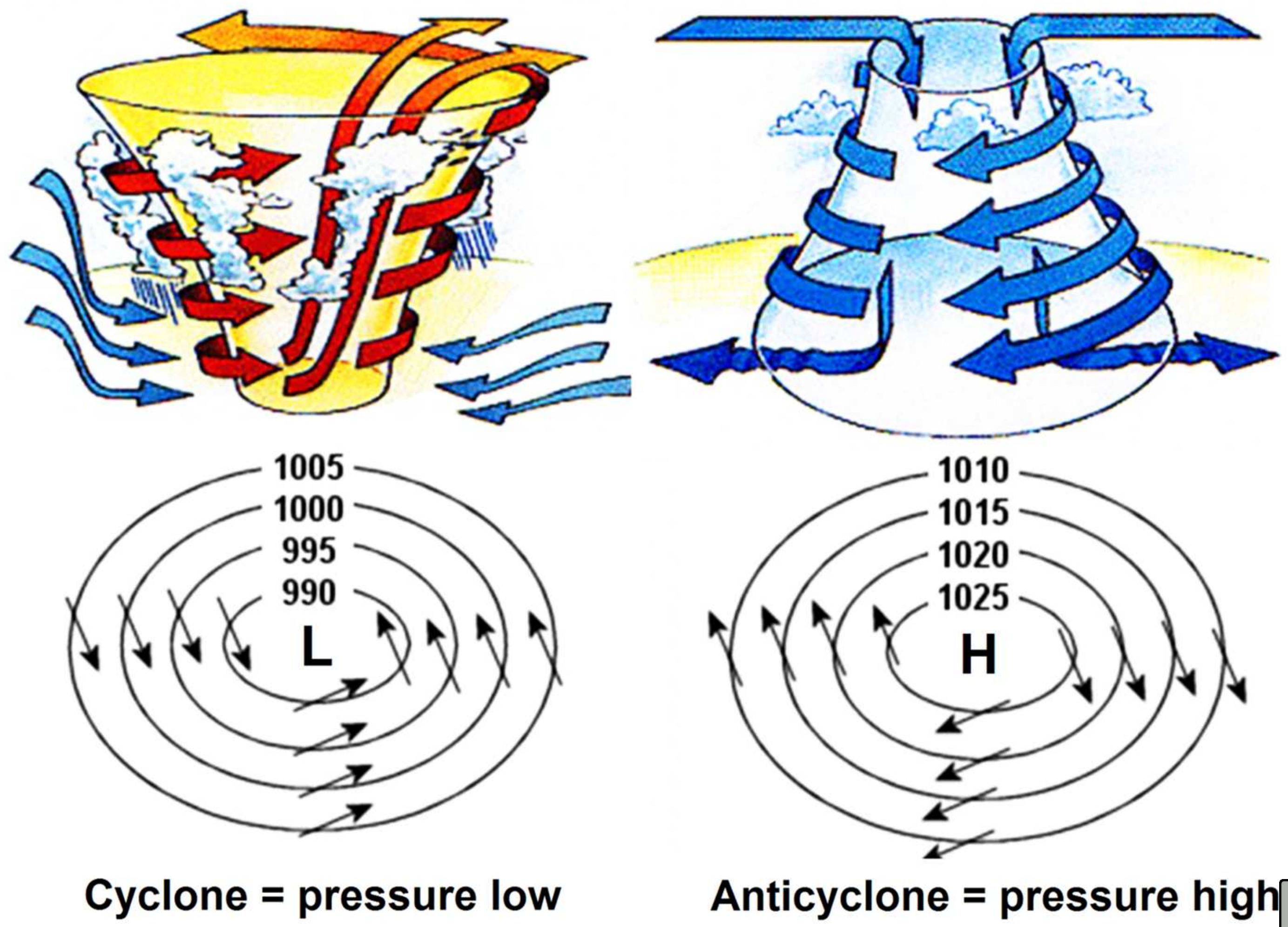
General rules for air circulation

- Differences in absorbed and emitted solar energy (Source: Seinfeld, J., H., Pandis, S., N.: Atmospheric Chemistry and Physics)



General rules for air circulation

- Local changes in pressure = main moving force for wind (Source: Seinfeld, J., H., Pandis, S., N.: Atmospheric Chemistry and Physics)



General rules for air circulation

- Other factors that influence air movements
  - Coriolis force = inertial force caused by the rotation of the Earth:

    In the northern hemisphere it causes twisting of moving masses to the right, and in the southern hemisphere twisting to the left, ie. from the direction of movement;

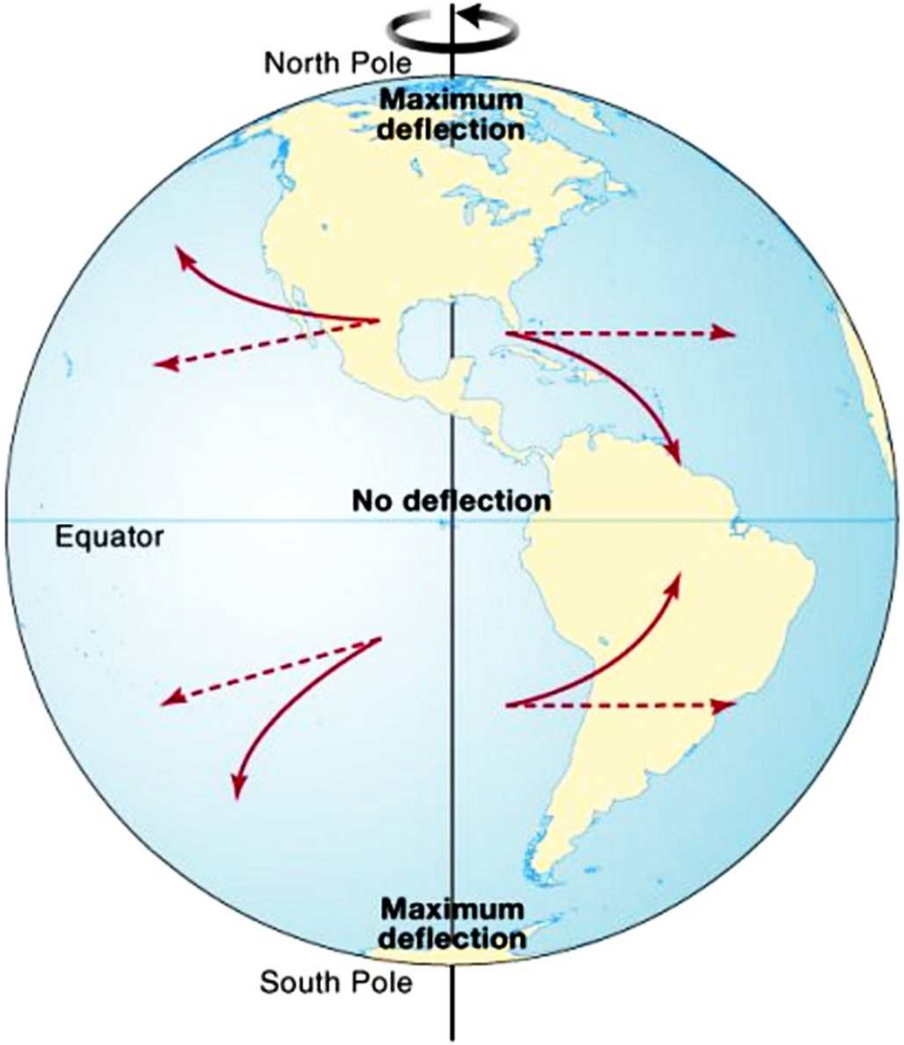
    CF has zero value at the equator and increases with latitude;

    It affects the airflow and movement of ocean currents;

    CF is visibly manifested only in larger wind systems ⇒ deflection from the horizontal pressure gradient (previous slide);
  - Friction = force against the direction of air movement;
  - Centrifugal force - affecting the flow, if this takes place along a curvilinear trajectory;
- Result: air flows to the lower pressure side and is deflected by a certain angle from the direction of the horizontal pres gradient.

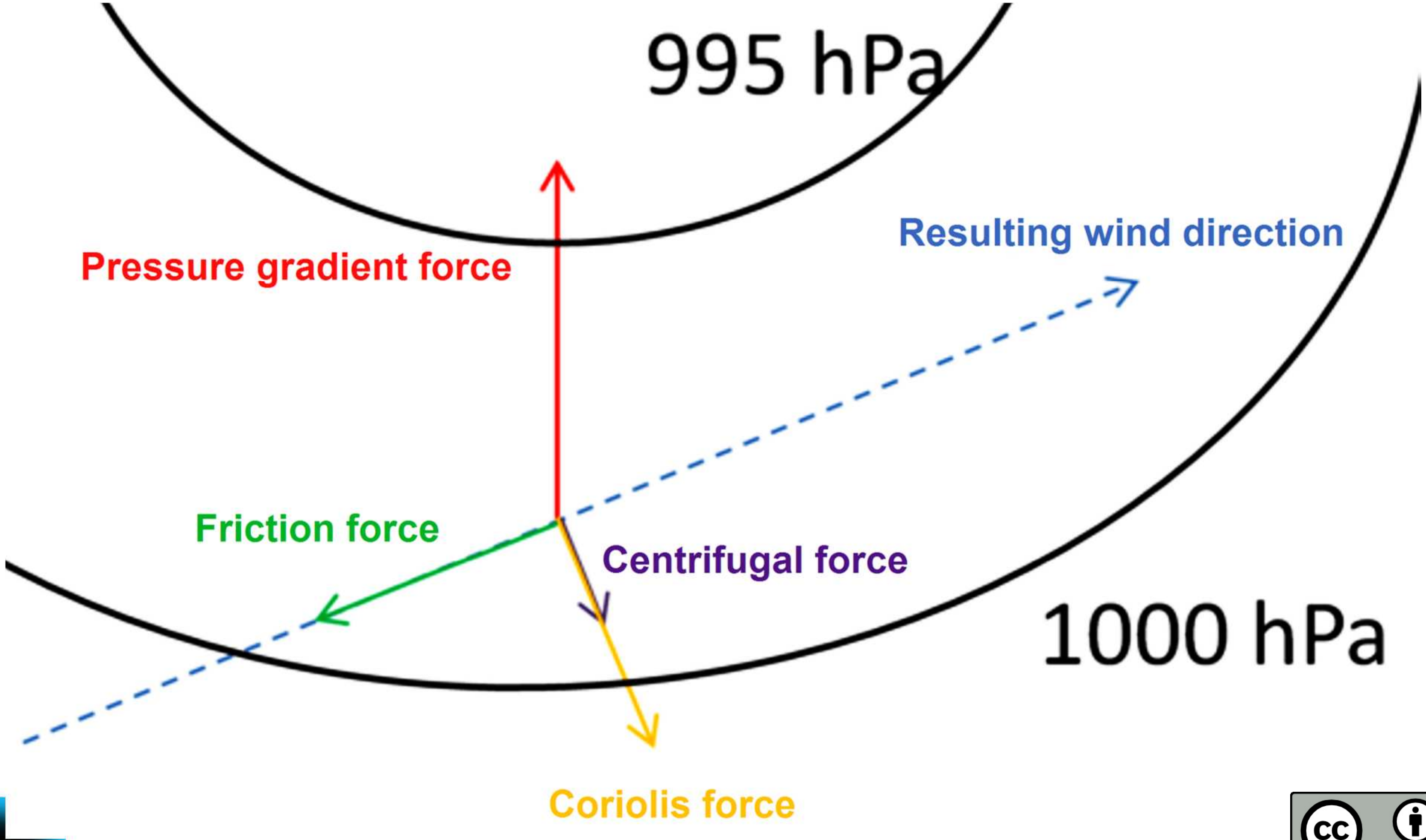
General rules for air circulation

- Demonstration of deflections from the straight trajectory, caused by Coriolis force



General rules for air circulation

- Example of vector determining of the wind direction, taking account of the above mentioned factors (Source: In-počasí.cz):



General rules for air circulation

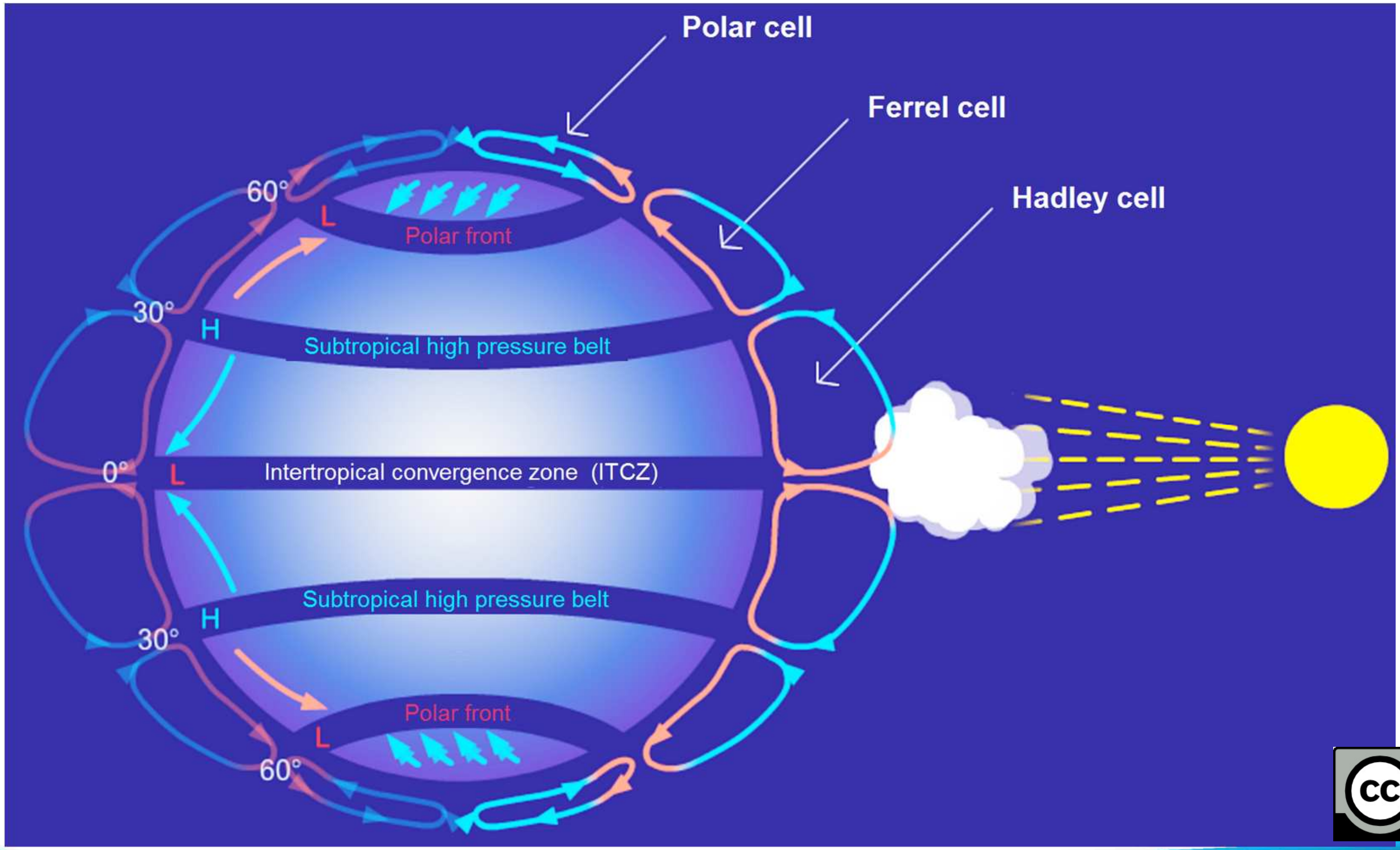
- Global circulation of atmosphere has following properties:

  (Source: http://is.muni.cz/do/rect/el/estud/pedf/ps14/fyz_geogr/web/pages/04-cirkulace.html)

  - Mostly vortex (circulating) character of air movement (eg. Cyclonic flow);
  - The predominance of horizontal movements over the vertical;
  - The predominance of zonal winds (along parallel lines) over movements along meridian;
  - Variability of atmospheric circulation and its components;
  - Changes in direction and velocity of flow from layer to layer;
  - Prevailing westerly transfer of air in the troposphere and lower stratosphere in moderate latitudes.

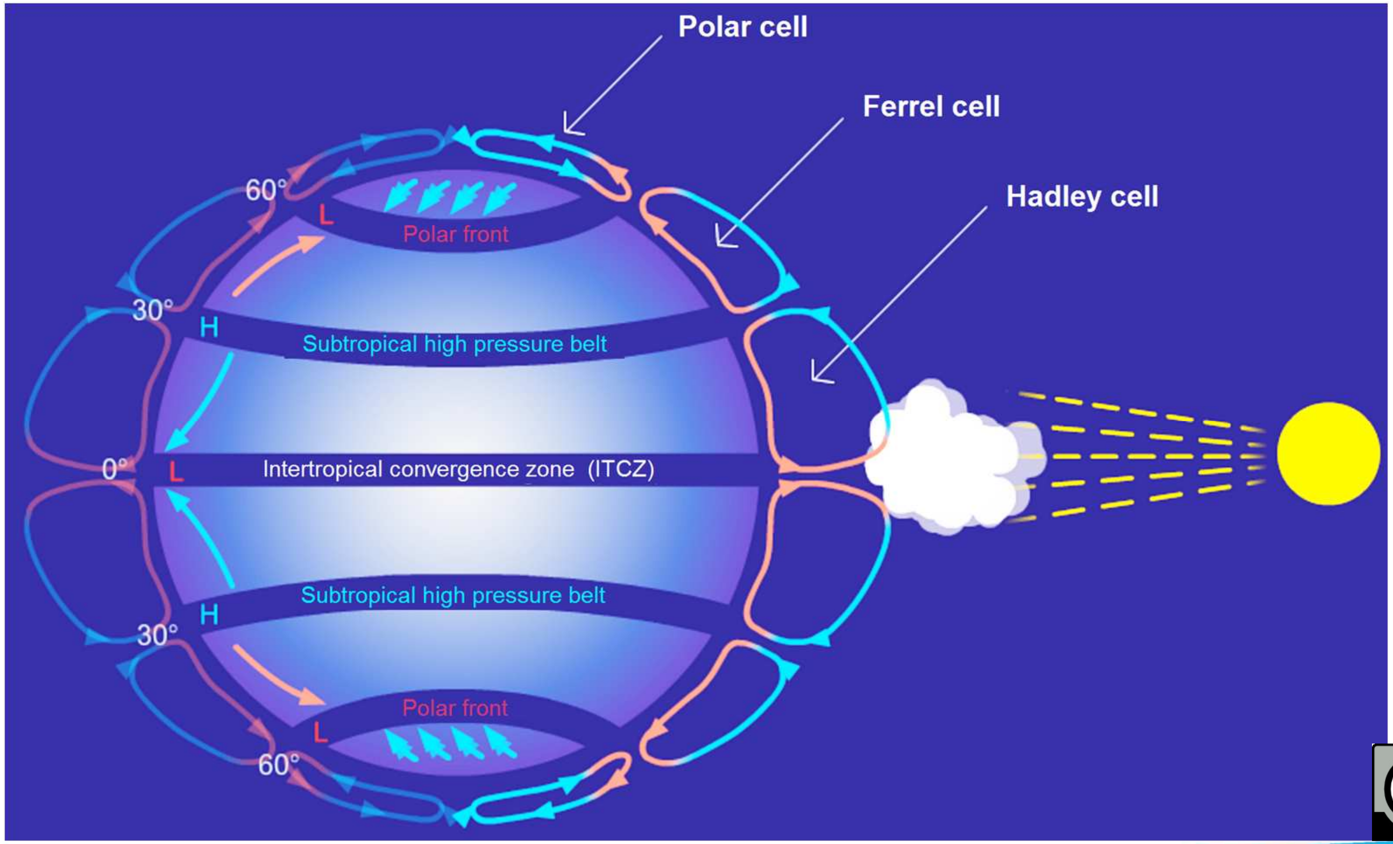
Movement of air in atmosphere

- Hadley cell – the air in the low pressure area along the equator (ITCZ) rises up to the upper border of Troposphere, after that it flows simultaneously to the North and South; after reaching 30 °of latitude dry air descends and forms high pressure belts (desert areas); after that it either returns to equator or it is pushed to moderate temperature latitudes.



Movement of air in atmosphere

- Polar cell – on 60° of North and South latitude the warm air rises to the upper border line of Troposphere, then it is cooled down close to the poles and descends in polar areas ⇒ area of high pressures.
- Ferrel cell – dominating West air flows grace to circulation between Hadley and polar cell.

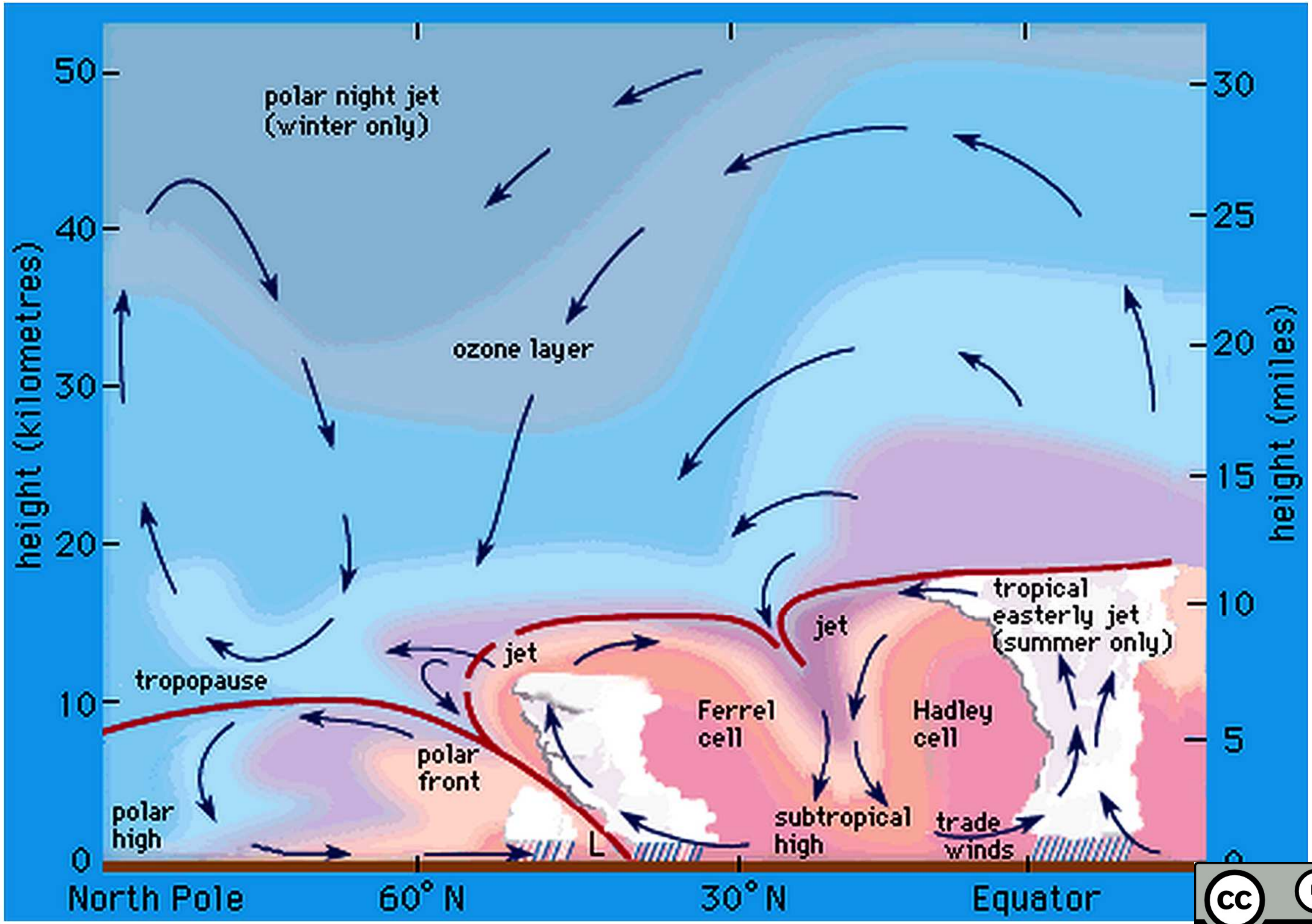


Atmospheric Jet Streams

- Types of atmospheric jet streams (Source: In-počasí.cz)
  - Tropospheric jet stream;
    - Polar Jet Stream (localization ca. 60°, between polar and Ferrel cell)
    - Subtropical Jet Stream (in winter ca. 30°, in summer shift to ca. 40°, between Ferrel and Hadley cell)
    - Equatorial Jet Stream (over the equator)
  - Stratospheric jet stream;
  - Low level jet stream;

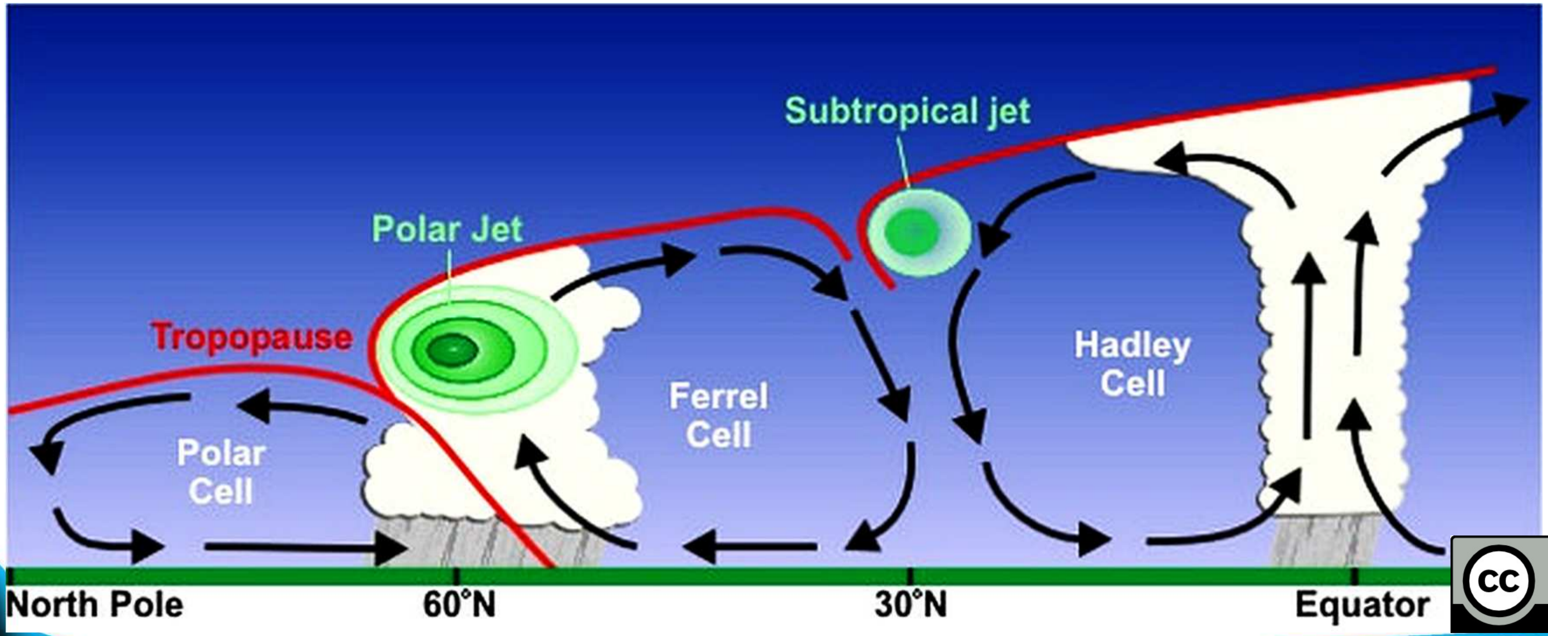
Atmospheric Jet Streams

- Vertical localisation of jet streams (for north hemisphere)



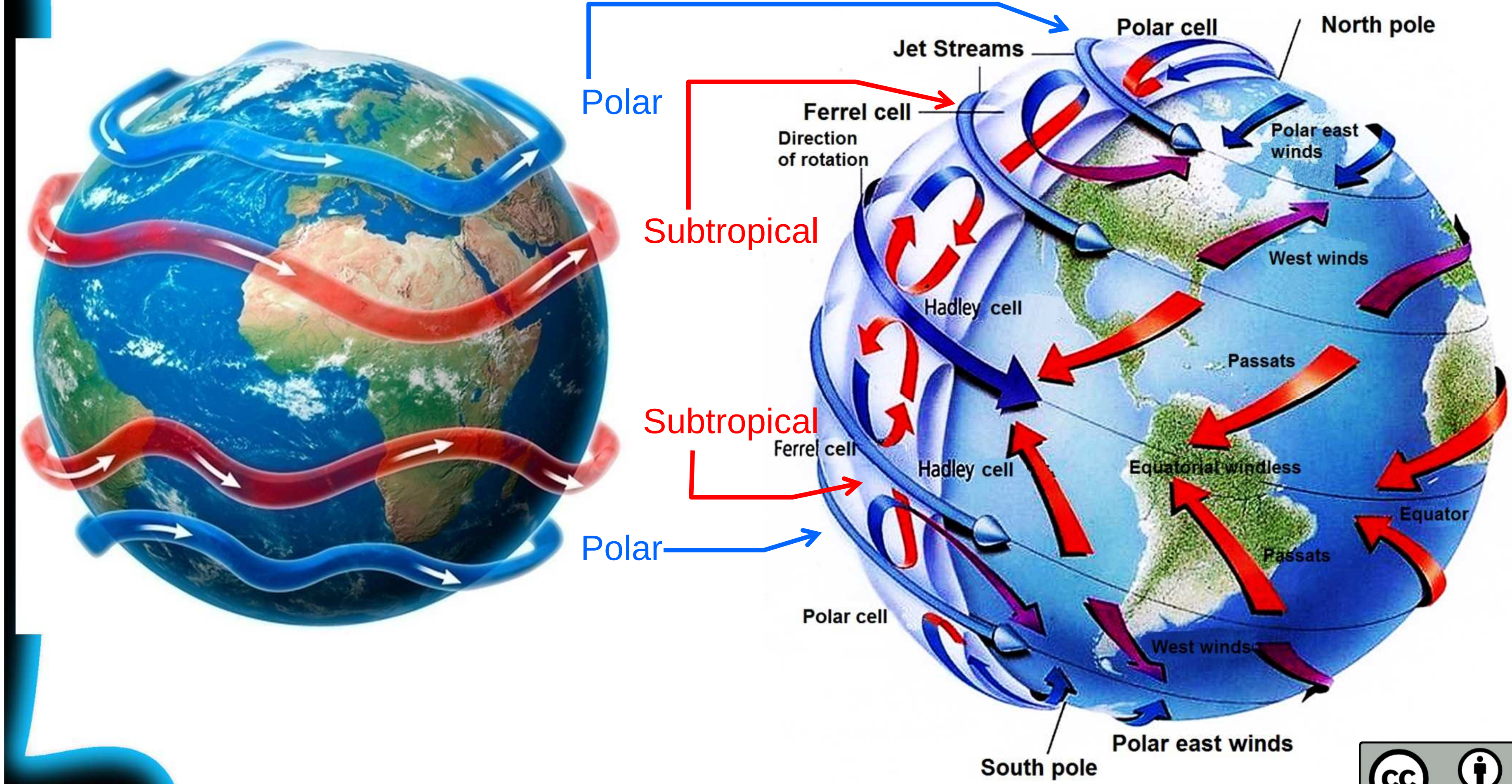
Tropospheric Jet Stream

- Shape, driving force and direction of Jet Stream
  - Direction: from west to east;
  - Shape: approximately shape of wave hose or pipe, leading alongside the parallels of latitude;
  - Driving force: generated by temperature differences in various latitudes;
- Speed of Jet Stream
  - average velocity > 30 $m \cdot s^{-1}$ (108 km/h), maximum speed > 700 km/h



Tropospheric Jet Stream

- Horizontal direction of Jet Stream locomotion + tropospheric cells



Tropospheric Jet Stream

- Importance of Jet Stream (for north hemisphere)
  - influencing weather in Europe and Asia;
  - north-south waving caused by so called Rossby's waves, which make additional pressure to west side;
  - The force of jet streams is usually bigger than Rossby's waves ⇒ waves of jet streams moves from west to east;
  - Sometimes the power of Rossby's waves is equal to the jet stream ⇒ stopping jet stream movement ⇒ long-term uniform pressure distribution ⇒ extremes in weather:

    meanders bent to north attract warm air from the south latitudes

    meanders bent to south attract cold air from the north latitudes.
  - Jet stream transports huge air masses to a long distances (including pollutants).

Tropospheric Jet Stream

- Appearance and properties of Jet Stream
  - The shape similar to the hose-like channels with a significantly higher flow rate – defined by isotachs;

Note: Isotach = imaginary line connecting points with the same wind speeds, water and the movement of some meteorological phenomena

  - Margins of the jet streams are characterized by a sharp increase (gradient) of wind speed - about 10 $m \cdot s^{-1}$ (36 km/h) per 1 km of lateral distance.
  - Vertical location: typically 1-2 km below the tropopause (on the border of neighbour air masses with significantly different temperatures);
  - Beware! Jet Stream is potentially dangerous for aircrafts, however, when flying in the direction of the jet stream, the significant fuel savings is achieved.

Tropospheric Jet Stream

- Particular streams of the tropospheric Jet Stream (Source: In-počasí.cz)
  - Polar Jet Stream

    Collision of cooler air from the north and the southern warm air from warmer areas, localised between Polar and Ferrel cells.

    PJS does not entirely form a continuous belt around the Earth, but it is represented by sub-bodies moving alongside the longitude and latitude as well.

    The intensity of PJS increases with the onset of winter.

    Stronger polar jet stream localised around 60-50° latitude, but due to the effect of waving it extends well below 30°;

    Vertical localization 7-12 km

Tropospheric Jet Stream

- Particular streams of the tropospheric Jet Stream (Source: In-počasí.cz)
  - Subtropical Jet Stream

    Average localisation 30°, between Ferrel and Hadley cell; on the border line between tropical and cooler air;

    Vertical localisation 10 to 16 km (see the changes of Tropopause height according to the latitude);

    SJS is more stable than the Polar Jet Stream and it is in fact continuous (unbroken into parts).

    Summer shift by 10° to poles, in average (over the continent more significant than over the seas);

    Velocity higher than Polar Jet Stream: > 50 $m.s^{-1}$ (180 km/h).
  - Equatorial Jet Stream

    Over the equator, on the border between north and south Hadley cells; Vertical localisation 15 to 20 km;
    Opposite flowing than other Jet Streams (from the east).

Other Jet Streams

- Characterisation of the stratospheric Jet Stream (Source: In-počasí.cz)
  - Vertically localised over the tropospheric Jet Streams (ca. 30 – 50 km);
  - Very fast stream with isotach about 60 $m.s^{-1}$ (216 km/h);
  - During winter it descends down to the edge of Tropopause = 12 km;
  - Direction of flowing changes during calendar year: In winter it flows from the west; in summer from the east.

    In summer time the stratospheric Jet Stream loses the velocity and typical character of jet streams;
  - The most significant stratospheric Jet Stream in winter and around 70° latitude.

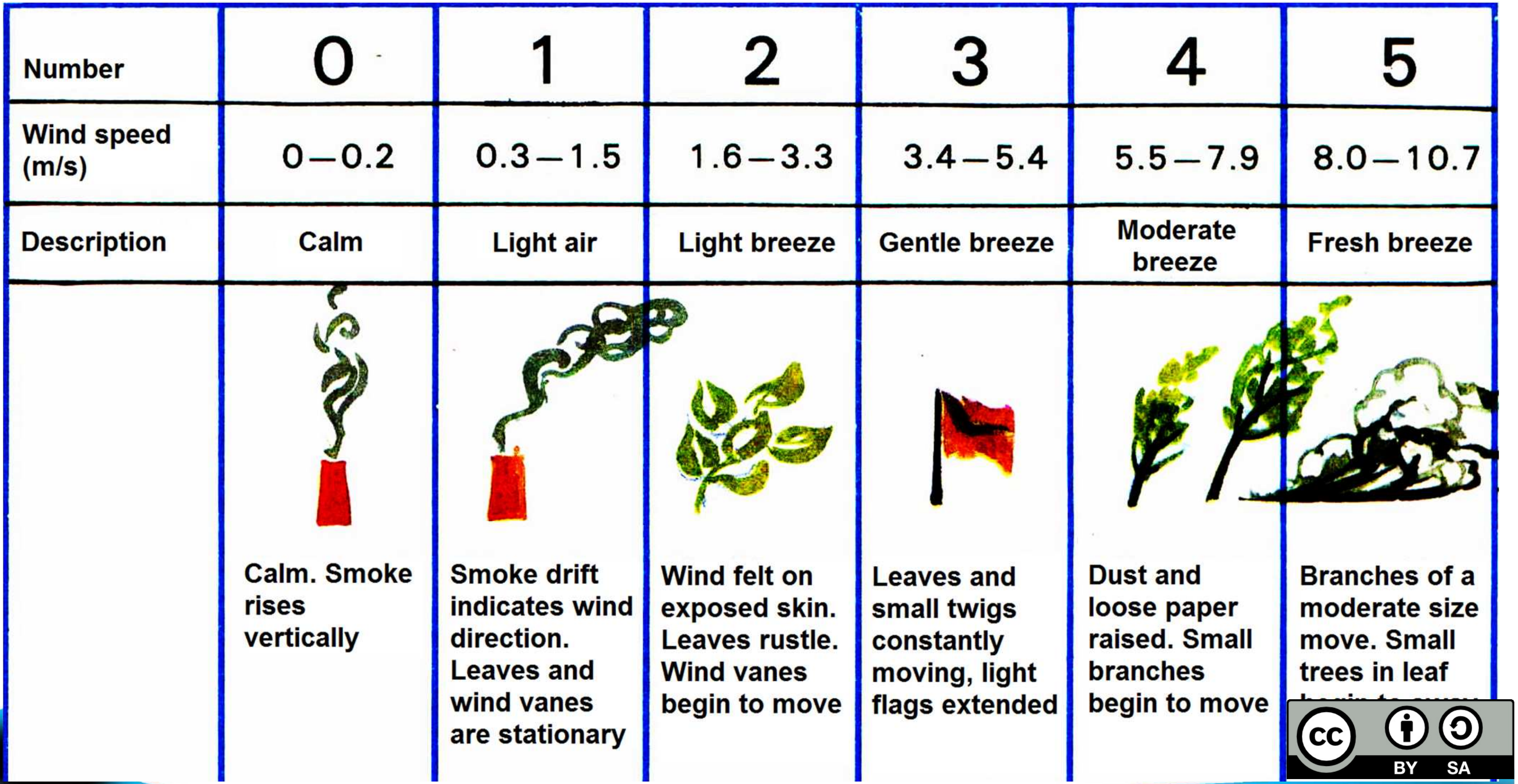
Other Jet Streams

- Properties of low level Jet Stream (Source: In-počasí.cz)
  - More types of powerful wind in low altitudes;
  - In fact pipe of very fast air, moving alongside before the cold front;
  - Night low level Jet Stream is formed due to night temperature inversion;
  - So called sting jet, moving along quickly growing cyclones with rapid pressure decrease, is very dangerous ⇒ It may damage building roofs, breaks trees and so on.
  - Climatological low level Jet Stream exists only on the north hemisphere.

    For example: Somalian Jet Stream removes humidity from the Somalian region and transfer it to form Asian monsoons.

Local flux in troposphere

- Beaufort wind force scale (Source: http://www.rmets.org/weather-and-climate/observing/beaufort-scale)
  - Author sir Francis Beaufort, British Rear Admiral (1774 – 1857),
  - original for naval purposes, below table = „continental“ version;



Number	0	1	2	3	4	5
Wind speed (m/s)	0–0.2	0.3–1.5	1.6–3.3	3.4–5.4	5.5–7.9	8.0–10.7
Description	Calm	Light air	Light breeze	Gentle breeze	Moderate breeze	Fresh breeze
	Calm. Smoke rises vertically	Smoke drift indicates wind direction. Leaves and wind vanes are stationary	Wind felt on exposed skin. Leaves rustle. Wind vanes begin to move	Leaves and small twigs constantly moving, light flags extended	Dust and loose paper raised. Small branches begin to move	Branches of a moderate size move. Small trees in leaf

Local flux in troposphere

- Beaufort wind force scale (Source: http://www.rmets.org/weather-and-climate/observing/beaufort-scale)
  - Author sir Francis Beaufort, British Rear Admiral (1774 – 1857),
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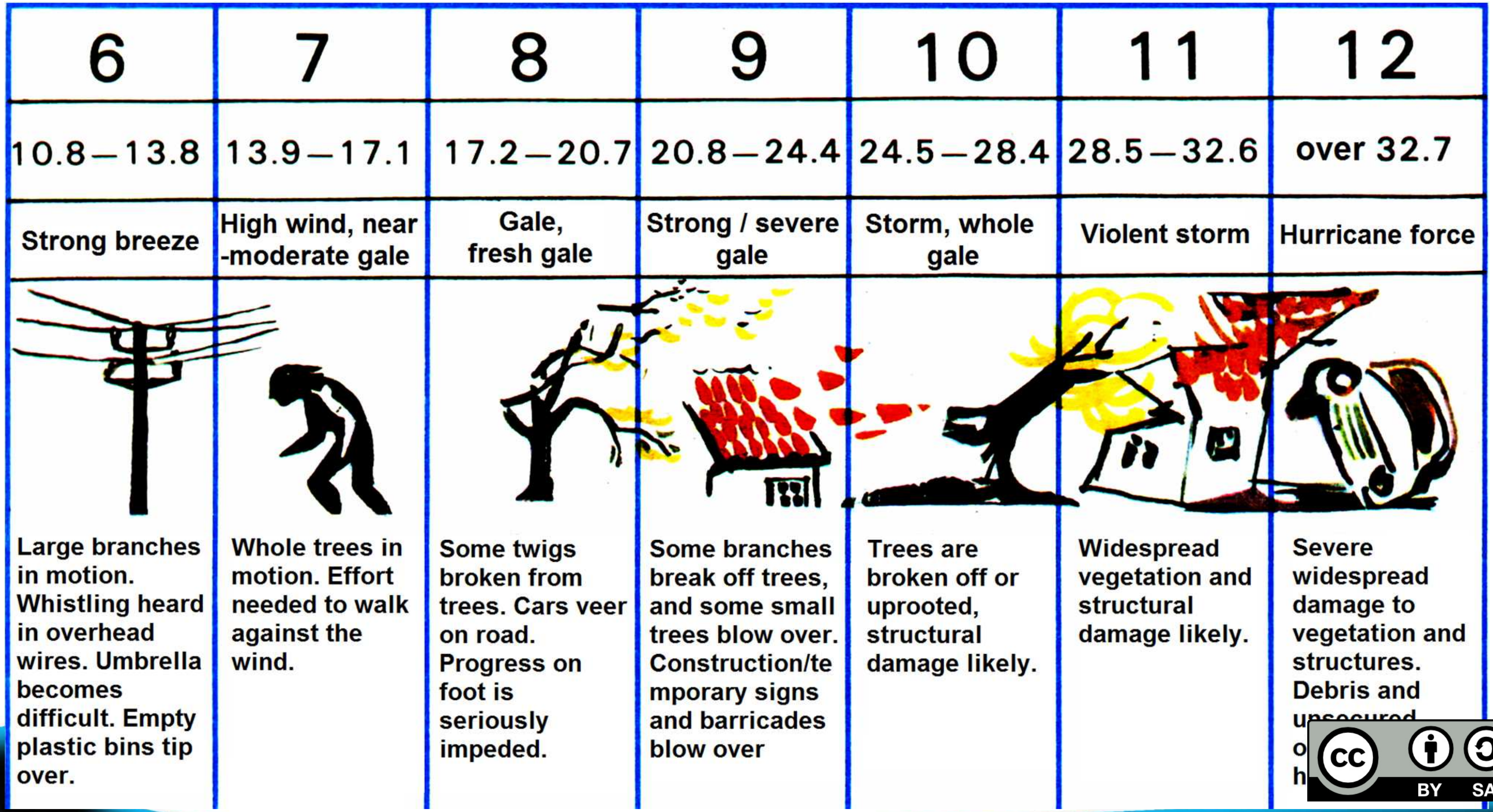


6	7	8	9	10	11	12
10.8 – 13.8	13.9 – 17.1	17.2 – 20.7	20.8 – 24.4	24.5 – 28.4	28.5 – 32.6	over 32.7
Strong breeze	High wind, near -moderate gale	Gale, fresh gale	Strong / severe gale	Storm, whole gale	Violent storm	Hurricane force
Large branches in motion. Whistling heard in overhead wires. Umbrella becomes difficult. Empty plastic bins tip over.	Whole trees in motion. Effort needed to walk against the wind.	Some twigs broken from trees. Cars veer on road. Progress on foot is seriously impeded.	Some branches break off trees, and some small trees blow over. Construction/temporary signs and barricades blow over	Trees are broken off or uprooted, structural damage likely.	Widespread vegetation and structural damage likely.	Severe widespread damage to vegetation and structures. Debris and unsecured o h

Local flux in troposphere

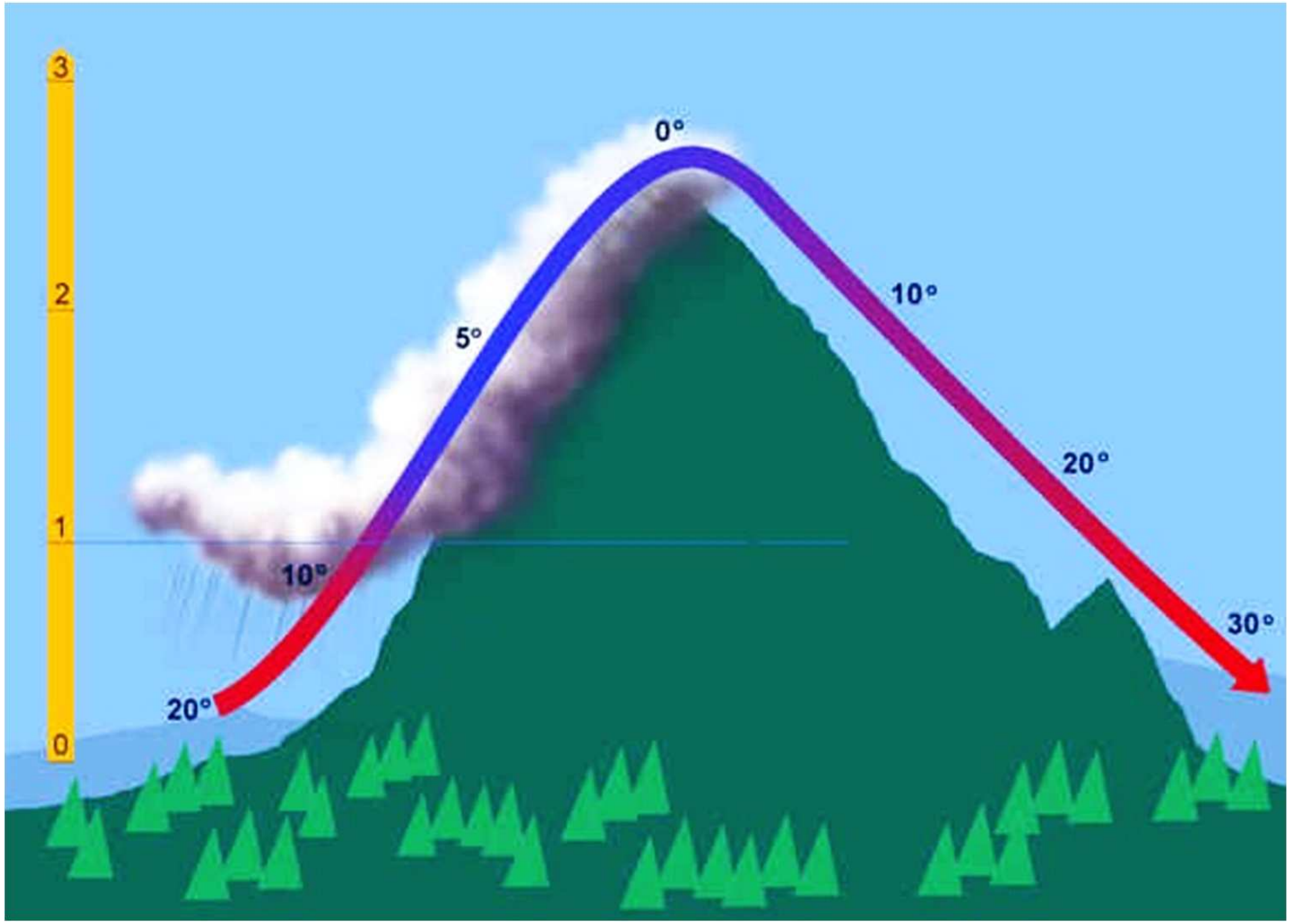
- Long-distance winds
  - Passats: Tropical winds resulting from circulation in Hadley cells. They flows from areas of high pressures in subtropical latitudes (30 - 40 °) to the low pressure area above the equator.

    In the area between 30 - 40° north and south latitude passats draw moisture and transmit it to the equatorial rainforests. In the north hemisphere P. flows from the northeast, and in the south hemisphere from the southeast.
  - Monsoon: Regular seasonal winds providing rainfall in South and Southeast Asia.

Summer monsoon created by higher heating of the land compared to the ocean. Pressure low formed over continent ⇒ wet air from the ocean flows to the high mountains, over which it cools and forms rainfalls. Winter monsoon is dependent on uneven cooling, when the dry blowing over the ocean carries a snowstorm over Japan.

Local flux in troposphere

- Local winds – influenced by effect of high relief upon the air circulation
  - Foehn (föhn): dry, warm wind flowing down over the leeward side of the mountain slopes.



Local flux in troposphere

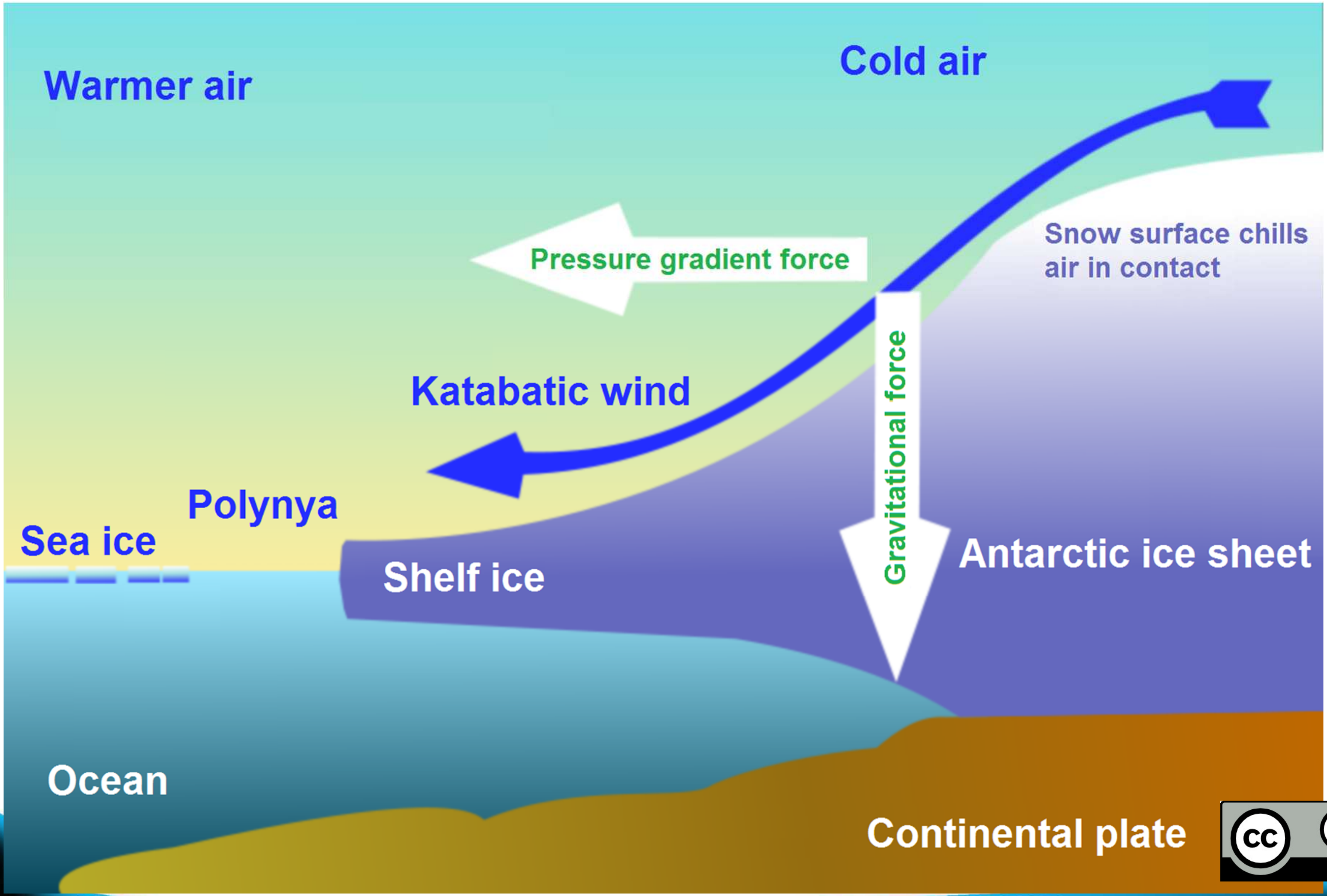
- Local winds – influenced by effect of high relief upon the air circulation
  - Breeze: Coastal wind that blows between the sea and the coast in the summer as a result of uneven heating of the water and the land, changing the direction of the pressure gradient.

    Direction: afternoon colder air form sea to land; in the night from the coast to sea;
  - Bora: Overflowing cold air over the mountain barriers lining the coast. First accumulated, then overflows passes and saddles with a sharp drop in temperatures (underflows the warm air and causes waves).
  - Mistral: Synonym for bora used in south France.
  - Katabatic winds:

    Cold air flows down by gravity from the upper position into the lower (e.g. Iceberg wind); In fact the of bora.

Local flux in troposphere

- Katabatic winds – gravitation underflow of the cold wind underneath the warm air (with lower density)



Local flux in troposphere

- Local winds – influenced by effect of high relief upon the air circulation
  - Mountain and valley winds:

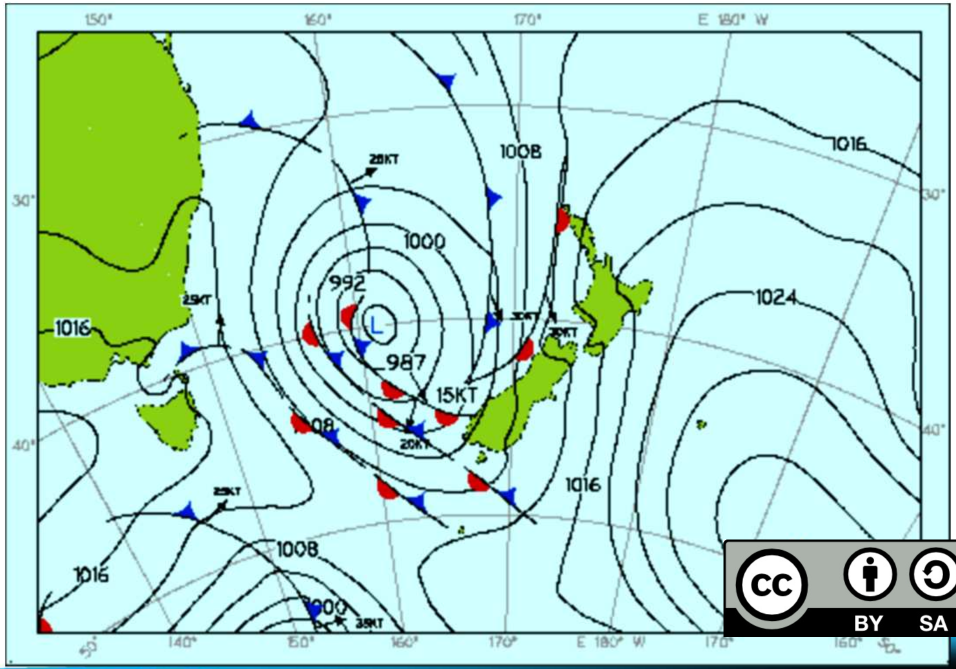
    Warm air rises up from the valleys during a day (valley wind). In the night, however, cold air descend the same way back from the mountains to the valleys (mountain wind). The above mentioned flux is combined with transverse circulation on the hillsides (rising the warm air during a day, descending of cold air during a night).
  - Blizzard:

    Wet circulation flowing from the sea to the land and transporting mainly snow precipitation. Normally it appears in northern latitudes. Wind speed ca. 15 $m.s^{-1}$ (54 km/h).
  - Tornado:

    Very quickly ascending spiral air flow, created during unequal temperature and pressure distribution nearby the surface. Wind speed may exceed 200 km/h.

Issues of meteorology

- **Synoptic meteorology (SM)**
- SM studies atmospheric phenomena and processes on the macroscopic scale.
- Obtained information is periodically inscribed into synoptic (weather) maps.
- Analysis of information in the map enables to forecast the weather, which is based on observation of appearance, evolution and movement of cyclones, anticyclones, air masses and atmospheric square areas.
- Synoptic maps visualize data, both in horizontal and vertical directions (so called isobaric levels).
- Data acquired using:
  - aerological measurement
  - meteorological radars
  - meteorological satellites



Issues of meteorology

- **Synoptic meteorology**
- Synoptic analysis = comparison of values measured and drawn into the synoptic maps. Synoptic analysis is based on following principles:
- Complexity

  = The weather characteristics are mutually interconnected and conditioned each other.

  Values of one characteristic are compared in different locations, in different altitudes and during certain time.
- Three-dimensional behavior

  Observation and detection of values of meteorological characteristics is realised simultaneously (concurrently) at several altitude levels.
- Time consecution

  Comparison of measured meteorological characteristics is realised in more subsequent time intervals ⇒ observation of weather evolution during time.

Issues of meteorology

- **Synoptic meteorology**
- Working procedure for synoptic map analysis:
  - Determination of stable and unstable air masses, based on type of clouds and form of precipitations (rainfall), localization and identification of frontal fractures;
  - Drawing of lines expressing hourly trends of air pressure (isobaric lines);
  - Determination of geographic location of warm, cold and occluded fronts;
  - Determination of front type and direction of movement of isobars in case of gradient wind (changes of vectors of winds);
  - Comparison of above data with height maps of absolute and relative baric topography;

- Condition for successful forecasts:

Knowledge of precise values about actual state of atmosphere.

Issues of meteorology

- **Synoptic meteorology**
- Acquisition of precise values about actual state of atmosphere:
  - A network of terrestrial stations each 1 or 6 hours transmits the encoded message containing data about: clouds, range of vision, relative humidity, precipitations, snow coverage, air temperature, dew point temperature, direction and speed of wind, air pressure and its trend;
  - Aerological stations (4 times per day at the same time around the World) release meteorological balloons with analytical aeroprobes, e.g. Czech Republic stations: Prague-Libus and Prostejov;

    Altitude range ca. 32 km

    Data acquisition:

After reaching the limit altitude the balloon cracks and the probe falls down using a parachute; following parameters are measured each 5 s: temperature, pressure, humidity, dew point, direction and speed of wind + several times per year additional data about O_3 and radioactivity.

- Long distance detection: meteorological satellites, radars, flash detections systems etc.

Issues of meteorology

- Aerological station – releasing of aeroprobe using meteorological balloon = weather balloon (Source: CHMI)

Issues of meteorology

- **Synoptic meteorology**
- Classification of weather prognoses:

– Very short term	0–12 hours	synoptic evaluation
↳ Nowcasting	0–2 hours	synoptic evaluation
– Short term	1–3 days	numerical models
– Medium term	4–8 days	numerical models + models of deterministic chaos theory
– Long term	months	knowledge of relations among parts of climatic system (e.g. Asia – beginning of monsoon period and so on)
– Prognosis of climate	decades, centuries	very complicated

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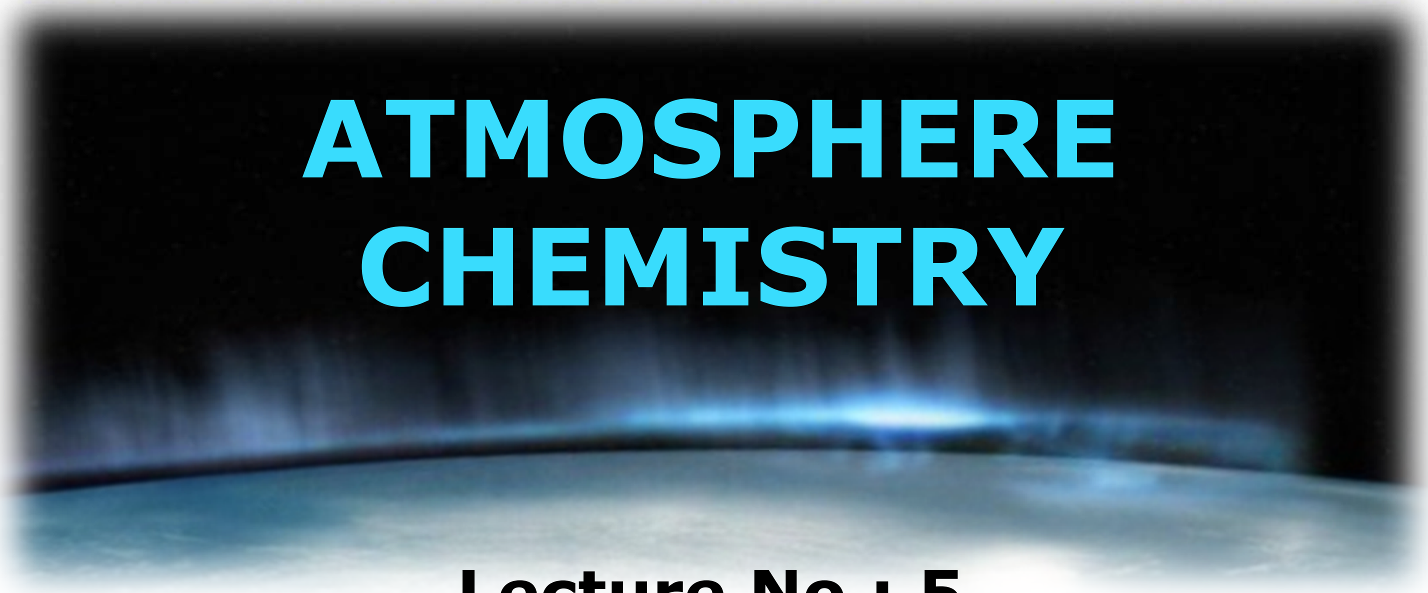


ATMOSPHERE CHEMISTRY

Lecture No.: 5

Organisation of study

- Lecturer: Marek Staf, MSc., Ph.D., phone: +420 220 444 458
  e-mail: marek.staf@vscht.cz,
  web: http://web.vscht.cz/~stafm/
  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 - oral form
- Note:

Scope of lecture 5

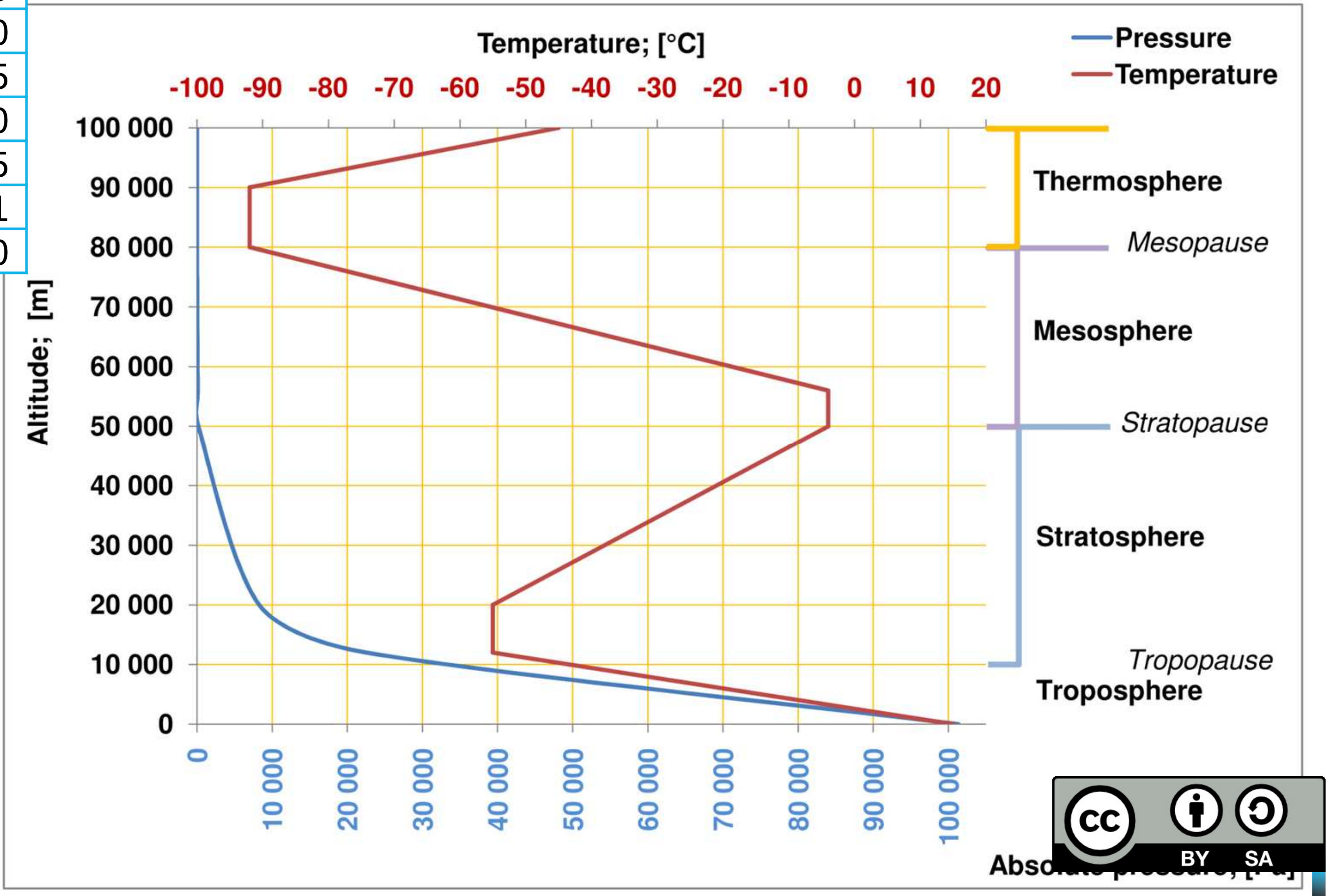
Basic reactions in the atmosphere, homogeneous and heterogeneous reactions

- Common characteristics of atmospheric reactions
- Problems of active and passive air sampling
- Distribution of reactants appearing in the air
- Distribution of reactions according to various criteria
- Monomolecular reactions
- Bimolecular reactions
- Termolecular reactions
- Photochemical reactions – ways of excitation and losing the excessive energy
- Main acid base reactions in the atmosphere
- Characteristics of nuclear reactions and natural radioactive bac

Common signs of reactions in air

- Low concentrations of reactants – low partial pressures and total pressure;

Altitude [km]	Temper. [℃]	Pressure [Pa]
0	15	101 325
12	-55	22 600
20	-55	8 300
50	-4	195
56	-4	90
80	-92	5
90	-92	1
100	-45	0



Common signs of reactions in air

- Main components leading atmospheric reactions:
  - acidic components
  - oxidizing components
- Laboratory simulation of stratospheric (and higher) reactions is problematic:
  - very low pressures components are released from walls of sampling containers and cans (desorption) ⇒ undesired interference;
  - differences in reaction kinetics; in high altitudes low concentration of substances absorbing energy released during some reactions ⇒ slow reaction rate; in laboratories the wall of apparatus absorbs energy higher by order of magnitude ⇒ much faster reactions
  - risk of involvement of the apparatus itself into the reaction:

    catalytic effect of materials, which the apparatus is made of

    adsorption of some compounds on the apparatus surface c
    of the material with reactants (e.g. with radicals etc.)

Possibilities of air sampling

- Distribution of sampling techniques

Active sampling= sample is taken with additional energy using external force than diffusion; active element is pump (inlet or outlet) or vacuum (suction into evacuated sampling can)

- → sampling together with whole matrix (air)
- → sampling with isolation of selected components

Passive sampling = free diffusion flow of molecules of sampled substance from air to collection media till reaching equilibria concentration of analyte in both environments;

- → only sampling with isolation of selected components

Possibilities of air sampling

- Active sampling with collecting whole matrix
  - Example of sampling into evacuated sampling canister (producer e.g. SUMMA®)
  - Material – stainless steel with electrochemically polished internal surface + in some cases equipped with silica layer
  - Sampling through special valve (mechanical or electromagnetic), assuring constant sampling time and gas flow.
  - Sampling stopped with residual vacuum   5 kPa due to changes in barometric pressure.
  - Alternative method is sampling into special bag.

Possibilities of air sampling

- Active sampling with isolation of selected components

  (Source: http://www.population-protection.eu)

  - Approaches using filtering of the air through active element, where analysed substance is selectively and quantitatively captured.
  - Following processes serve for capture:

    Absorption in solvents

    Adsorption on solid sorbents

    Filtration using dust filters

  - Realisation of capture is provided e.g. by sampling gas pump with adjustable flow rate (usually range 0 – 5 $l.min^{-1}$).
  - Pump is equipped with correctly calibrated gas flow meter or gas meter displaying flowed volume.

Possibilities of air sampling

- Active sampling with isolation of selected components

  (Source: http://www.population-protection.eu)

  - Example: adsorption of organic compounds using sorbent in sampling tube.
  - 3 groups of different sorbents available:
    - Non polar sorbents type I. on the basis of active coal (Carbotrap, Carbosieve, Anasorb and so on) ⇒ sorption of aliphatic hydrocarbons including polycyclic;
    - Hydrophilic sorbents type II. with positive surface charge on the basis of silica gel ⇒ sorption of carboxylic acids and their derivatives.
    - Partially hydrophilic polymer sorbents type III. with negative surface charge (Amberlite XAD2, Tenax and so on) ⇒ sorption of polar derivatives of hydrocarbons.

Possibilities of air sampling

- Example of utilisation of the sorption tube
  - Sorption tubes supplied either welded and pre-activated (type I.), or they require additional activation, immediately before application (silica gel 150 °C with N_2 flow, polymeric Tenax 80 °C with He flow)
  - Before sampling both edges of tubes must be break off, or the caps must be removed and the tube is connected to the pump inlet.

Tenax tubes before application

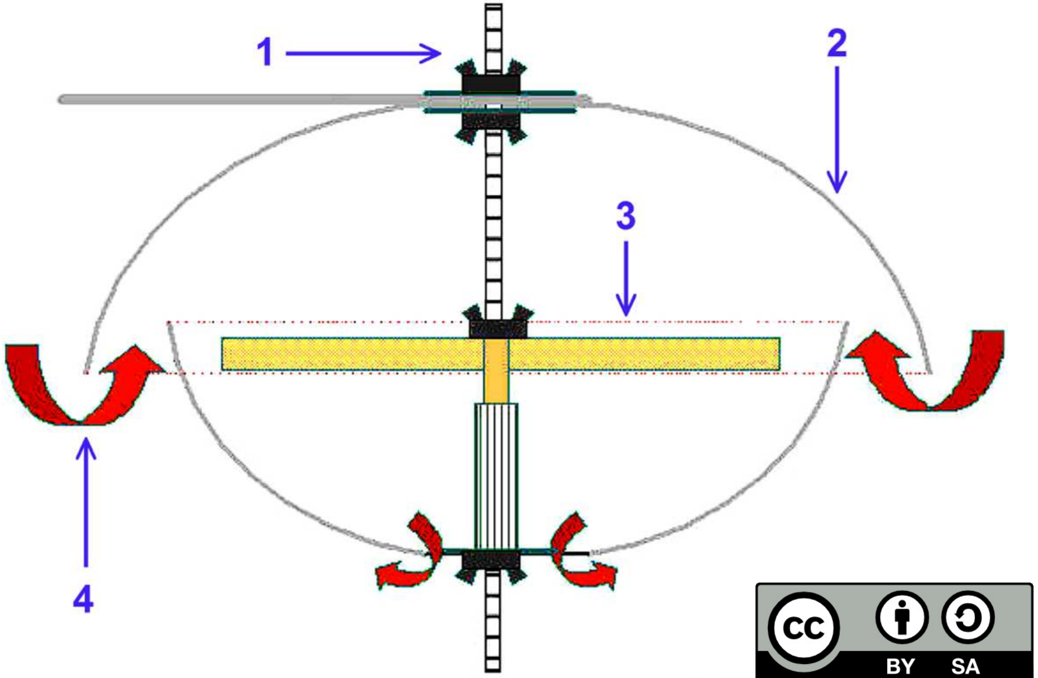
Hermetic capsule for saturated tubes

Possibilities of air sampling

- Passive sampling with isolation of selected components

  (Source: http://www.population-protection.eu)

  - Separation is based on difference of concentration of analyte in the air and in the sorbent. Sampling realised either during fixed time interval or till reaching equilibria concentration.
  - Sorbents: polyurethane foam, XAD resin, polyethylene semipermeable membrane with triolein filling etc.



1 – fixing screw

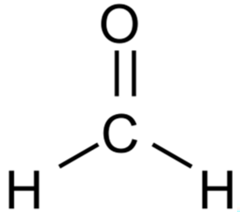
2 – stainless steel
hemispheric cover

3 – sorbent

4 – free circulation of air

Distribution of reactants

- Primary energy for initialisation of reactions = solar irradiation;
- Distribution of reactions according to presence of the above mentioned energy:
  - Day reactions; basic reactant = hydroxyl radical HO•
  - Night reactions; basic reactant = nitrate radical NO_3•
- Other gaseous reactants (distribution into groups may overlap):
  - Inorganic oxides; CO, CO_2, NO, NO_2, SO_2
  - Oxidants; O_3, H_2O_2, NO_3•, , HO•, HO_2•, ROO•
  - Reducing substances; CO, SO_2, H_2S, hydrocarbons
  - Organic compounds; in clean atmosphere only CH_4

    near polluters higher C_xH_y and derivatives
  - Photochemically active; NO_2,  (formaldehyde)

Distribution of reactants

- Other gaseous reactants (distribution into groups may overlap):
  - Acids; H_2SO_4
  - Bases; NH_3
  - Salts; NH_4HSO_4
  - Unstable components; HO•, other radicals, electrically excited NO_2^*

- Other components of atmosphere entering into the reactions:
  - Liquid particles = place, where reactions in solution take place
  - Solid particles = Surface for heterogeneous reactions (possibly surface-catalyzed reactions)

Both types of particles allow also descending of absorbed gases to lower atmospheric layers.

Distribution of atmospheric reactions

- The highest number of reactions: Troposphere
  - Sufficient partial pressures of components + sufficient temperature (penetration of irradiation > 330 nm)
  - Contrariwise the amount of UV irradiation with shorter wavelengths is filtered by ozonosphere;
- Basic distribution of reactions:
  - Homogeneous reactions

    Run only in gaseous phase

    Products of homogeneous reactions influence course of the reactions heterogeneous (e.g. oxidative influence of O_3, H_2O_2)
  - Heterogeneous reactions

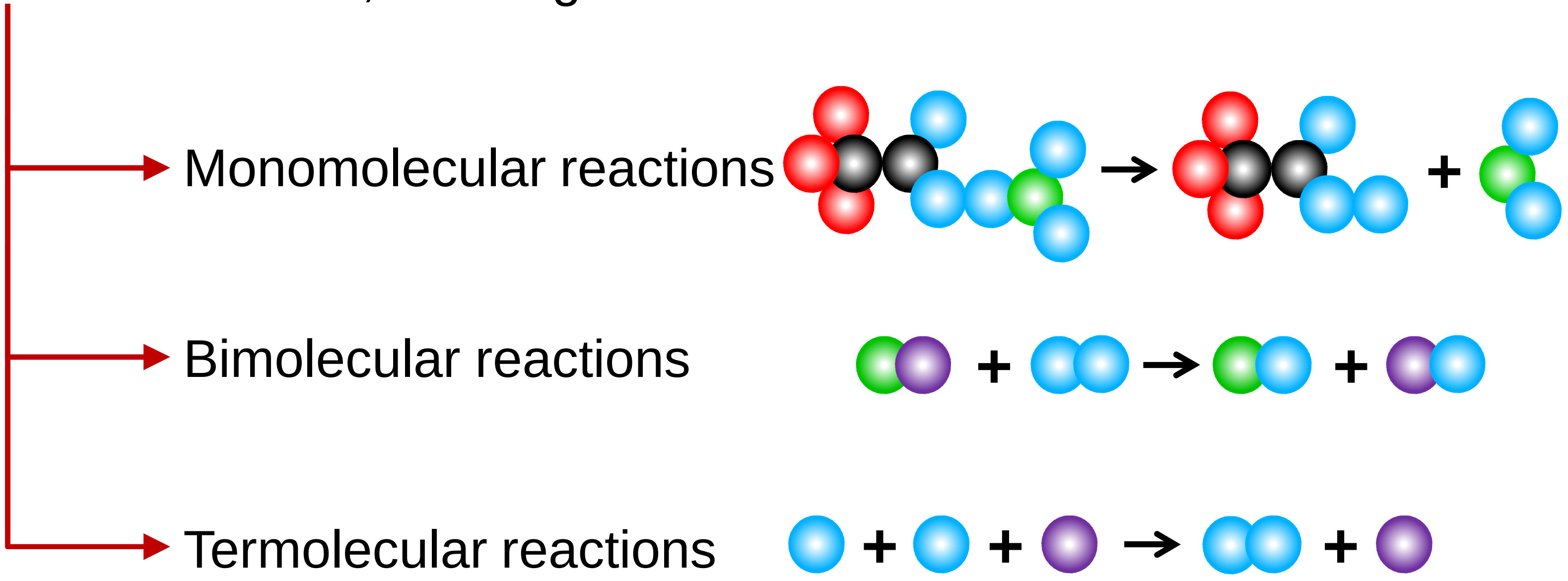
    Interaction of microphysical processes with chemical reactions;

    → adsorption = process on the surface of solid particles

    → absorpce = process in liquid phase (water droplets)

Distribution of atmospheric reactions

- Distribution of homogeneous reactions
  - One of the possibilities of distribution is according to number of atoms or molecules, entering the reaction:



Monomolecular reactions

Bimolecular reactions

Termolecular reactions

Distribution of atmospheric reactions

- Distribution of reactions according to chemical basis of process:
  - Photochemical reactions
    - Photooxidation
  - Acid base reactions
  - Nuclear reactions
  - Reactions of oxygen
  - Reactions of water
- One concrete reaction can accomplish more cathegories together.
  - e.g. Reaction can be at the same time: homogeneous, bimolecular, acid base and so on.

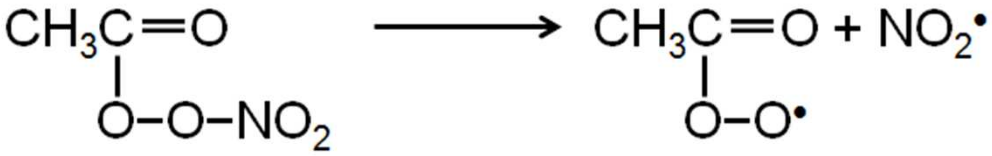
Distribution of atmospheric reactions

- **Homogeneous monomolecular reactions**
  - Principle is in cleavage of molecule into two or more products.
  - Main mechanism is absorption of heat energy.
  - Initial molecule must be, therefore, thermolabile and must have excess of energy, which is induced by following ways:

    Thermal excitation by elastic collision with third substance (it does not participate on the reaction)

    Photoexcitation ⇒ photolytic reaction
  - Examples of the most important reactions:

    Decomposition of peroxyacetyl nitrate to nitrogen dioxide:



$$CH_3C(=O){-}O{-}O{-}NO_2 \longrightarrow CH_3C(=O){-}O{-}O^{\bullet} + NO_2^{\bullet}$$

Stratospheric decomposition of chlorine dioxide:

$$O{=}Cl{=}O^{*} \longrightarrow Cl + O_2$$

Distribution of atmospheric reactions

- **Homogeneous bimolecular reactions**
  - Main principle is increasing of energy in the system of two molecules, which collided together (so called kinetic collision theory of gases).
  - Increase of energy occurs due to overcoming repulsive force between the molecules, in case they have sufficient kinetic energy in the moment of collision.
  - Reaction rate is directly proportional to initial concentrations of both reactants.
  - 3 basic types of bimolecular atmospheric reactions are following:
    - Exchange of atoms or groups
      - ionospheric ion-molecular exchanges
    - Addition
    - Substitution reaction, type metathesis

Distribution of atmospheric reactions

- **Homogeneous bimolecular reactions**
  - Reaction on the principle of exchange of atoms or groups;

    Following reactions in the atmosphere have this mechanism:

    - Hydrogen – atom transfer

      $$O(^1D) + H_2O \rightarrow 2OH^\bullet$$

      where O(^{1}D) is Oxygen atom in excited singlet state

    - Exchange Hydrogen– atom

      $$CH_4 + OH^\bullet \rightarrow H_2O + CH_3^\bullet$$

    - Exchange Oxygen– atom

      $$O_3 + O \rightarrow 2O_2$$

Distribution of atmospheric reactions

- **Homogeneous bimolecular reactions**
  - Ion-molecular reactions

    Reaction mechanism typical for ionosphere – abundance of ions in troposphere is lower by order of magnitude, so this reaction mechanism is not usual

Charge transfer

$$O_2^+ + N_2 \rightarrow NO + NO^+$$

or $$N_2^+ + O_2 \rightarrow N_2 + O_2^+$$

Ion – ion recombination

$$NO^+ + NO_2^- \rightarrow NO + NO_2$$

Associative detachment

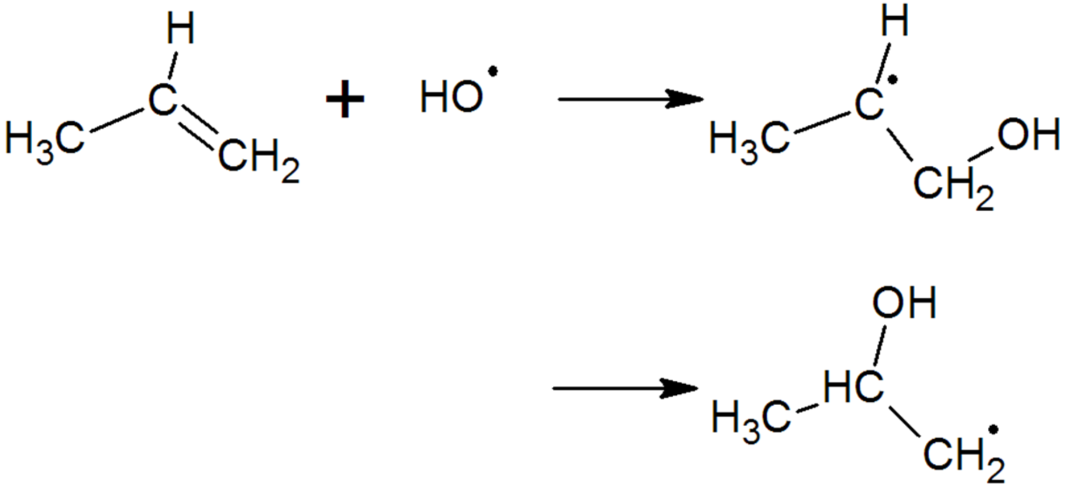
$$O_2^- + O \rightarrow O_3 + e^-$$

Distribution of atmospheric reactions

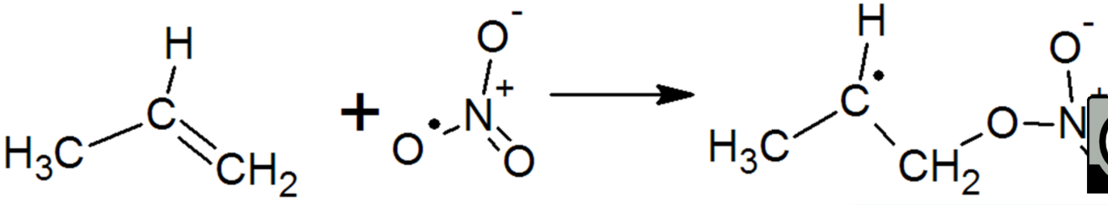
- **Homogeneous bimolecular reactions**
  - Reactions on the basis of addition;

    Either 2 molecules combines together, or (more often) radical is adopted by a neutral molecule; Examples:

    - Reaction of hydroxyl radical with propylene:



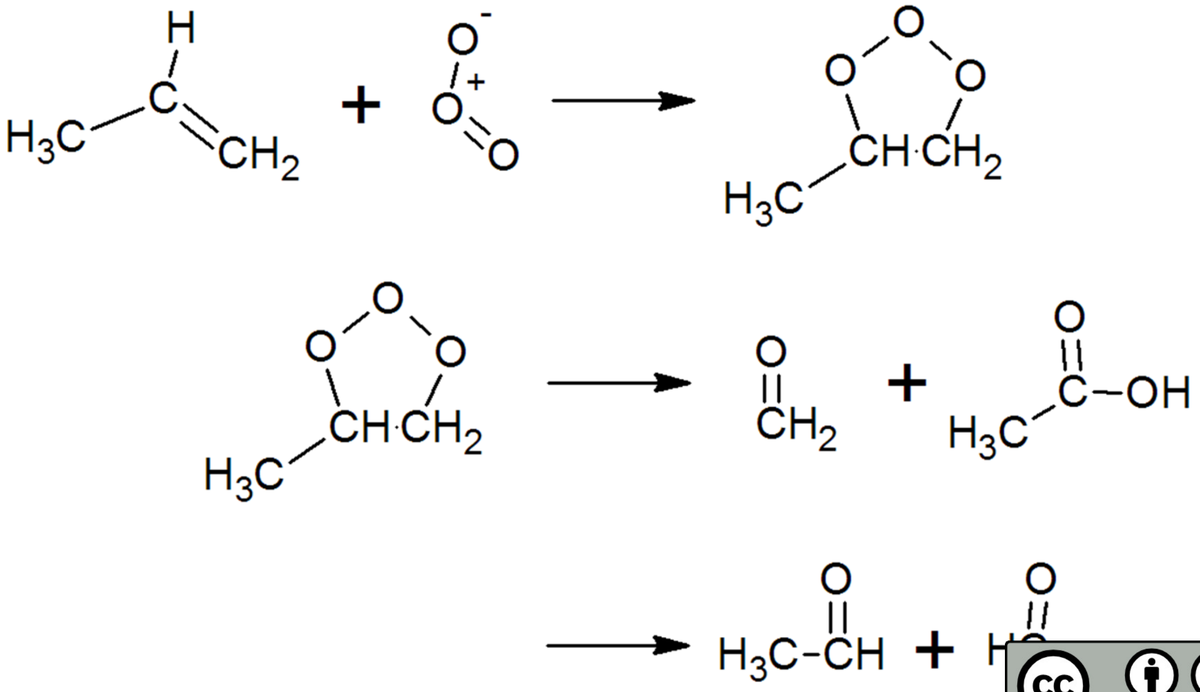
    - Reaction of nitrate radical with propylene:



Distribution of atmospheric reactions

- **Homogeneous bimolecular reactions**
  - Reaction on the basis of substitution type metathesis

Less frequent type of atmospheric reaction with formation of transition state with more reaction centers and subsequent cleavage of the intermediate into products: Example – ozonolysis of propylene with primary addition of O_3 on double bond of olefine (so called ozonide)



Note: in fact bimolecular addition, followed by monomolecular cleavage of an intermediate (adduct)

Distribution of atmospheric reactions

- **Homogeneous termolecular reactions**
  - Common principle is recombination of 2 molecules, atoms or radicals in presence of third particle, which condition the reaction course by absorption of excessive energy.
  - 2 particles, entering the reaction, usually contain excess of energy ⇒ second condition for reaction course. Examples:

Combination of atoms of O to form the molecule:

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

Importance of M: removal of energy from O_2, otherwise the energy exceeding the limit causes homolytical molecule cleavage.

Generation of Ozone:

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

Oxidation of nitrogen oxide by oxygen (see chapter NO_x):

$$NO + NO + O_2 \rightarrow 2NO_2$$

Reactions distribution by mechanism

- **Photochemical reactions**
  - Reactions with the highest importance for atmospheric chemistry;
  - First step for realisation of the photochemical reaction = absorption of light quantum by molecule;
  - Absorption of energy induces excitation of the molecule;
  - In the atmosphere, there are 3 types of unstable, very reactive particles:
    - Electronically excited molecules (e.g. NO_2^*)
    - Free radicals (atoms or molecular fragments with unpaired electrons)
    - Atomic or molecular ions

Reactions distribution by mechanism

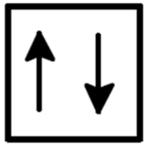
- **Photochemical reactions**
  - Excitation allowable by absorption of UV + VIS irradiation (low E ⇒ lowest excited states):

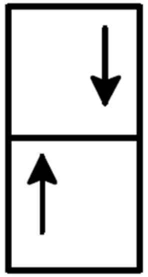
Excited singlet state

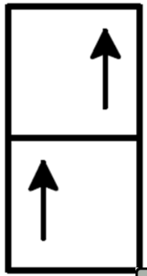
= one of the electron pair from the highest occupied orbital shifts into the higher orbital and has opposite spin than its counterpart

Excited triplet state

= e^- in the higher orbital and its counterpart in the initial orbital have identical spin


base singlet state


excited singlet state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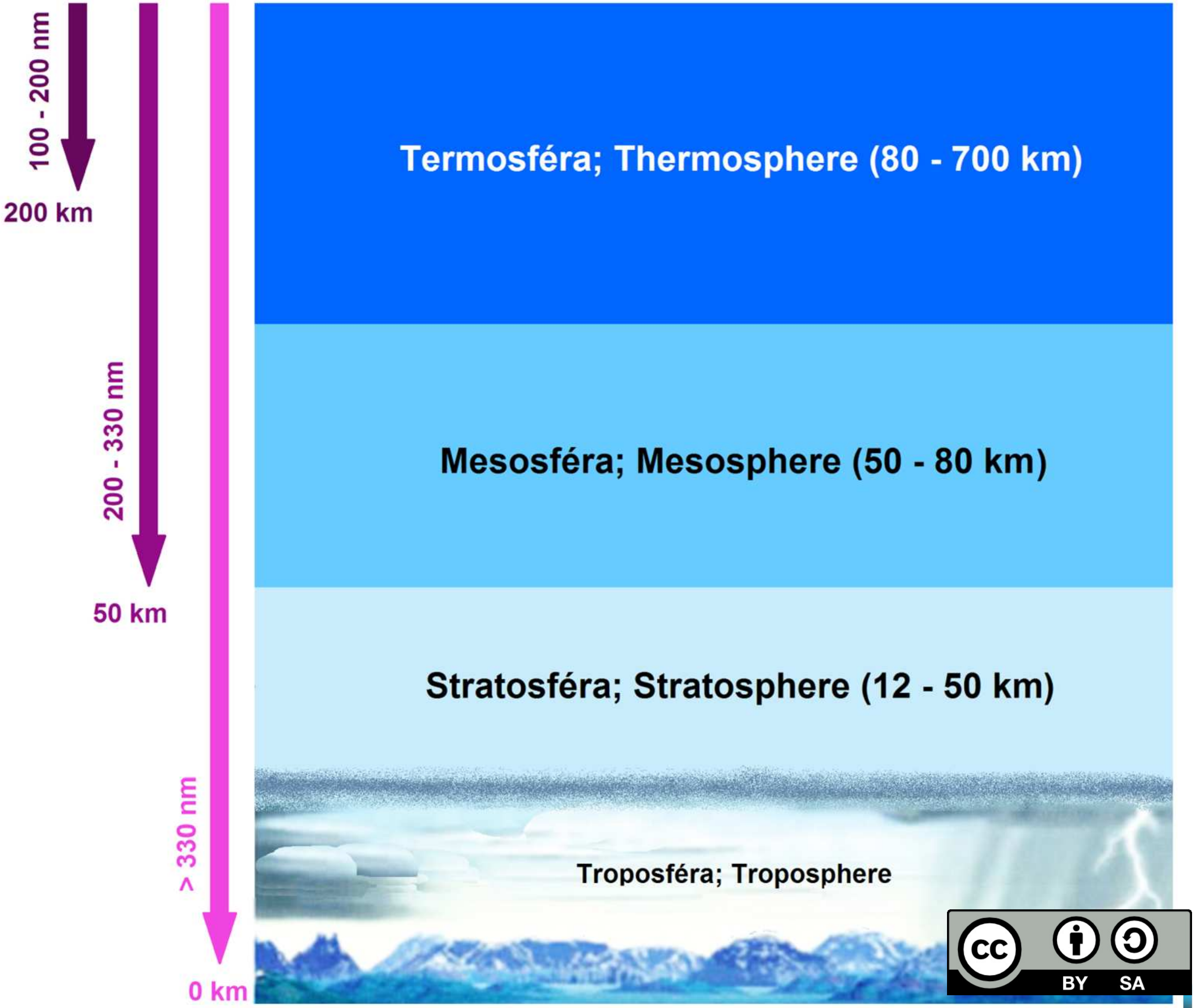
Reactions distribution by mechanism

- **Photochemical reactions**

Irradiation

throughtput

– see 1st lecture



Reactions distribution by mechanism

- Photochemical reactions
  - General range of wavelengths, involved into photochemical reactions: 280 – 750 nm; Irradiation with shorter wavelengths does not penetrate to lower atmosphere;
  - Infrared irradiation does not have sufficient energy for particles excitation (absorption in IR part of spectrum only increases kinetic energy ⇒ elevation of atmospheric temperature);
  - NO_2 is maximum absorbing gas among photochemical reactants:

between 300 – 370 nm	90 % dissociation into NO + O
between 370 – 420 nm	decrease from 90 % to 0 %
over 420 nm	does not react

  - Furthermore significant participation in photochemical reactions have: O_3, formaldehyde, higher aldehydy a ketones, nitrous acid;
  - Within wavelengths available in troposphere don't react: SO
    CO, C_xH_y and derivatives except karbonyl compounds.

Reactions distribution by mechanism

- **Photochemical reactions**
  - After excitation the particle has excessive energy, which is unloaded alternatively by the following ways:
    - **Energy transmission to another particle**, which gets higher translation energy and subsequently releases it as heat;

$$O_2^* + M \rightarrow O_2 + \overset{\overset{HEAT}{\uparrow}}{M}$$

    - **Dissociation of excited molecule**, example – formation of atomic oxygen in higher layers of atmosphere;

$$O_2^* \rightarrow O + O$$

    - **Direct reaction with another substance**: creation of another molecules or one molecule and cleaved atom and so on.

$$O_2^* + O_3 \rightarrow 2O_2 + O$$

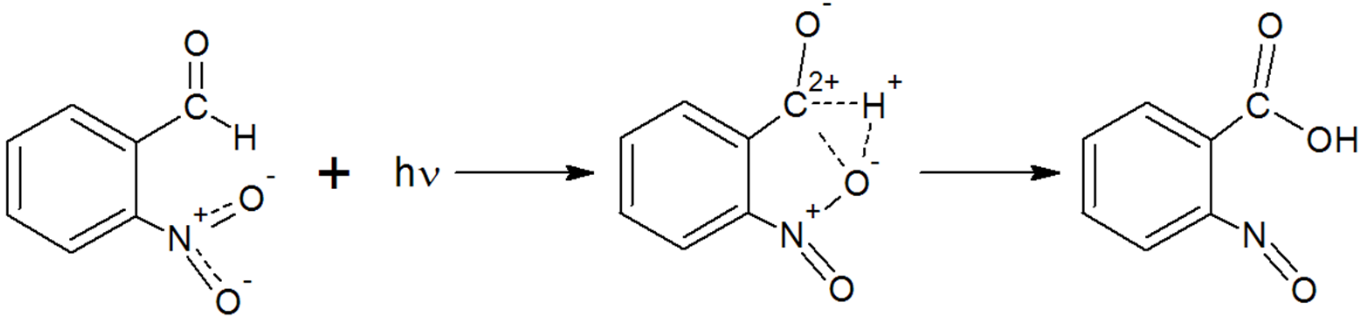
Reactions distribution by mechanism

- **Photochemical reactions**
  - After excitation the particle has excessive energy, which is unloaded alternatively by the following ways:

Deactivation by collision: excited particle gives energy to another particle, which is excited secondarily;

$$O_2^* + K \rightarrow O_2 + K^*$$

Spontaneous isomerisation, energy is consumed for change of structure of the molecule: example transformation of o−nitrobenzaldehyde into o-nitrosobenzoic acid;



Photoionization, loss of electron

$$N_2^* \rightarrow N_2^\bullet + e^-$$

Reactions distribution by mechanism

- **Photochemical reactions**
  - After excitation the particle has excessive energy, which is unloaded alternatively by the following ways:

→ **Luminescence** = lost of energy via irradiation of electromagnetic quantum, e.g. reaction of nitrogen dioxide as the main reactant in photochemical smog;

$$NO_2 + h\nu \rightarrow NO_2^*$$

$$NO_2^* \rightarrow NO_2 + h\nu$$

3 variants of luminescence:

→ Fluorescence (immediate irradiation, so called re-emission)

→ Phosphorescence (irradiation with time delay)

→ Chemiluminescence (after excitation by chemical reaction)

$$O_3 + NO \rightarrow NO_2^* + O_2$$

$$NO_2^* \rightarrow NO_2 + h\nu$$

Reactions distribution by mechanism

- **Acid base reactions**
  - Reactions involves acidic compounds: CO_2, SO_2, NO_x, and basic compound: $Ca(OH)_2$, $CaCO_3$, NH_3
  - In average, the atmosphere is slightly acidic due to dissolving of CO_2 in water aerosol and its subsequent partial dissociation:

$$CO_2(g) \xrightarrow{water} CO_2(aq)$$

$$CO_2(aq) + H_2O \xrightarrow{dissociation} H^+ + HCO_3^-$$

SO_2 and NO_x, react by the similar way, however they yield stronger acids ⇒ acidic deposition ⇒ eutrophication of water, damaging vegetation.

Note. Above mentioned effects discussed in more details within lectures aimed at sulphur and nitrogen oxides.

Reactions distribution by mechanism

- **Acid base reactions**
  - Concentration of basic compounds in air is lower due to its low pH;
  - $Ca(OH)_2$ and $CaCO_3$ emitted into atmosphere in a form of dusty particles from mining activities and limestone treatment for building materials. Subsequent reaction with atmospheric acids, present in water aerosol:

$$Ca(OH)_2(s) + H_2SO_4 \longrightarrow CaSO_4(s) + 2H_2O$$

  - Among bases, ammonia is the most important; NH3 emitted via biological mechanisms:
    - biological decomposition of nitrogen-containing compounds with animal and vegetal origin
    - bacterial reduction of nitrates

$$NO_3^- + 2\{CH_2O\}_{biomas} + H^+ \rightarrow NH_3(g) + 2C$$

Reactions distribution by mechanism

- **Acid base reactions**
  - Generated ammonia is dissolved in water aerosol and further reacts with atmospheric acids:

$$NH_3(aq) + H_2SO_4(aq) \longrightarrow NH_4HSO_4(aq)$$

$$NH_3(aq) + HNO_3(aq) \longrightarrow NH_4NO_3(aq)$$

  - Mentioned processes have both positive and negative impact:

neutralisation of acidic corrosive components (against acid rains)

generation of corrosive ammonia salts in a form of aerosol

Reactions distribution by mechanism

- **Nuclear reactions**
  - Atoms of heavy radioactive elements usually emits α particles (helions) or β particles (electrons).
  - Cores of radioactive elements transform into the cores of another element via decay chains. From the viewpoint of atmospheric chemistry Uranium decay chain is the most important;
  - Properties of U: bright silver metal, on air grey oxides formed on the surface, ρ_U = 19,01 g.cm^{-3} at 25 °C , (ρ_{Au} = 9,3 g.cm^{-3}, ρ_{Pt} = 21,45 g.cm^{-3}), melting p. 1132,3 ± 0,8 °C, appearance in minerals:

Autunite > 48 % U and Uraninite 88,15 % U (Source: .wikimedia.org/wiki/File:Uraninite-39029.jpg)

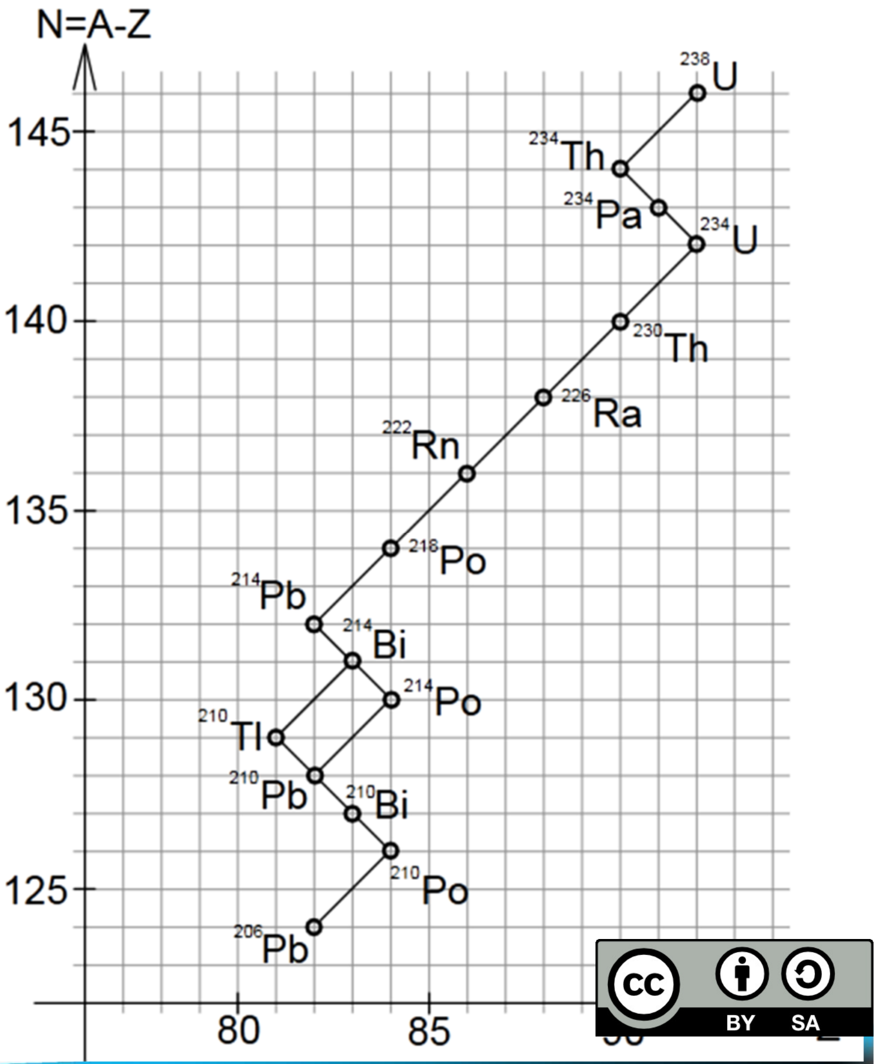
Reactions distribution by mechanism

- **Nuclear reactions**
  - Uranium 238 exists in Earth’s crust in rocks (ca. 50 % of initial weight already decayed since the planet formation)
  - In the decay chain, decay into Rn is the most important for air: 1st α-decay into Th, 5th α-decay into Ra, 6th α-decay into Radon

$$^{238}_{92}U \longrightarrow {}^{234}_{90}Th + {}^{4}_{2}He$$

$$^{226}_{88}Ra \longrightarrow {}^{222}_{86}Th + {}^{4}_{2}He$$

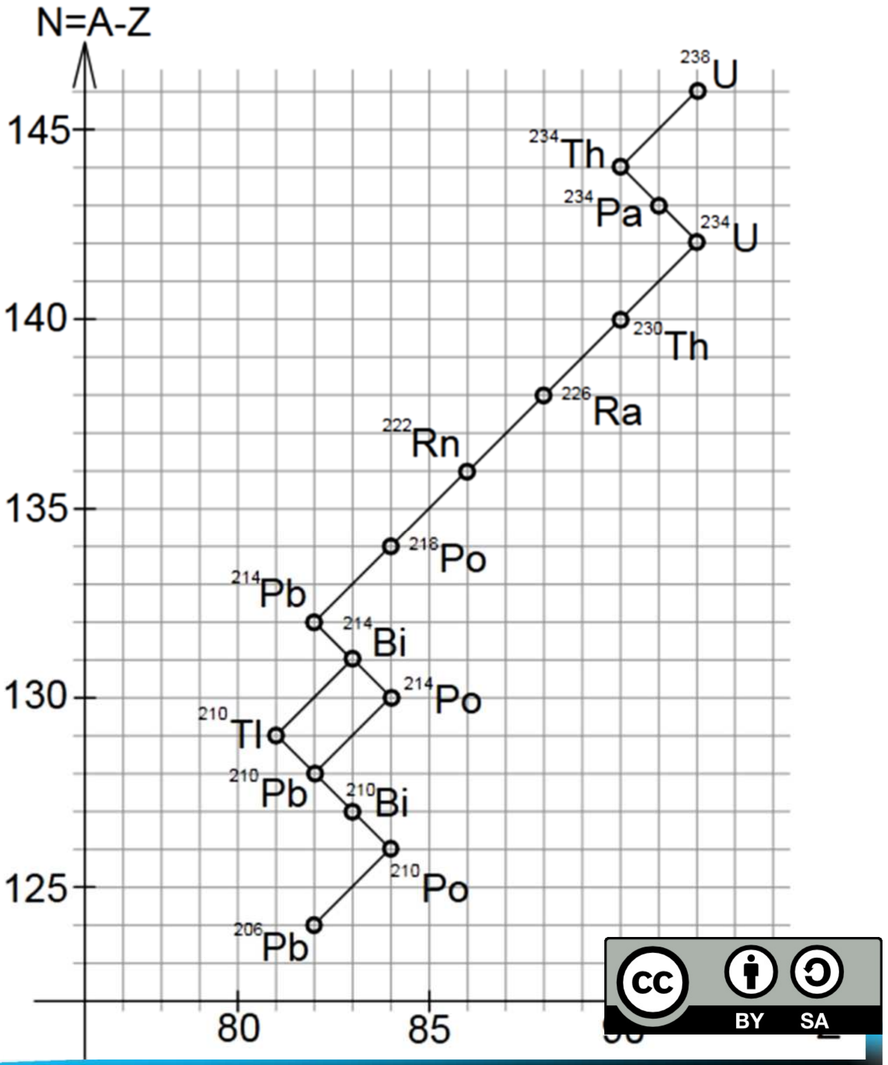
Isotope	Decay halftime
^{238}U	4,468 billion years
^{234}Th	24,1 days
^{226}Ra	1 600 years
^{222}Rn	3,824 days



(A = nucleon , N = neutron, Z = atomic, proton number)

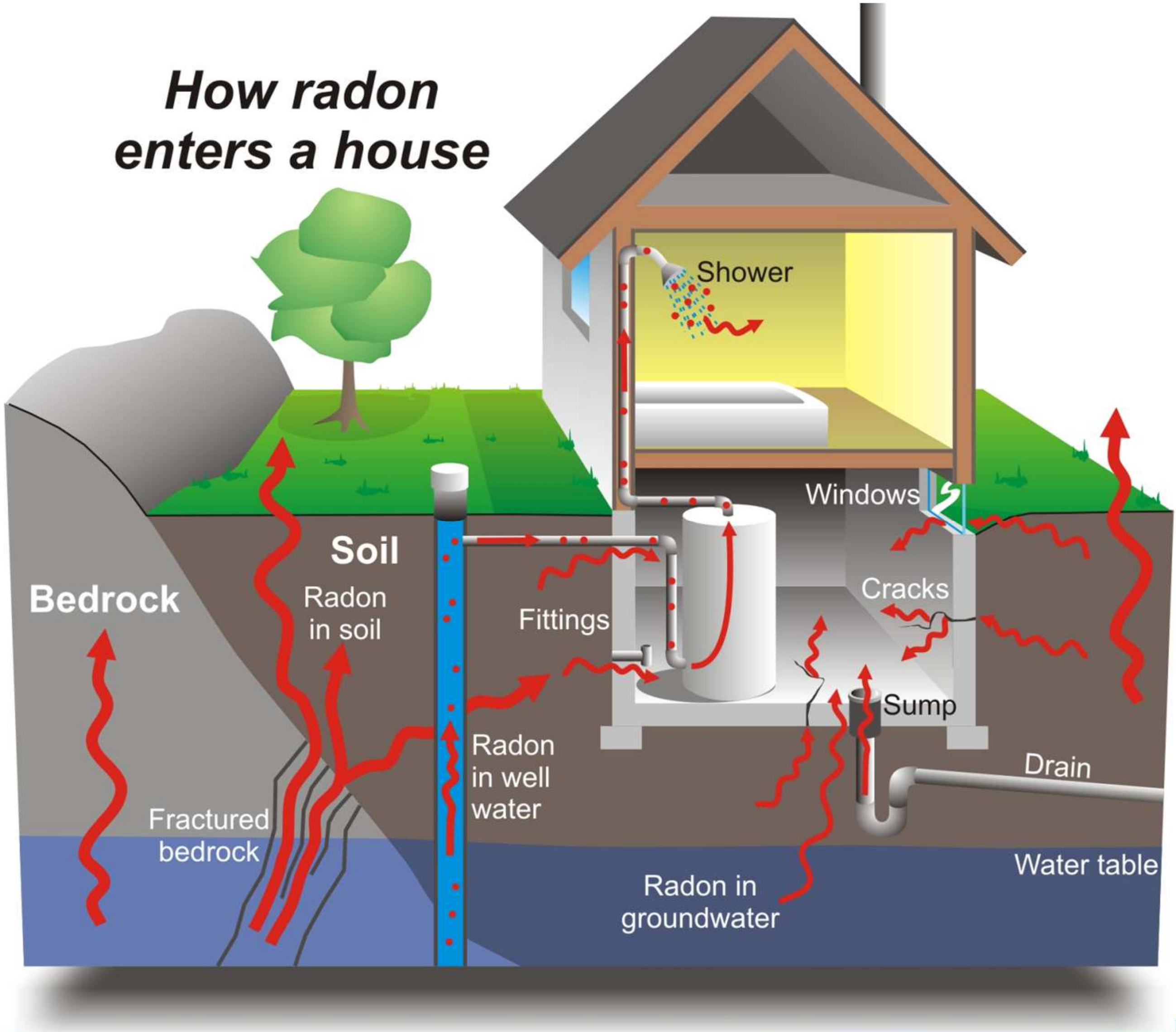
Reactions distribution by mechanism

- **Nuclear reactions**
  - Radon permeates through soil, rocks, bore holes and mines to the air.
  - Background concentration of Rn is responsible for 50 % of natural atmospheric radioactivity
  - Rn is not toxic itself.
  - Only products of its further decay are dangerous.
  - Isotopes Po, Pb, Bi are easily adsorbed onto dusty particles, which fraction < PM_3 penetrates into pulmonary alveolus and causes lung cancer.



Reactions distribution by mechanism

- Pathways of Rn leakage to houses (Source: www.rangerradonservicesinc.com)



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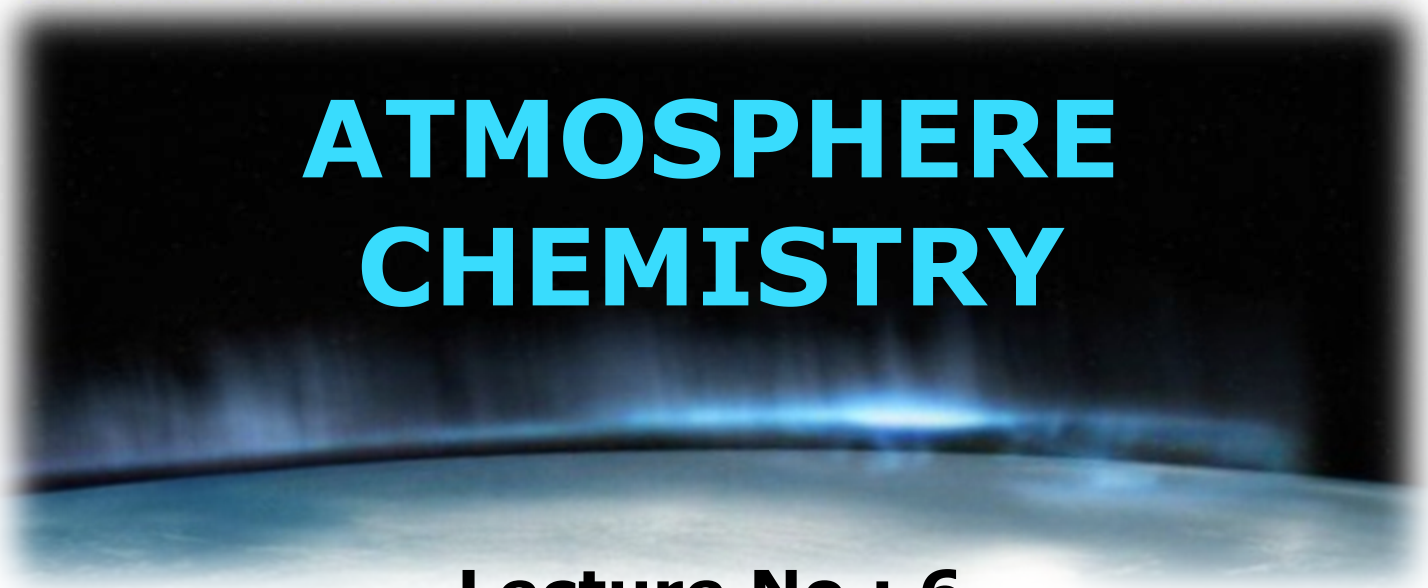

ATMOSPHERE CHEMISTRY

Lecture No.: 6

Organisation of study

- Lecturer: Marek Staf, MSc., Ph.D., phone: +420 220 444 458

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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 - oral form
- Note:

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Scope of lecture 6

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

- General classification of the all types of pollutants according to their effect
- Overview of the main greenhouse gases
- Mechanism of greenhouse gases impact
- 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 economical activity and GHG emissions
- Worldwide emissions of the major GHGs according to their chemical properties and industrial sector

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 - chemically, physically or due to their radioactivity damage health of plants and animals;
  - Substances damaging O_3 - decompose stratospheric ozone layer;
  - Greenhouse gases - change a balance between heat absorption and radiation from the atmosphere;
  - Precursors - in their initial form show no dangerous properties, but undergoes changes resulting in above mentioned properties, or they allow other compounds 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 for reporting 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

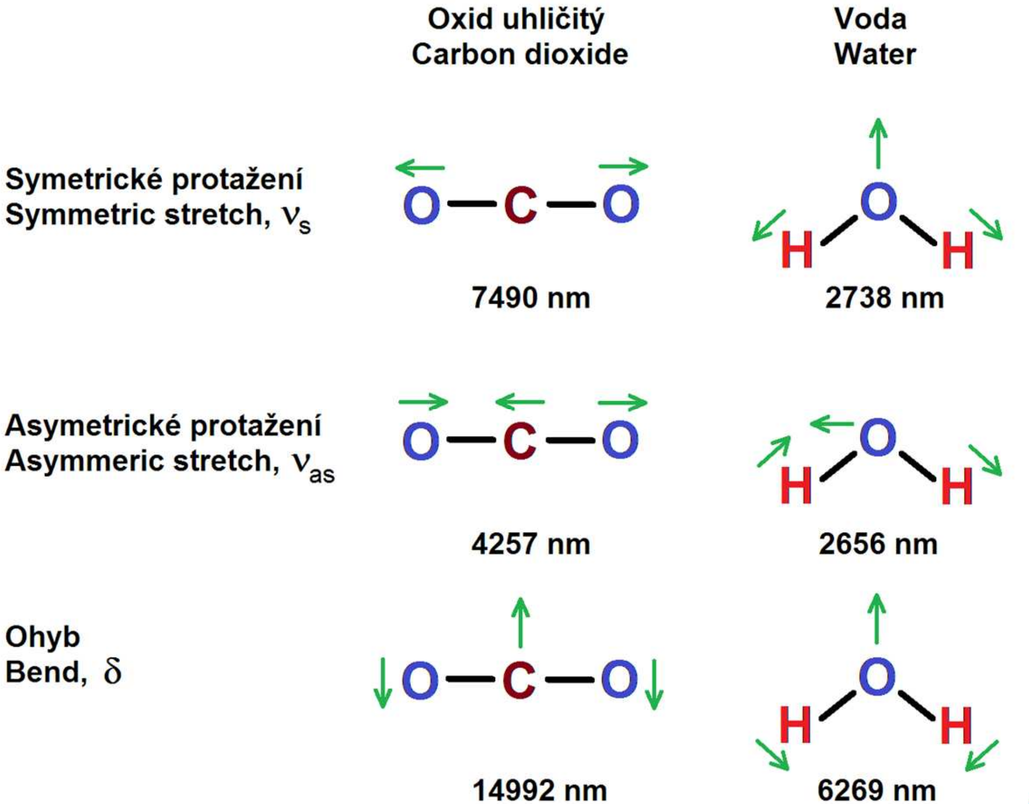
- Main greenhouse gases – distribution and abbreviations:
  - H_2O (vapour)
  - CO_2
  - C_xH_y (especially CH_4)
  - N_2O
  - F-gases a ClF-gases:
    - CFCs (chlorofluorocarbons)
    - HFCs (hydrofluorocarbons)
    - PFCs (perfluorocarbons)
    - SF_6 (sulfur fluoride)
  - O_3

Effect of greenhouse gases

- Mechanism of GHG impact:
  - Greenhouse gas must absorb irradiation in IR part of spectrum;
  - Quantum transition during IR absorption = values of molecular vibrations;
  - GHG molecule must change its dipole moment due to IR absorption;
    - Symmetric di-atomic molecules, like H_2, N_2, O_2, do not change dipole moment ⇒ they are IR inactive;
    - Molecules with different partial charges on the atoms, like CO, CO_2, N_2O, NO, HCl, change dipole moment ⇒ they are IR active;
  - GHG molecule must have sufficient lifetime in the atmosphere and must be present in sufficient concentrations (e.g. average content of H_2O = 0.4 % vol., average content of CO_2 < 0.04 % vol.).

Effect of greenhouse gases

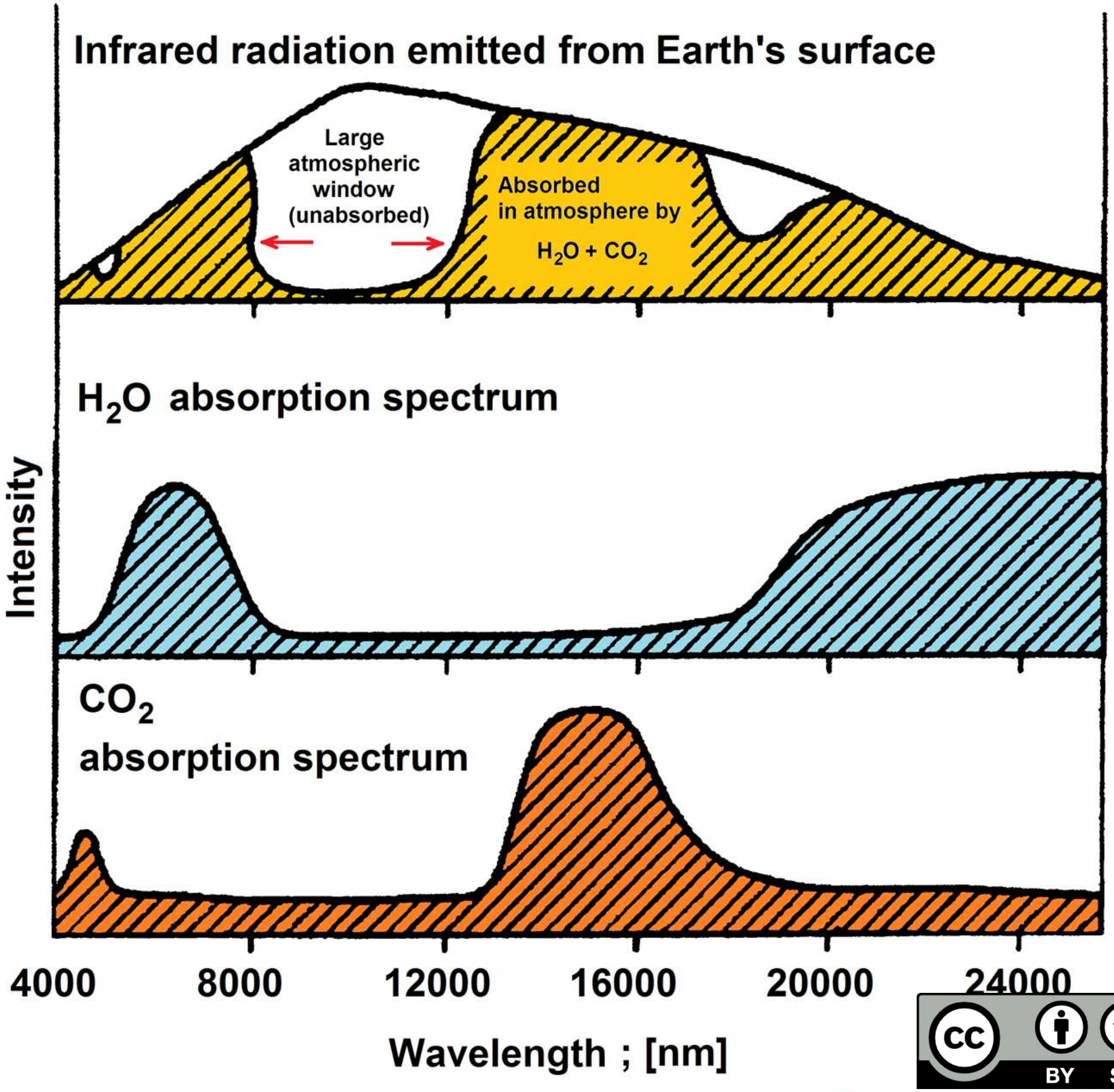
- Mechanism of GHG impact:
  - Each molecular vibration has its specific wavelength value, but 1 molecular vibration induces high number of various rotation levels ⇒ extension of absorption belt width.
  - Example – molecular vibrations of CO_2 and H_2O:



Effect of greenhouse gases

- Mechanism of GHG impact:

Due to extension of absorption belt width CO_2 and H_2O covers dominant part of IR irradiation, emitted by Earth’s surface back to the outer space



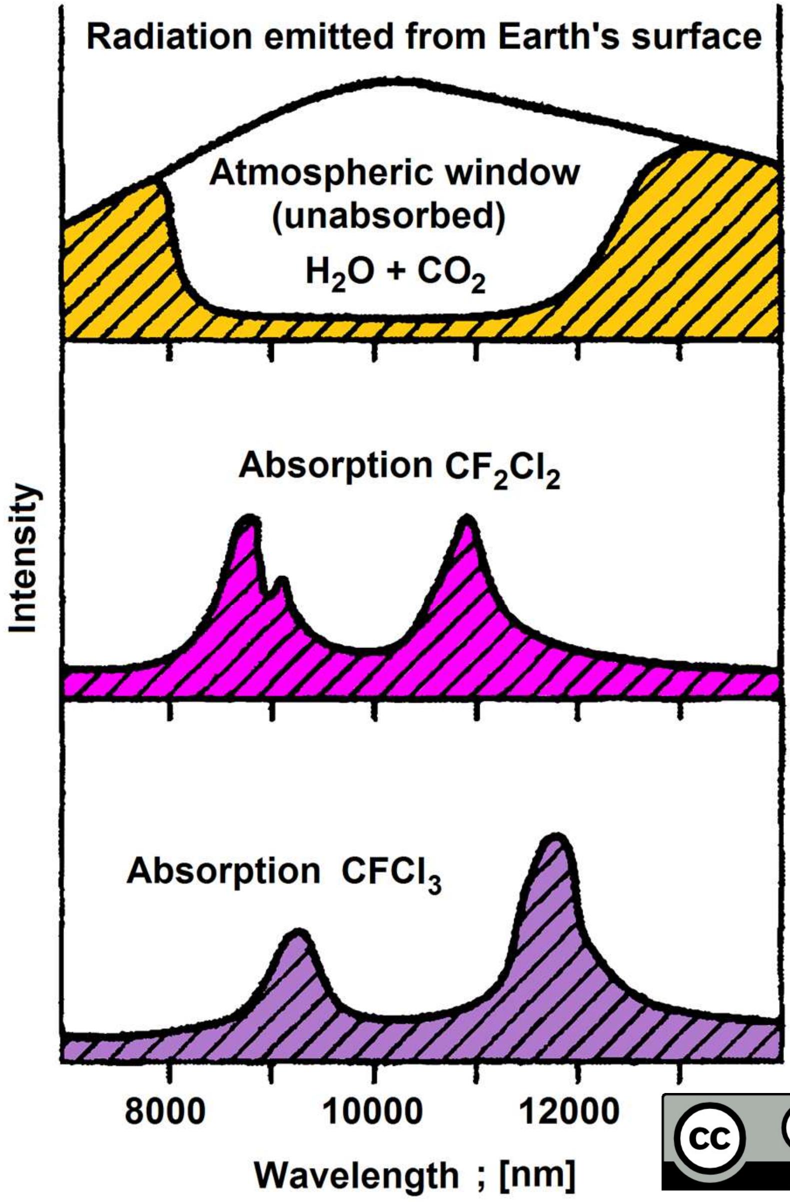
Effect of greenhouse gases

- 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 atmospheric window is much more 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 the gas;
  - It compares the amount of heat, retained by certain amount of the gas, relative to the same amount of CO_2;
  - It is expressed as a dimensionless factor related to CO_2, having factor 1 assigned;
  - GWP is calculated for a specific time frame, usually 20, 100 or 500 years;
  - E.g. In 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

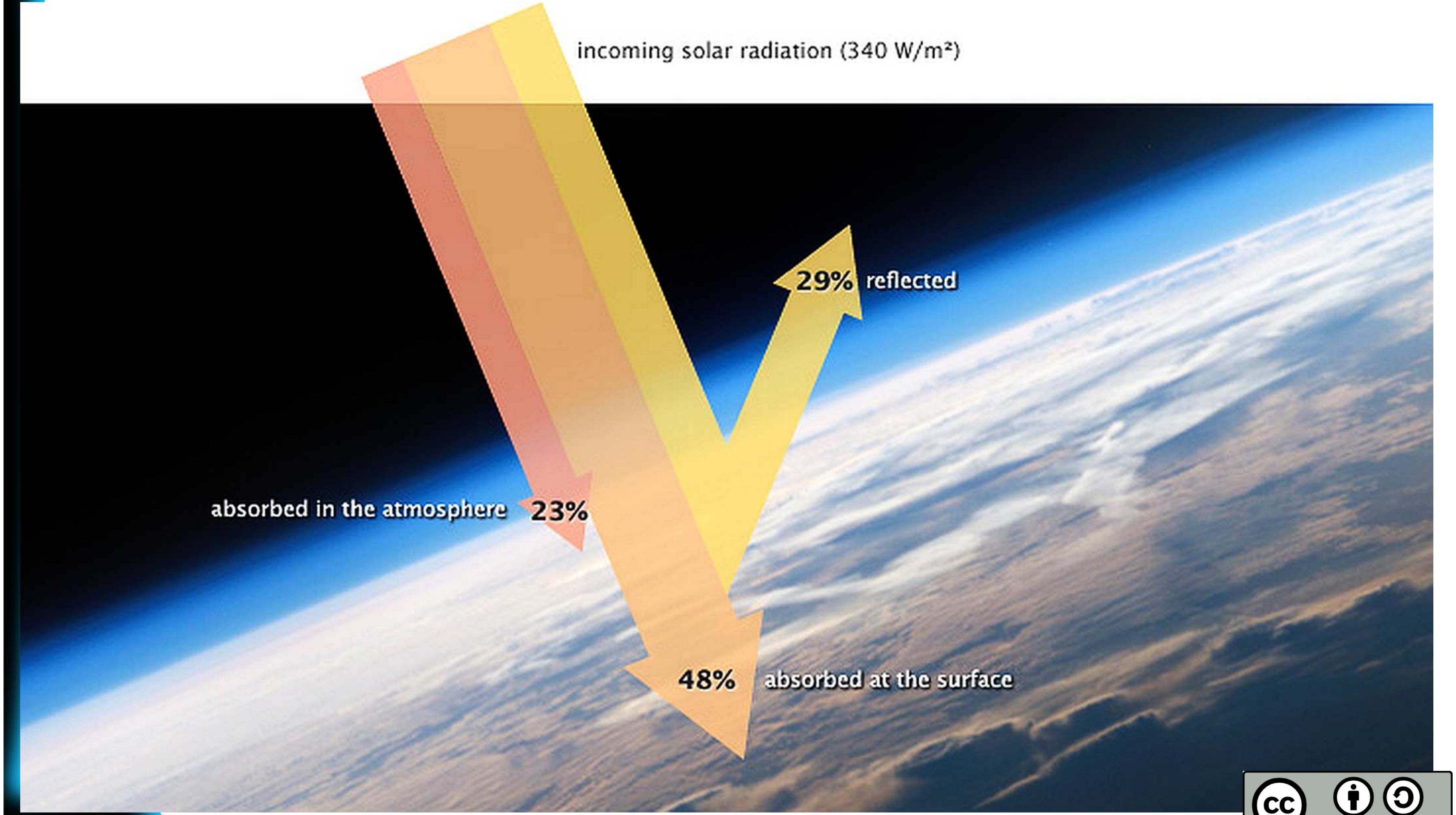
- Global warming potential, GWP
  - High GWP correlates with high absorption of IR part of spectrum and with long lifetime of the substance in the atmosphere.
  - Dependence of GWP on absorbed wavelength is more complicated. If the gas is absorbed at a particular wavelength, it does not have a large impact on its GWP, if the atmosphere already absorbs most of the radiation with this wavelength by the different way.
  - The gas has the greatest effect when it absorbs in the window, where the atmosphere is transparent. Dependence of GWP as a function of wavelength was determined empirically.
  - GWP of each greenhouse gas depends directly on its IR spectrum ⇒ 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 ⇒ warming of the system;
  - Negative radiative forcing = predominance of the emitted energy over absorbed energy ⇒ cooling of the system.

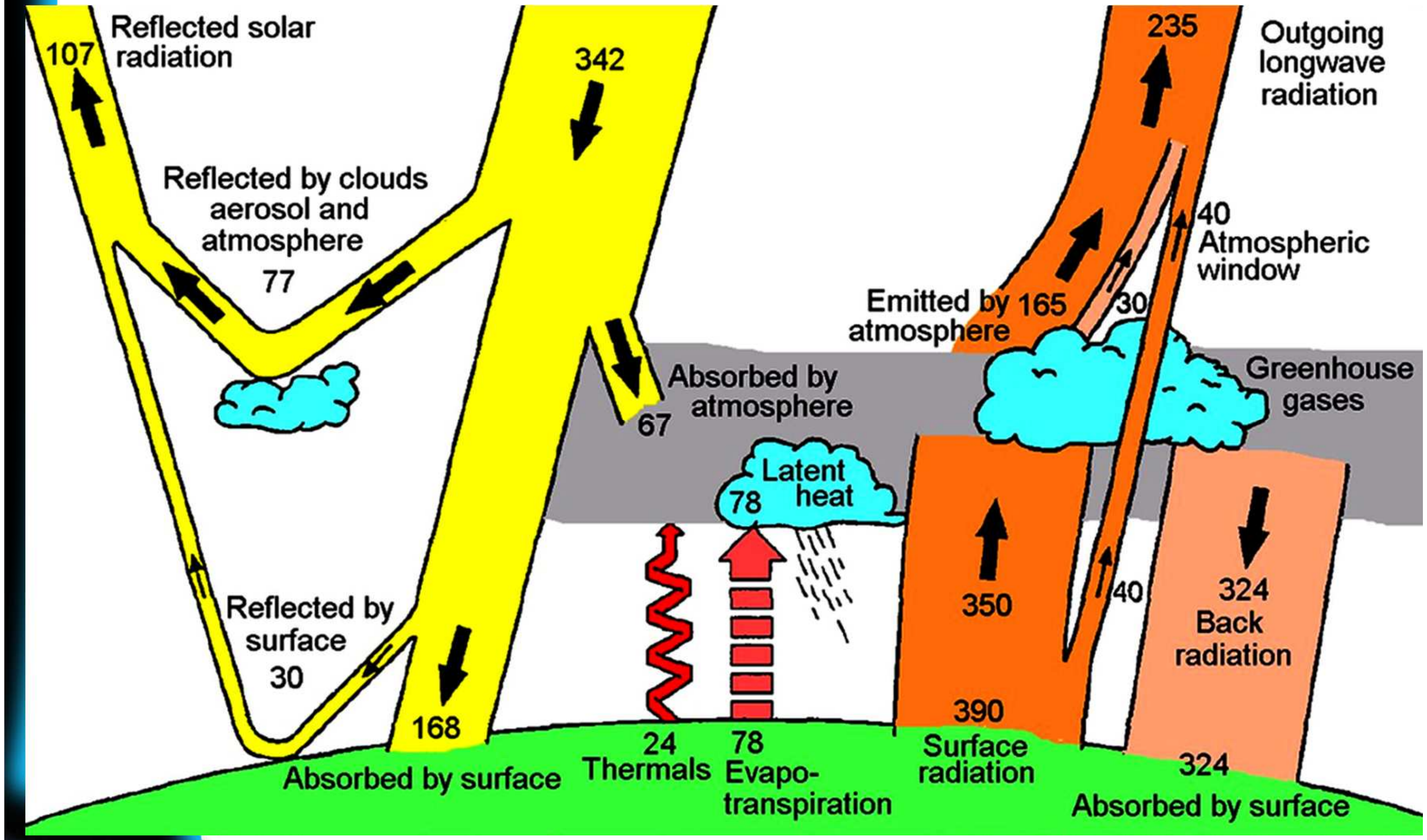
Calculation of GHG impact

- 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 showed 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
  - Radiative forcing gives simplified means for comparing various factors, which are supposed to influence the climate system.
  - Global Warming Potential (GWP) is one type of 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

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

  - Symbols in the figure above mean:

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

Abs$_i$ … Integrated infrared absorbance in ith interval;

F$_i$ … Radiative forcing in ith 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 the gas within the scale of all wavelengths, which are absorbed by the 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 third IPCC report.
  - GWP is defined as a ratio of the radiative forcing of 1 kg of the trace gas, integrated according to time, and radiative forcing of 1 kg of the reference gas.
  - Equation for calculation of the GWP for one concrete 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 whole selected time horizon;
  - For a majority of gases IR absorbance increases linearly with their abundance in the atmosphere;
  - Several important GHG 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 $CO_2 \Rightarrow$ 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 to overall IR absorption (saturation of corresponding wavelengths) if compared with the gases with different IR a bands $\Rightarrow$ This was considered for new GWP values.

Calculation of GHG impact

- Global warming potential (GWP)
  - Special problem – GWP calculation for water;
  - Unlike other GHG water is not decomposed in the environment ⇒ time scale of lifetime cannot be applied: Water vapour has IR spectrum containing higher number and wider absorption bands than CO_2;
  - Water vapour absorbs nonzero 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 Earth temperature is not equally distributed, continents differ from oceans as well as north 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. 0,0 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; + archiving of data and calculations for future checking by the international inspection team.

Monitoring of GHG

- National Greenhouse Gas Inventory:
  - Emissions of all GHG 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 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 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 fuels 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 the 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 Czech Republic this sector shows higher CO_2 capturing than it emissions ⇒ 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 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 emission from dumps:

1. It is supposed that 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 ⇒ 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

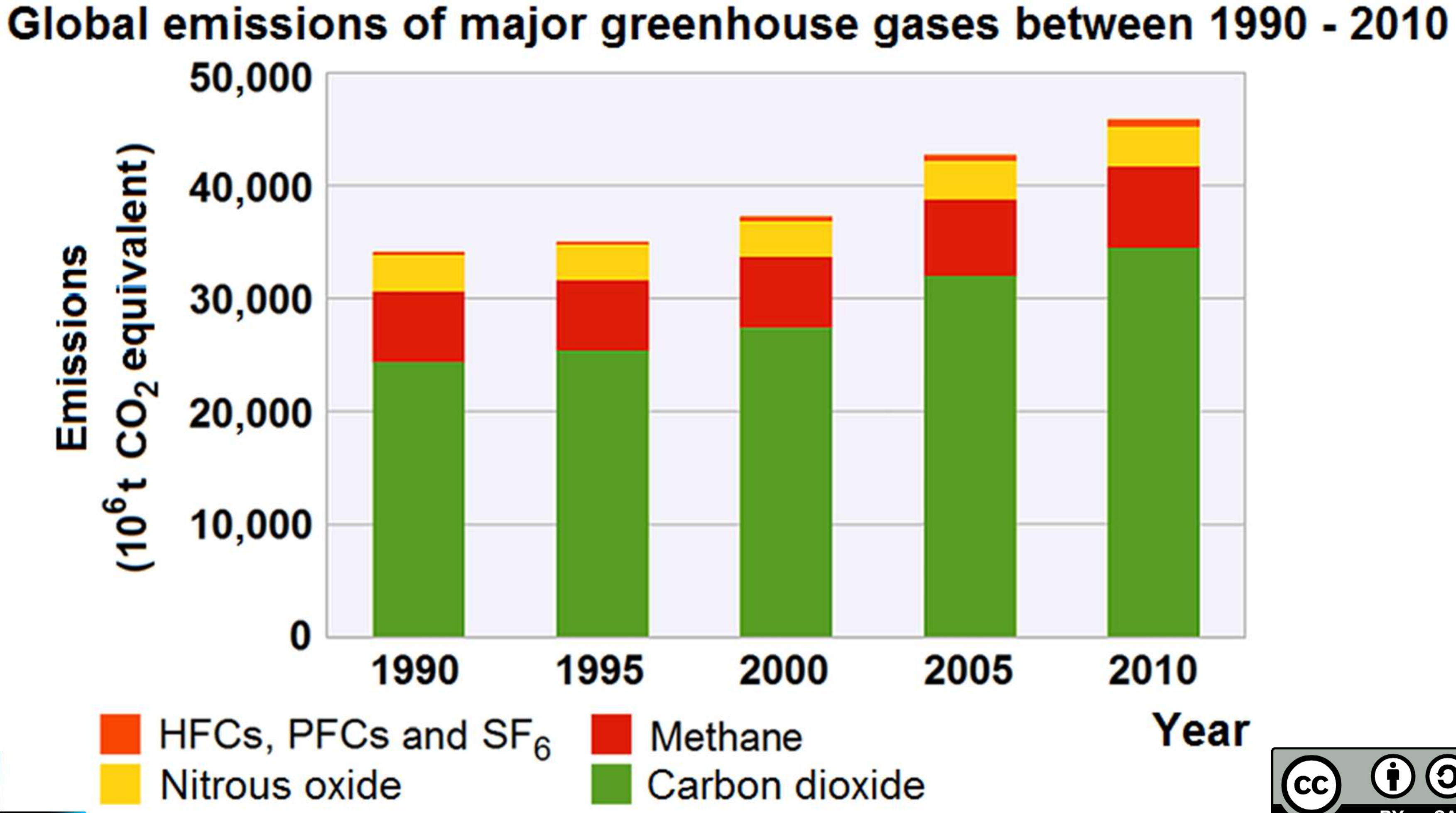
Monitoring of GHG

- **Production of greenhouse gases** (Source: Gomes; Carbon Dioxide Capture and Sequestration)
  - Values for preindustrial era were 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

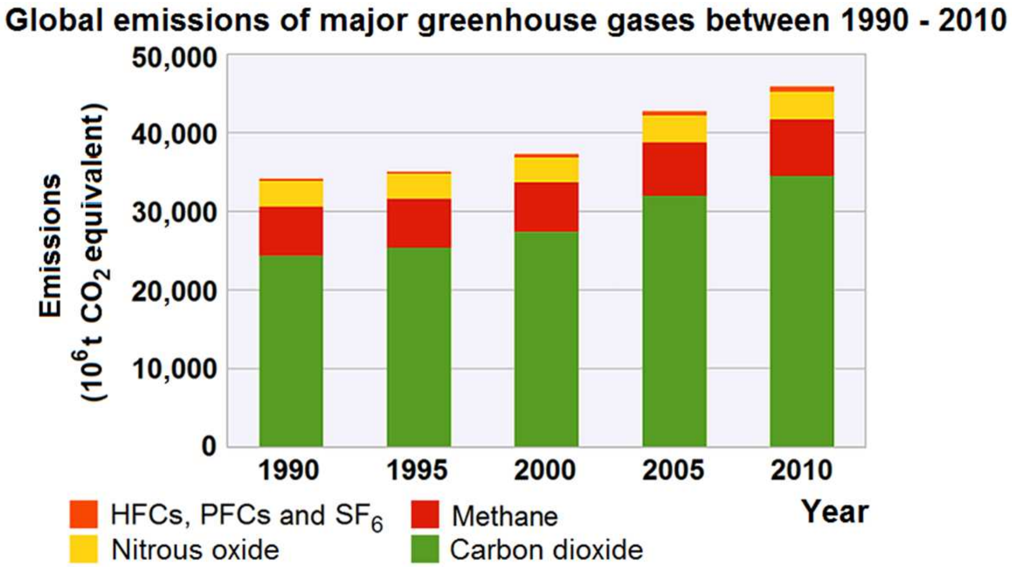
- **Production of greenhouse gases**
  (Sources: http://cait.wri.org, www.epa.gov/climatechange/indicators, http://faostat3.fao.org/faostat-gateway/go/to/download/G2/*/E))



Monitoring of GHG on global level

- Global emissions of greenhouse gases

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



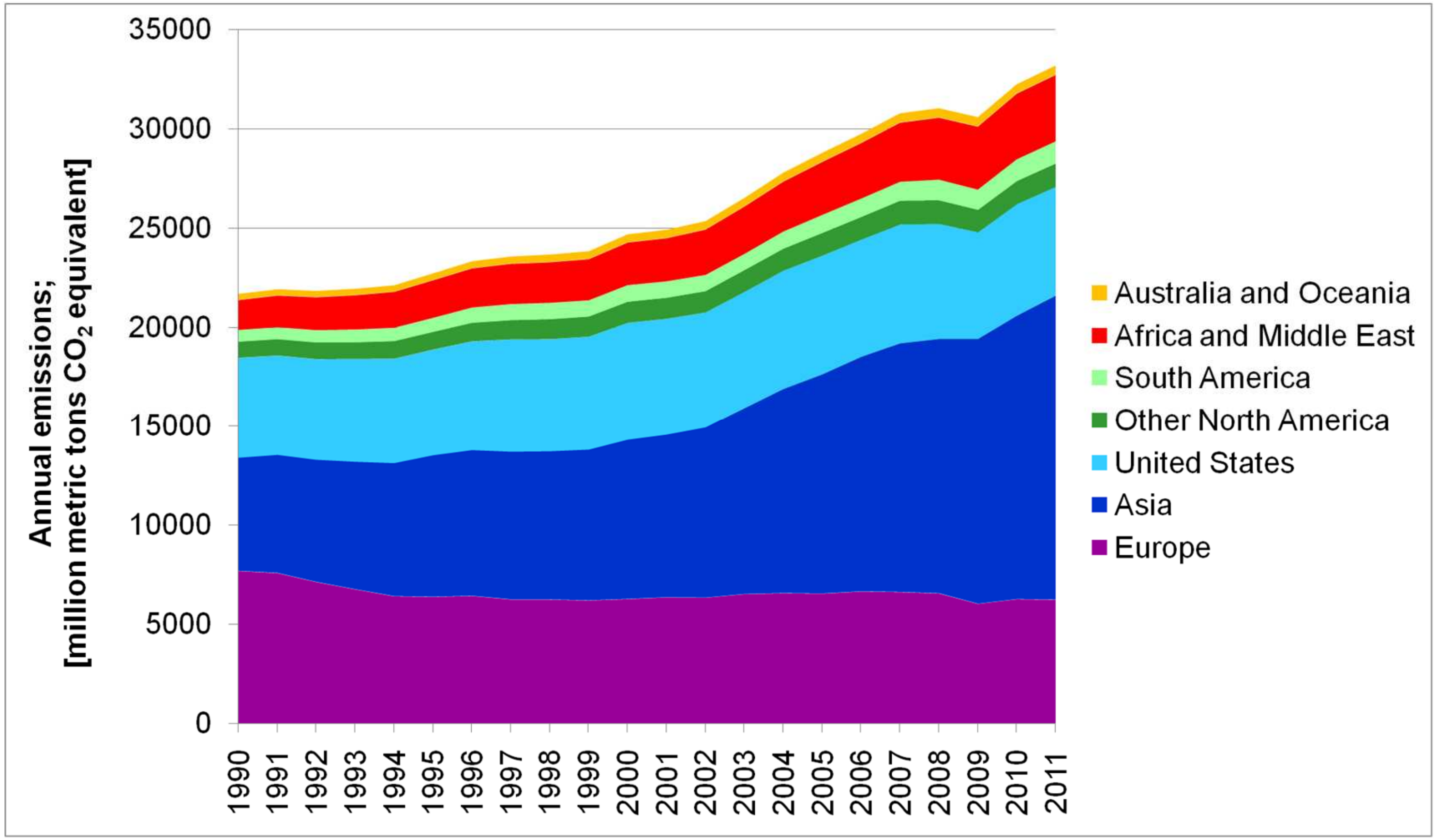
Global emissions of major greenhouse gases between 1990 - 2010

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	[illegible]

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)

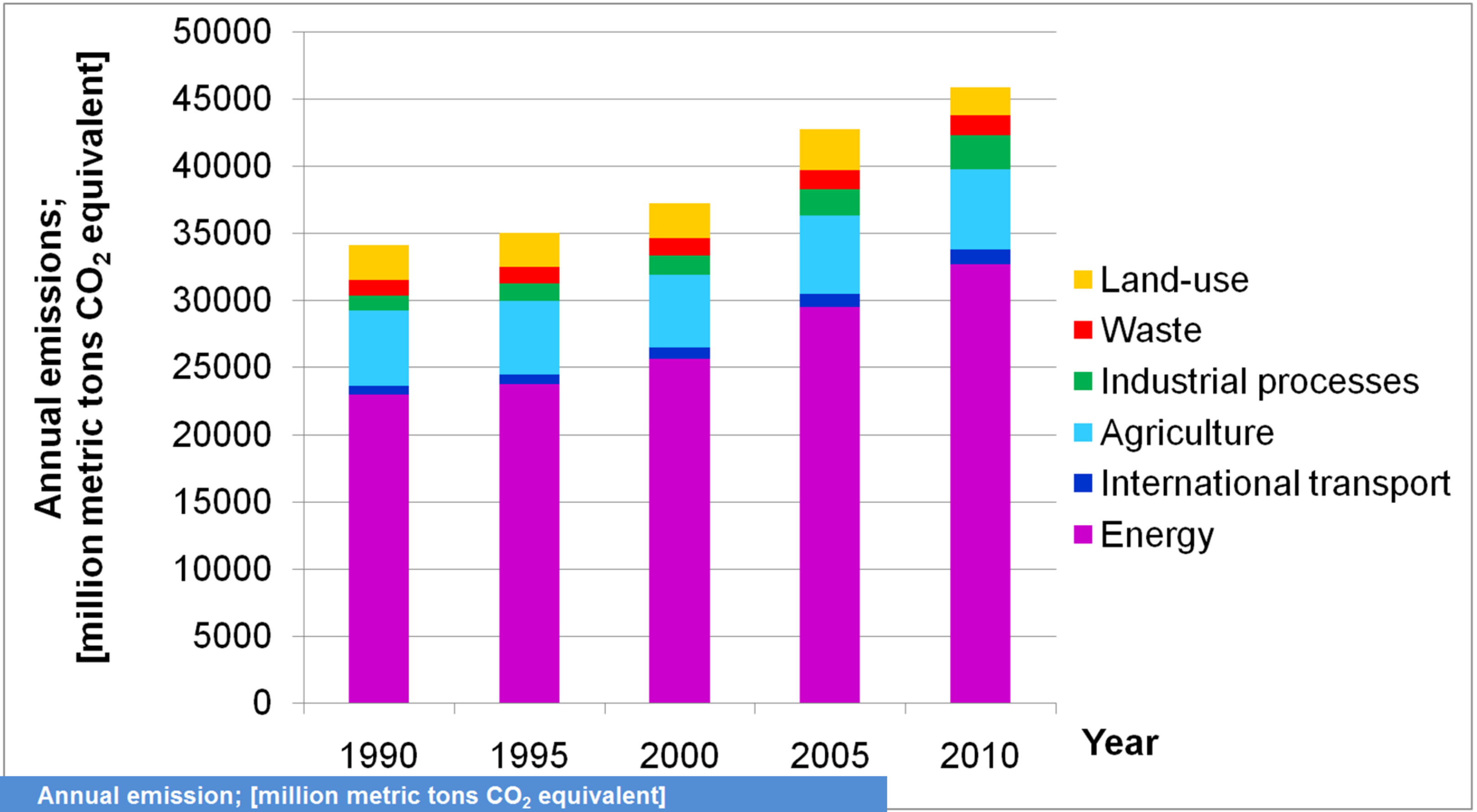


Region	Annual emission; [million metric tons CO_2 equivalent]																					
	1990	1991	1992	1993	1994	1995	1996	1997	1998	1999	2000	2001	2002	2003	2004	2005	2006	2007	2008	2009	2010	2011
Europe	7 678	7 575	7 123	6 752	6 405	6 374	6 420	6 242	6 236	6 195	6 263	6 349	6 330	6 513	6 557	6 537	6 644	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	[illegible]	[illegible]	[illegible]	[illegible]
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	[illegible]	[illegible]	[illegible]	[illegible]
South America	576	590	605	630	657	697	759	800	816	809	828	823	814	810	865	912	929	959	[illegible]	[illegible]	[illegible]	[illegible]
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	[illegible]	[illegible]	[illegible]	[illegible]
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 sector**

(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

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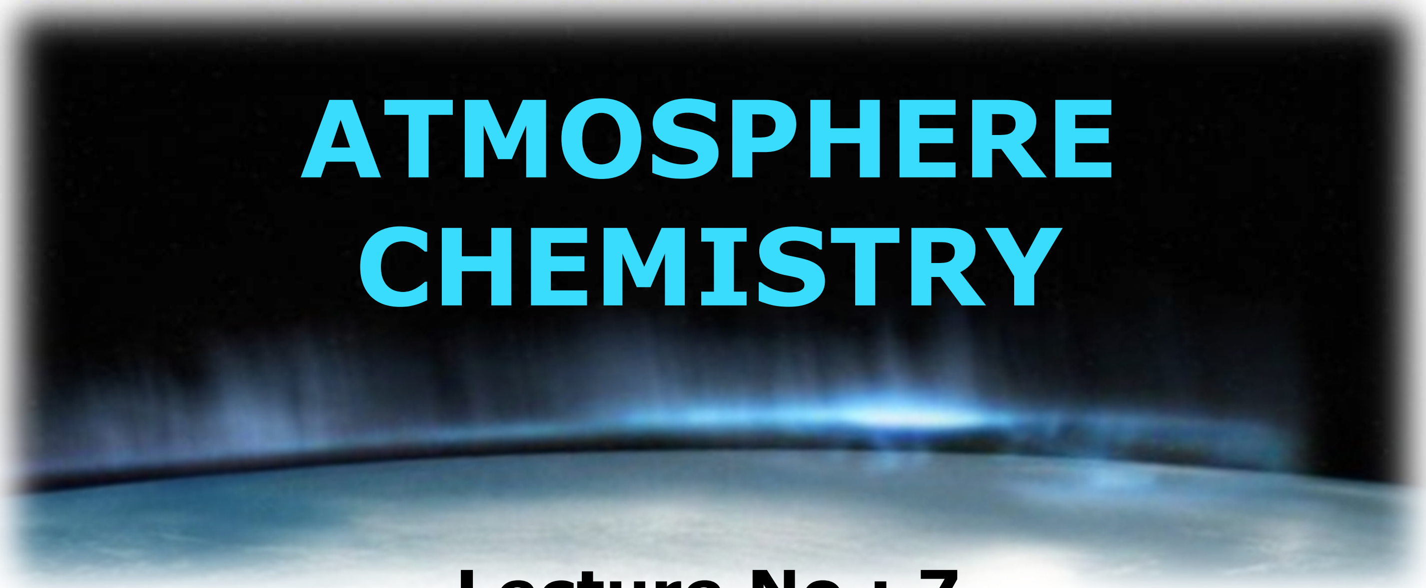

ATMOSPHERE CHEMISTRY

Lecture No.: 7

Organisation of study

- Lecturer: Marek Staf, MSc., Ph.D., phone: +420 220 444 458
  e-mail: marek.staf@vscht.cz,
  web: http://web.vscht.cz/~stafm/
  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 - oral form
- Note:

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Uveřejněné materiály jsou určeny studentům Vysoké školy chemicko-technologické v Praze jako studijní materiál. Některá textová i obrazová data v nich obsažená jsou převzata z veřejných zdrojů. V případě nedostatečných citací nebylo cílem autora/ů záměrně poškodit event. autora/y původního díla. S eventuálními výhradami se prosím obracejte na autora/y konkrétního výukového materiálu, aby bylo možné zjednat nápravu.

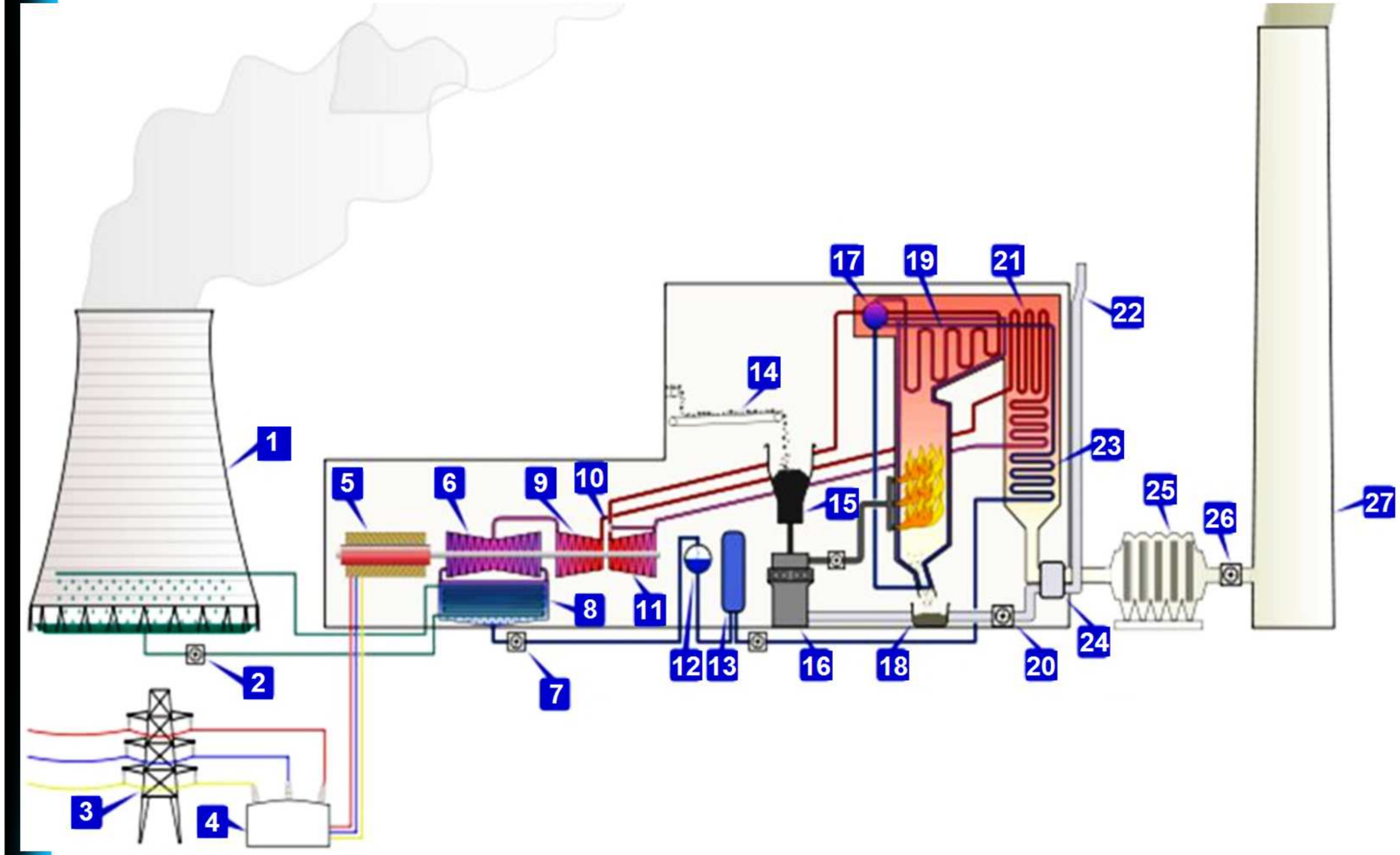
Scope of lecture 7

Pollutants and important chemical agents in the air – characterisation of the main greenhouse gases

- Power industry as the main source of carbon dioxide emissions
- Relationship between atmospheric concentration of CO_2 and global temperatures – difficulty of their projections to future
- Sources of hydrocarbons emissions and particularly methane
- Mechanism of atmospheric decomposition of methane
- Mechanism of atmospheric decomposition of higher hydrocarbons
- Sources of nitrous oxide emissions and its physico-chemical properties
- Manufacture of nitric acid as the main source of anthropogenic emissions of N_2O

Environmental issues of CO_2

- **Power industry – main source of CO_2** (Source: http://slideplayer.cz/slide/3668959/)



Legend:

1. Cooling tower
2. Cooling water pump
3. High voltage line
4. Transformer
5. Generator
6. Low pressure turbine
7. Water condensate pump
8. Condenser
9. Medium pressure turbine
10. Steam regulator
11. High pressure turbine
12. Venting
13. Water preheater
14. Coal feeding
15. Coal bin
16. Coal grinder
17. Steam boiler
18. Ash catchment
19. Steam superheater
20. Fan
21. Middle heater
22. Air inlet
23. Water economiser
24. Air pre
25. Flue gas cleaning unit
26. Flue gas fan
27. Stack

Environmental issues of CO_2

- **Relation between power industry and emissions of CO_2**

  (Source: Gomes; Carbon Dioxide Capture and Sequestration)

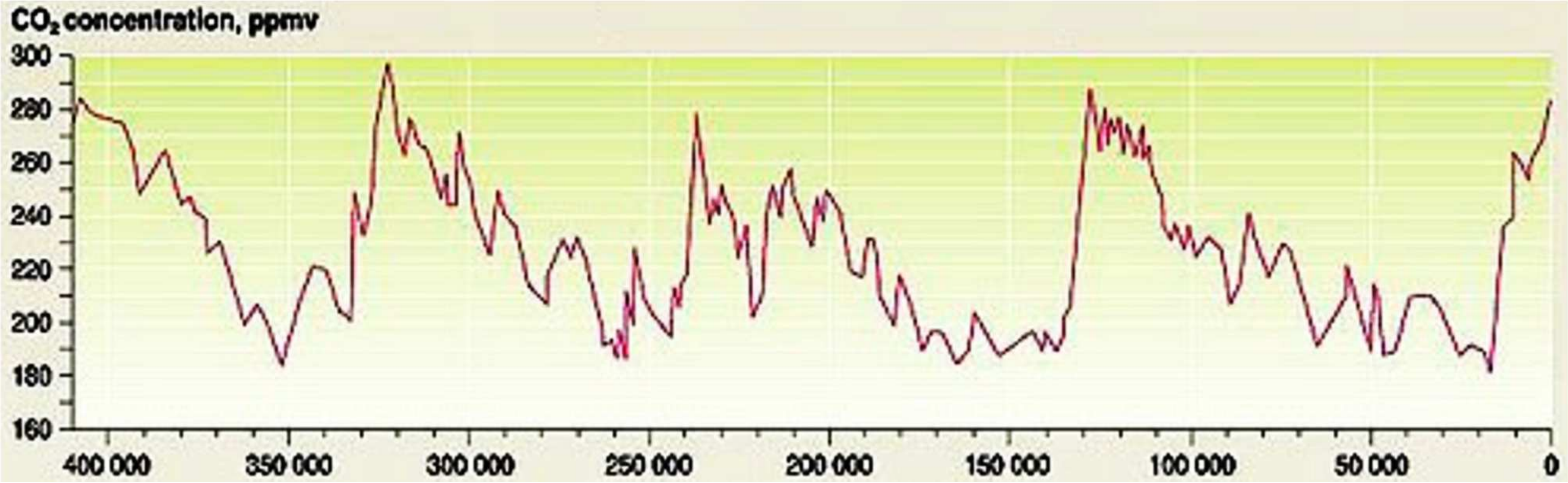
  - During 100 years (1900 – 2001) increase of:

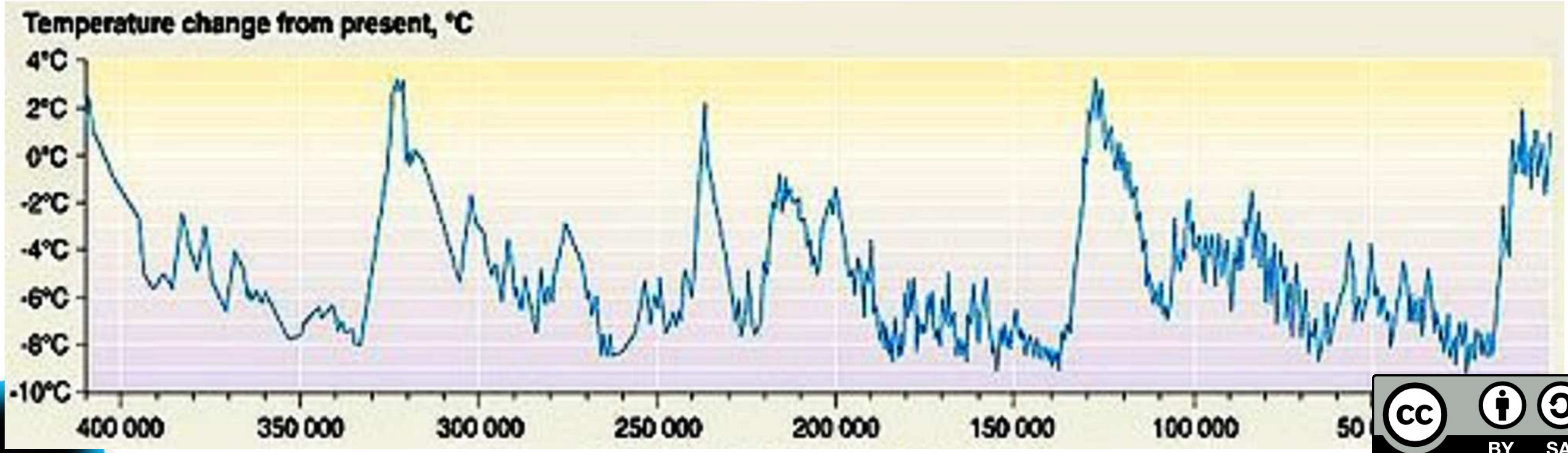
Population	by 250 %
Energy consumption	by 915 %
Content of CO_2 in the air	295 (1900)
	→ 315 (1960)
	→ 371 $ppm_{vol.}$ (2001)

  - According to IEA worldwide increase of energy consumption assumed between the years 2004 – 2030 by 57 %;
  - In 1960 Hawaii observatory Mauna-Loa commissioned. It monitors atmospheric concentration of CO_2 (values before the year 1960 only based on ice core analyses);
  - Since 1850 gradual increase of worldwide average temperature with accelerating trend since1970;
  - Causes don‘t proven till present ⇒ disputes still remaining;

Environmental issues of CO_2

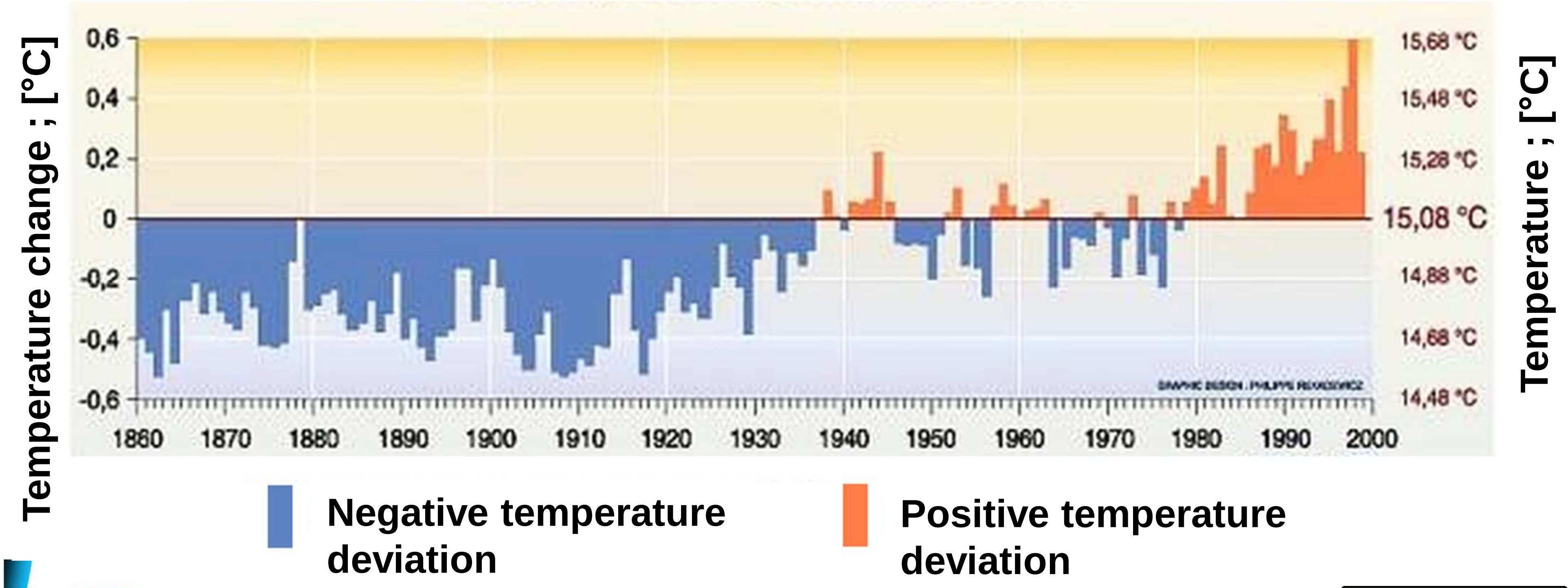
- **Variations in global temperatures over last 400,000 years** (Source: http://www.global-greenhouse-warming.com/ice-ages-and-sea-levels.html) – **Vostok ice core**





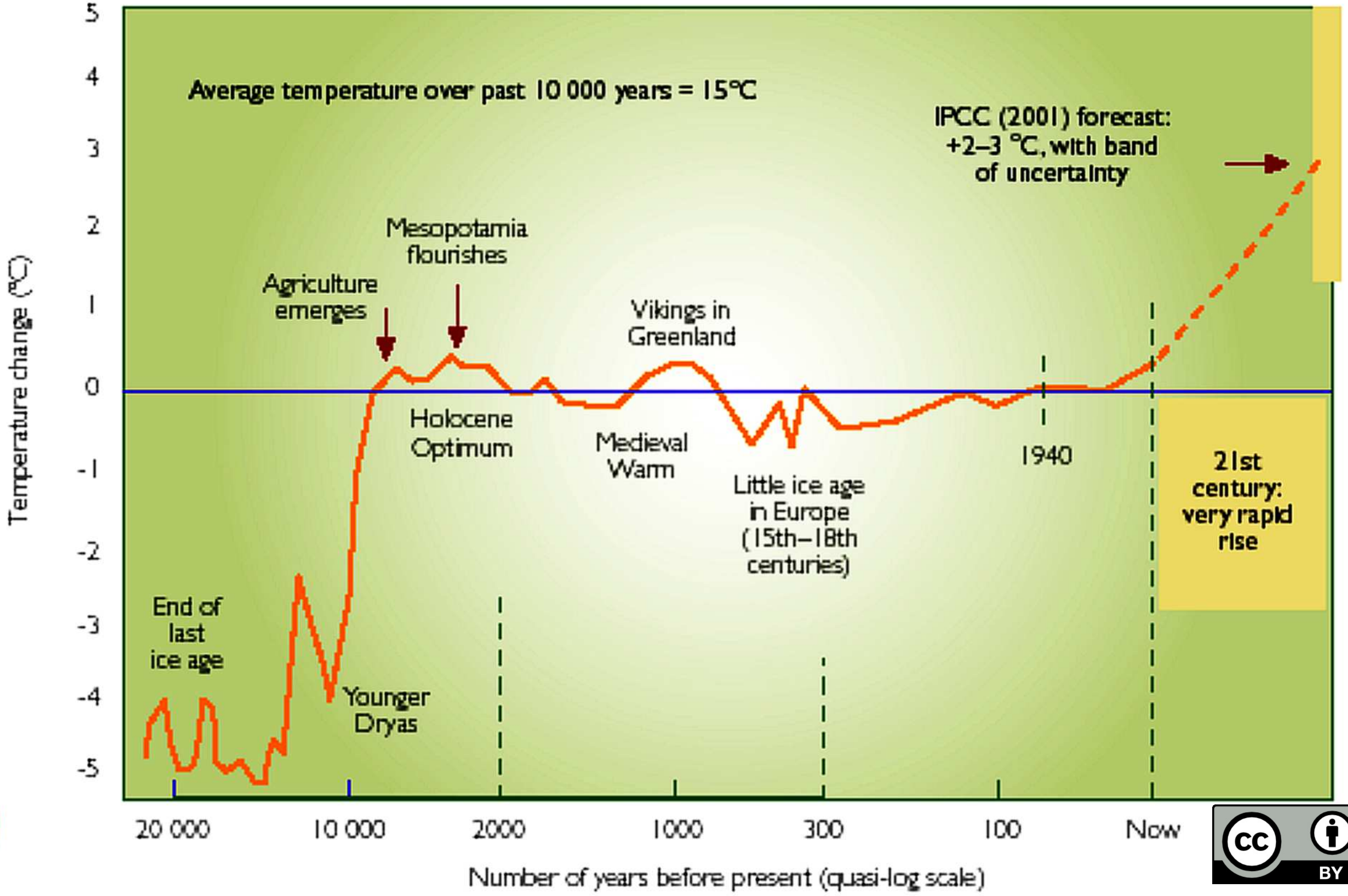
Environmental issues of CO_2

- History ca. 0.8 mil. years ago is mapped by the model EPICA (European Project for Ice Coring in Antarctica) – core drills into the iceberg with thickness of 3,270 m
- **Evolution of global temperatures between 1860 – 2000** (Source: Gomes; Carbon Dioxide Capture and Sequestration)



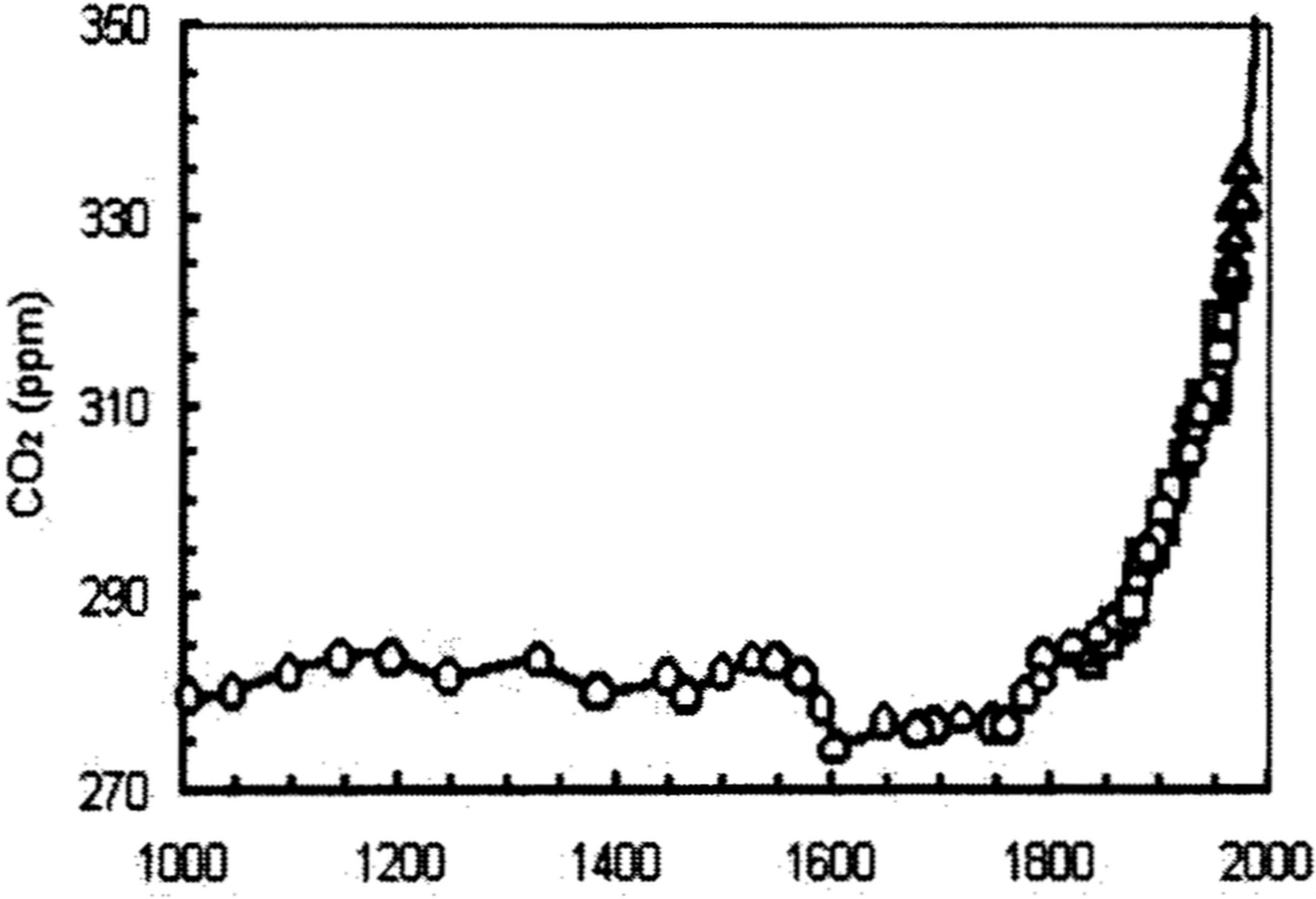
Environmental issues of CO_2

- **Variations in global temperatures over last 20,000 years** (Source: http://www.who.int/globalchange/climate/summary/en/)



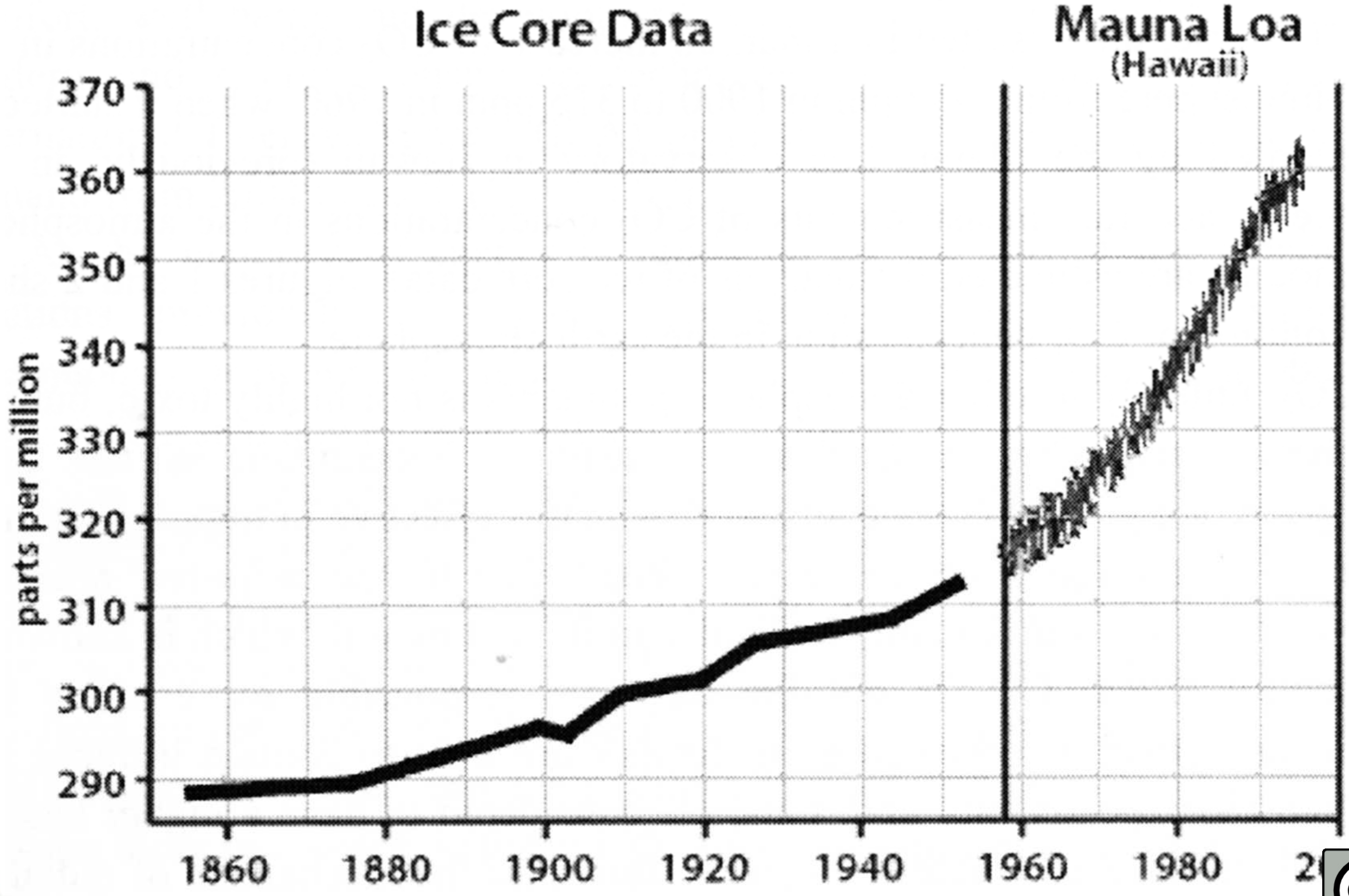
Environmental issues of CO_2

- **Historical variations of CO_2 content in atmosphere** (Source: Gomes; Carbon Dioxide Capture and Sequestration)



Environmental issues of CO_2

- **Historical variations of CO_2 content in atmosphere** (Source: Gomes; Carbon Dioxide Capture and Sequestration)



Environmental issues of CO_2

- **Anthropogenic emissions a retention of CO_2**

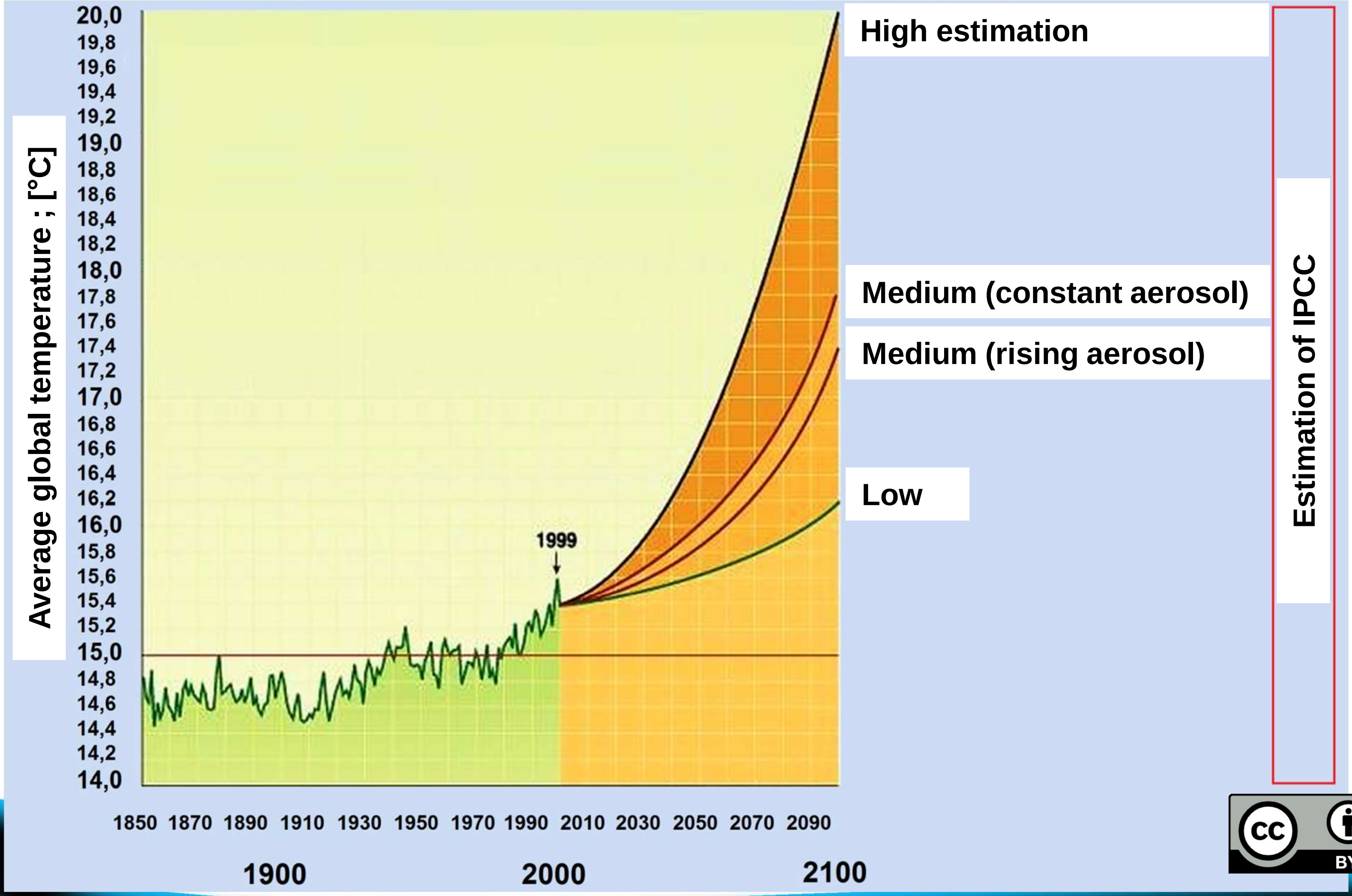
  (Source: Gomes; Carbon Dioxide Capture and Sequestration)

  - Climate theory:
    - The balance between UV and visible radiation absorbed by the planet and the reflection of infrared radiation into space;
    - Among all factors, examined in the period of rising temperatures, only atmospheric CO_2 concentration was changing.
  - The rise of CO_2 concentration in the atmosphere corresponds to only 55 % of total anthropogenic emissions ⇒ Natural mechanisms are still able to separate 45 - 50% of the CO_2 produced by human activities.
  - Retention capacity of the oceans is about 1.7 G (CO_2)/year (total retained about 38000 Gt (CO_2));
  - Retention capacity of the forests is around 1.4 Gt (CO_2)/year;
  - Based on it, scenarios of temperature variations were prepa

Environmental issues of CO_2

- **Scenarios of future global temperatures**

(Source: Gomes; Carbon Dioxide Capture and Sequestration)



Environmental issues of CH_4

- Basic characteristic of methane (Source: http://www.irz.cz/repository/latky/methan.pdf)
  - Boiling point at normal pressure -161°C;
  - Density at normal conditions 0,72 $kg.m^{-3}$ (compared to air with 1,29 $kg.m^{-3}$);
- Emissions sources (Source: http://www.irz.cz/repository/latky/methan.pdf)
  - Main emission sources are biological processes
    - Anaerobic processes (digestion) ⇒ final product of reduction of the organic compounds, e.g. biogas from moorlands;
    - Product of digestive activity of animals;
  - Share of biological CH_4 emissions on the total: 80 %;
  - Ratio between anthropogenic and natural emissions:

Anthropogenic: 60 %

Natural: 40 % (½ are

Environmental issues of CH_4

- Anthropogenic sources of methane

  (Source: http://www.irz.cz/repository/latky/methan.pdf)

  - Breeding of domestic animals, especially cattle (65-100 mil. t/year);
  - Emissions from mining and processing of fossil fuels (40-100 mil. t/year);
  - Biomass combustion (20 – 100 mil. t/year);
  - Biogas from waste landfills (biogas - 20 – 70 mil. t/year);
  - Rice cultivation (170 mil. t/year);
  - Production of chemical substances: acetylene, hydrogen, cyanides and methanol;
  - Black coal coke production;
  - Biogas from wastewater treatment plants with anaerobic stabilisation of sludge;

Environmental issues of CH_4

- Anthropogenic sources of methane

  (Source: http://www.irz.cz/repository/latky/methan.pdf)

- Share of methane from mining and distribution of natural gas:
  - Emissions due to leakage from natural gas processing facilities, transportation and distribution pipelines < 1 % of total anthropogenic emission ⇒ negligible importance!

Environmental issues of CH_4

- Lifetime and decay of CH_4 in air (Source: http://www.irz.cz/repository/latky/methan.pdf)
  - Lifetime of methane in atmosphere ca. 12 – 17 years;
  - Main mechanism of its decay in lower troposphere – **reaction with hydroxyl radical** by means of numerous reactions to CO_2: (share of this mechanism 91 %)

    2 possibilities of the course of initial phase:

    → In presence of NO_x:

$$CH_4 + OH^\bullet \longrightarrow CH_3^\bullet + H_2O$$

$$CH_3^\bullet + O_2 \xrightarrow{M} CH_3O_2^\bullet$$

$$CH_3O_2^\bullet + NO \longrightarrow CH_3O^\bullet + NO_2$$

→ Without presence of NO_x: (methylperoxy radical reacts to hydroperoxymethane, which is gradually transformed into formaldehyde)

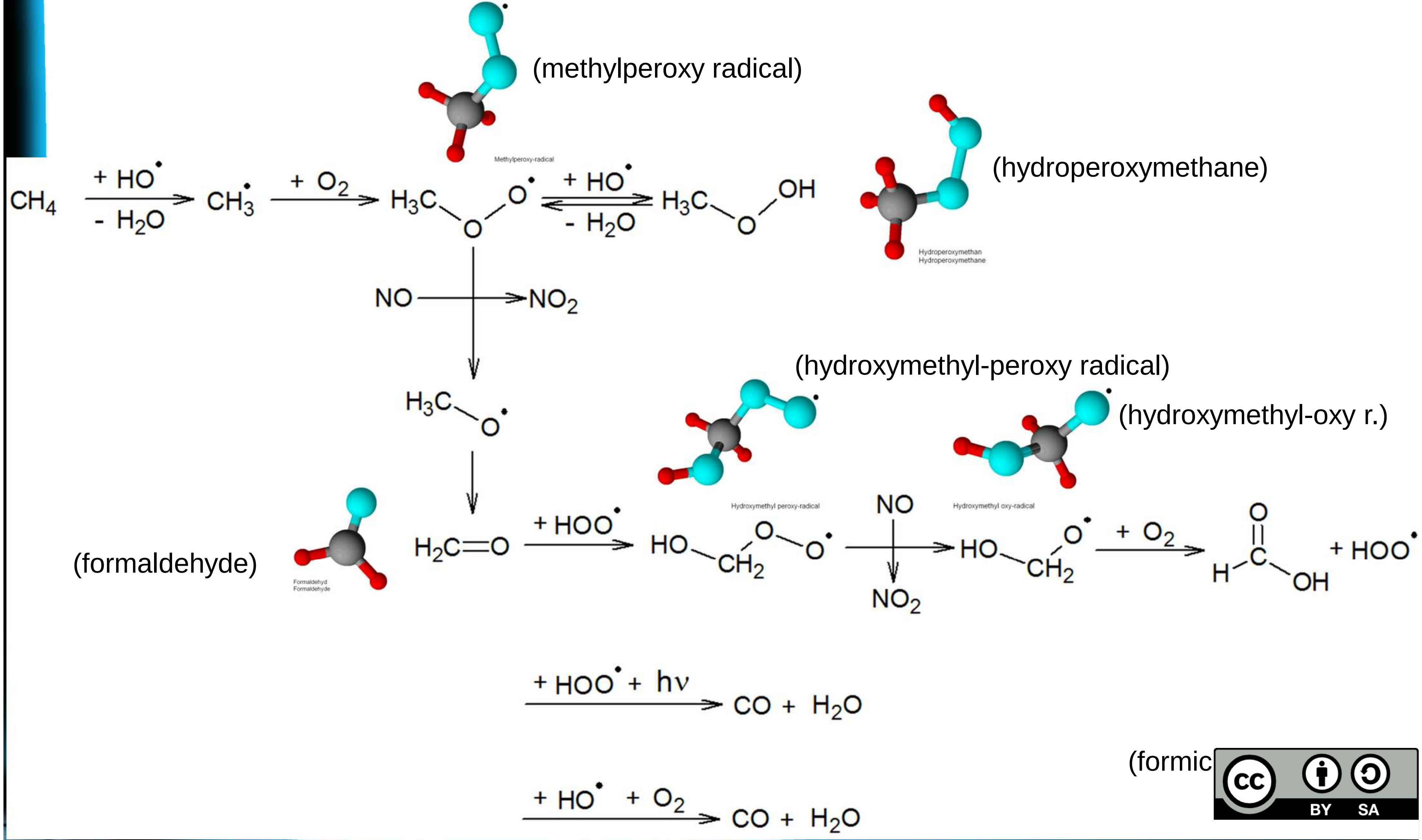
$$CH_3O_2^\bullet + HO_2^\bullet \longrightarrow CH_3OOH + O_2$$

$$CH_3OOH + h\nu \longrightarrow CH_3O^\bullet + OH^\bullet$$

$$CH_3O^\bullet + O_2 \longrightarrow HCHO + H$$

Environmental issues of CH_4

- Other transformations of CH_4 (Source: http://www.irz.cz/repository/latky/methan.pdf)



(methylperoxy radical)

(hydroperoxymethane)

(hydroxymethyl-peroxy radical)

(hydroxymethyl-oxy r.)

(formaldehyde)

(formic

Environmental issues of CH_4

- Lifetime a decay of CH_4 in the air (Source: http://www.irz.cz/repository/latky/methan.pdf)
  - Reaction with OH• in stratosphere plays minority role;
  - Methane is further decomposed by:

    Soil microorganisms (Share of this decomposition 4 – 7 %);

    Reaction with Chlorine atoms in thin upper layer of sea water (Share of this decomposition 2 – 5 %);
- Long term evolution of methane concentrations
  - Based on ice core analyses present concentrations are the highest within last 400000 years;
  - In 1750 concentration ca.7. 10^{-8} % vol.;
  - In 1998 17,45.10^{-8} % vol.;
  - Between 1999 – 2002 stagnation of the concentration rise at about 17,51.10^{-8} % vol.
  - After this plateau concentration increase started again;

Environmental issues of C_xH_y

- Transformation of higher alkanes
  - Reaction with hydroxyl radical ($HO^•$) – Fundamental atmospheric oxidation process;
  - Mechanism includes following steps:
    - Attacking random H on hydrocarbon chain
    - Oxygen addition onto formed alkyl-radical → creation of alkylperoxyl radical
    - Reaction of alkylperoxyl radical with NO
      - Oxidation NO → NO_2 and reduction of alkylperoxyl radical to alkyloxy radical

        or
      - Formation of alkyl nitrate

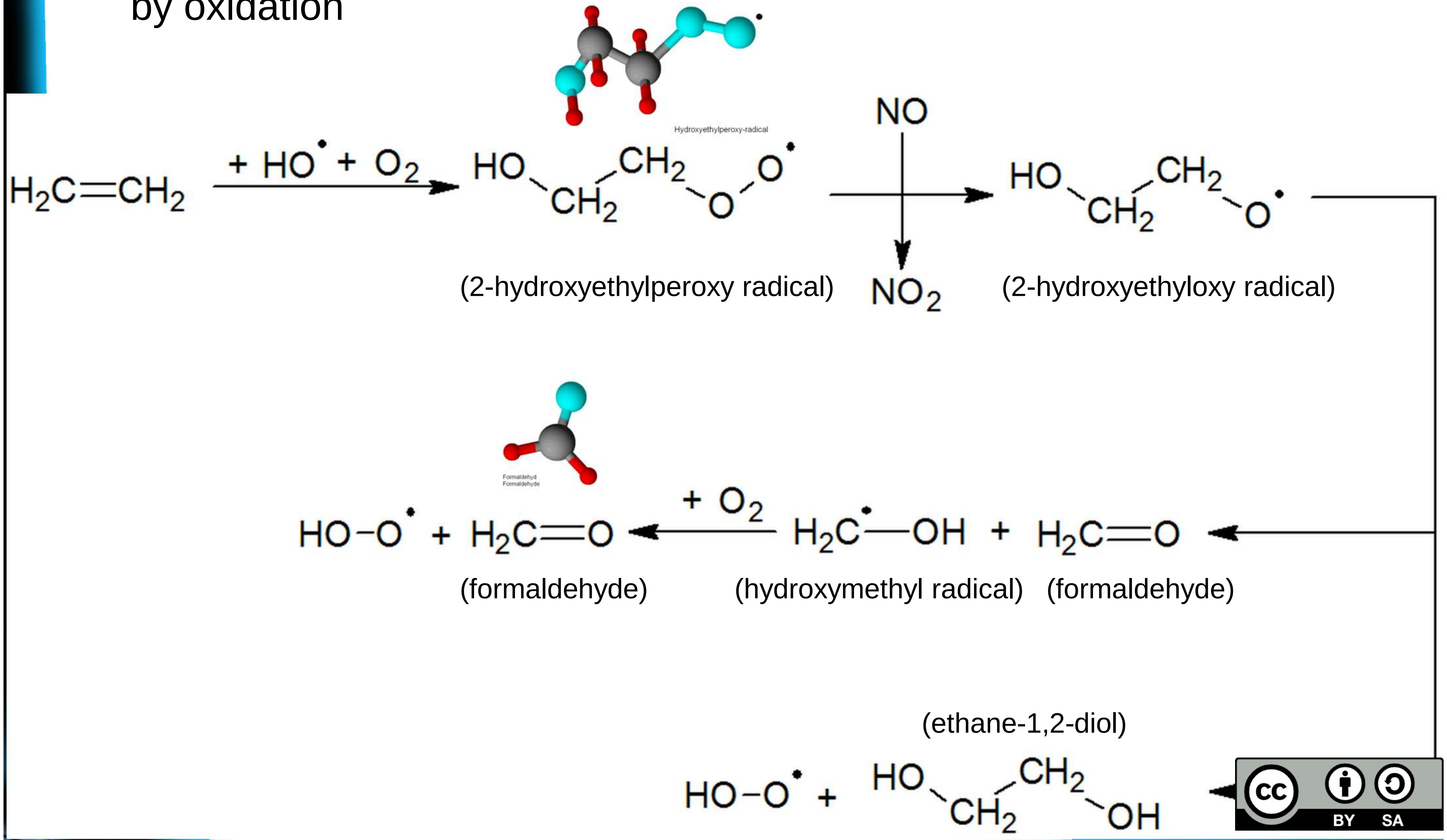
Note. The ratio of the last two mechanisms is growing in favour of alkyl nitrate with the number of C in the initial hydrocarbon ch

Environmental issues of C_xH_y

- Transformation of alkenes
  - Due to double bonds they react also with ozone and slowly with oxygen atoms;
  - 3 types of basic reactions:
    - Addition of $HO^{\bullet}$ onto double bond and subsequent oxidation
    - Reaction with $O_3 \rightarrow$ formation of Crieg radicals
    - Reaction with $HO^{\bullet}$ with initial attacking H on the random location on the hydrocarbon chain (same mechanism as for alkanes):
      - Creation of alkyl radical
      - Addition of oxygen to form alkylperoxyl radical with subsequent reaction with NO:
        - Oxidation $NO \rightarrow NO_2$ and reduction alkylperoxyl radical to alkyloxy radical
        - Or creation of alkyl nitrate

Environmental issues of C_xH_y

- Transformation of alkenes – Addition of $HO^\bullet$ onto double bond, followed by oxidation



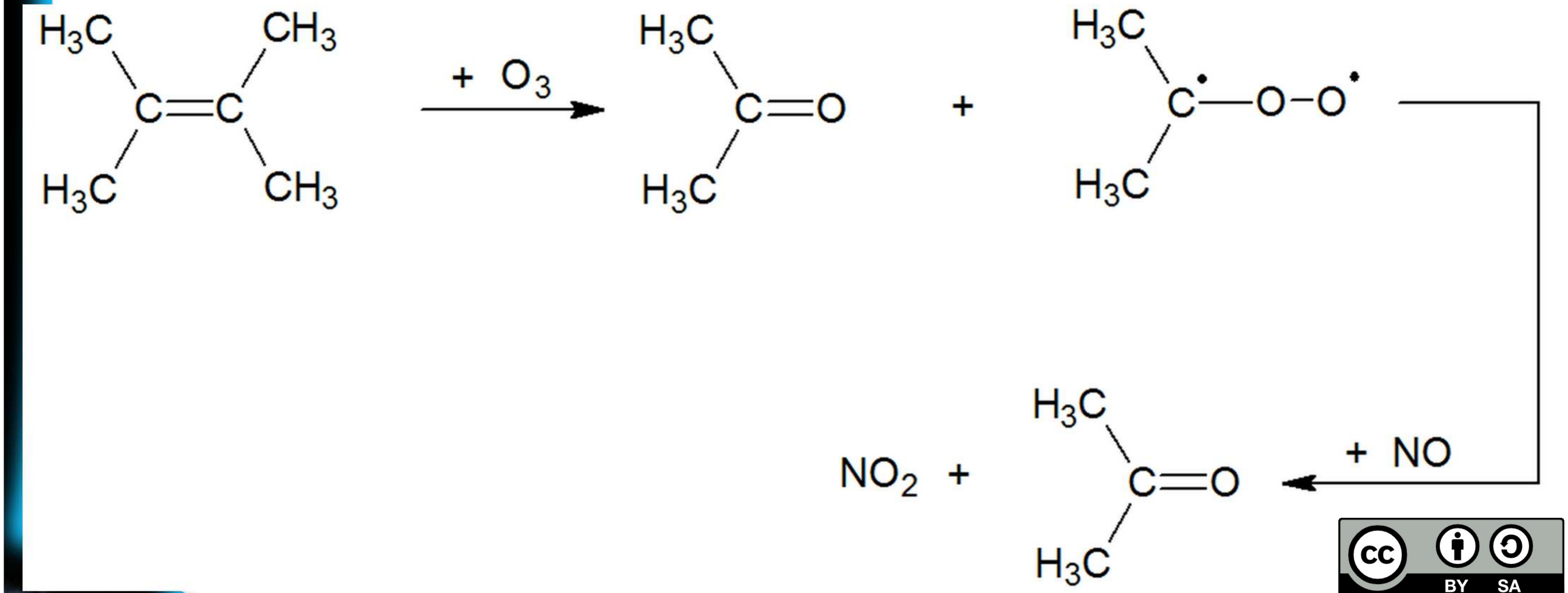
(2-hydroxyethylperoxy radical) (2-hydroxyethyloxy radical)

(formaldehyde) (hydroxymethyl radical) (formaldehyde)

(ethane-1,2-diol)

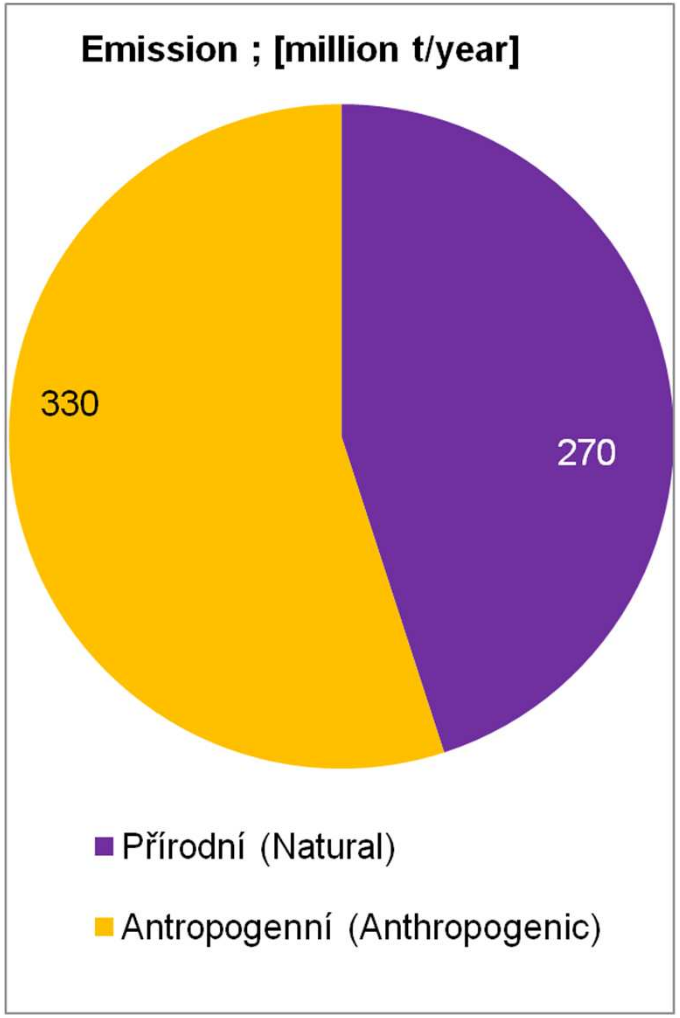
Environmental issues of C_xH_y

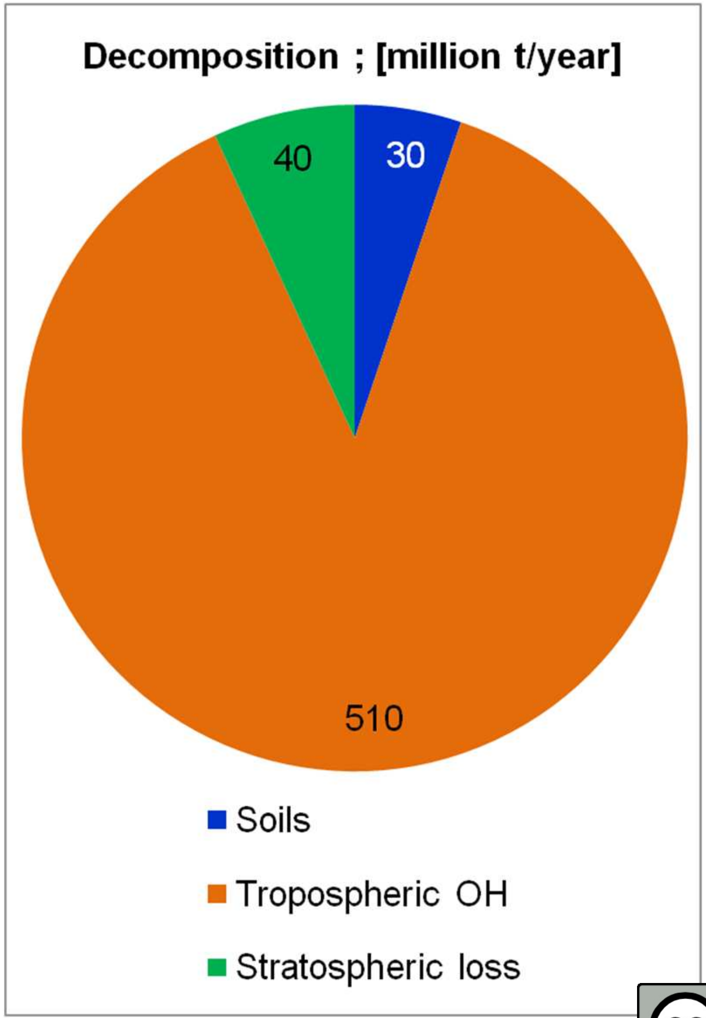
- Transformation of alkenes – reaction with O_3 → Crieg radicals
  - Crieg alkylperoxyl biradicals – strongly oxidative ⇒ oxidize NO to NO_2, NO_2 to NO_3^- (see chapter acid deposition), SO_2 to SO_3 etc.;
  - Double bond of the alkene is cleaved to form aldehyde (or ketone) and alkylperoxyl biradical, so called Crieg radical:



Environmental issues of CH_4

- Ratio between emission and decay of CH_4
  (Source: http://www.irz.cz/repository/latky/methan.pdf)



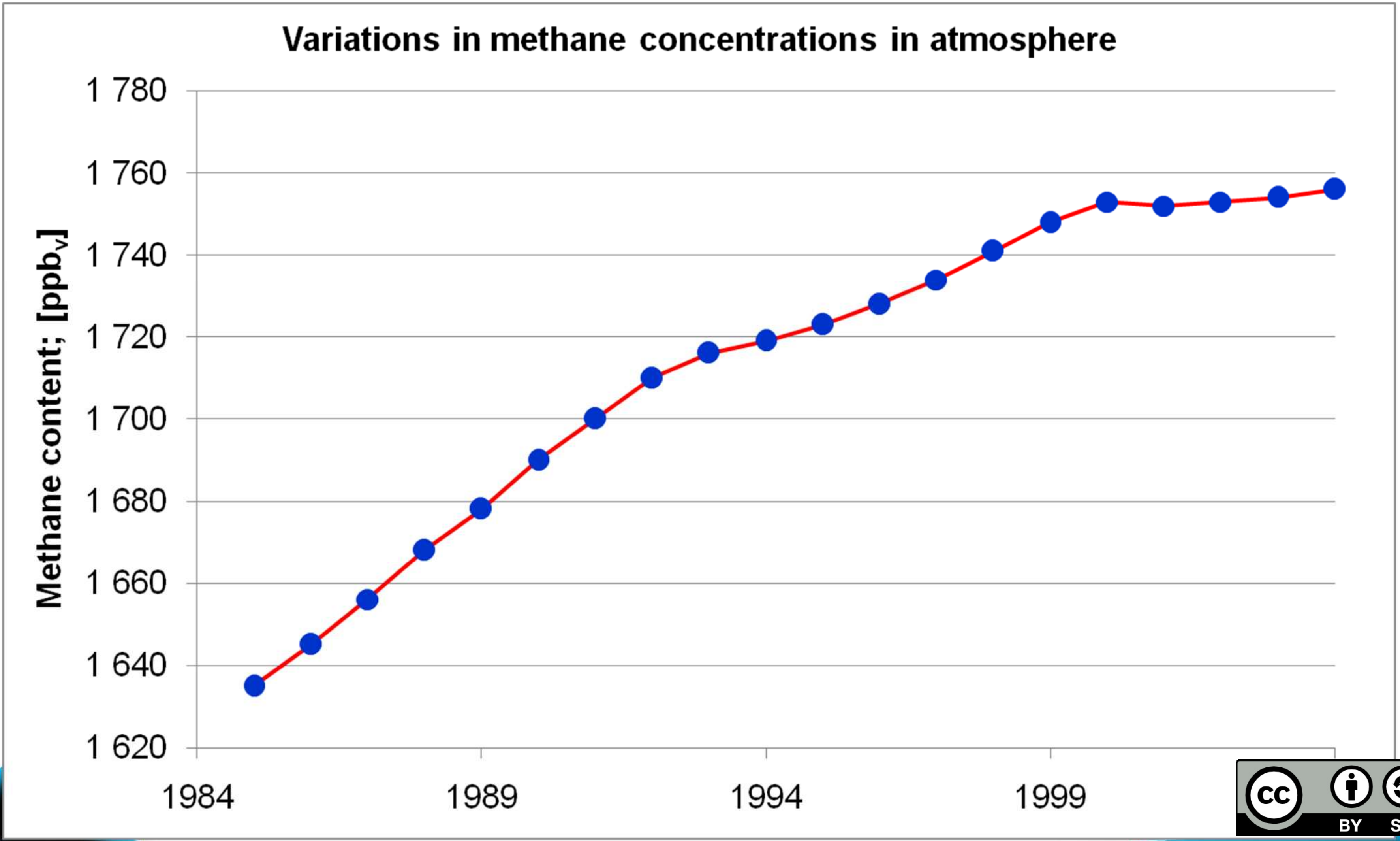


Overall misbalance + 20 mil. t/year

Environmental issues of CH_4

- Changes in atmospheric concentration of methane between 1984 - 2004

  (Source: http://www.irz.cz/repository/latky/methan.pdf)



Environmental issues of N_2O

- Nitrous oxide is a member ox the group of nitrogen oxides: nitrogen monoxide NO, dioxide NO_2, azoxid N_2O, N_2O_3 and N_2O_5;
- **Formation of N_2O** (Source: IPCC)
  - N_2O is created in initial phase of combustion at lower temperatures;
  - Content in flue gas is ca. by two orders lower than thermal NO

    (NO up to 0,3 % vol.; N_2O max. 3.10^{-6} % vol.)

    In fluidized bed combustors significantly higher N_2O concentrations max. 2.10^{-4} % vol.;
  - It is important greenhouse gas;
  - Average lifetime in atmosphere is 114 years;
  - GWP of nitrous oxide:

    according to EEA formerly published GWP(N_2O) = 298

    according to US EPA 310

    presently EU ETS in conformity with EPA 310;

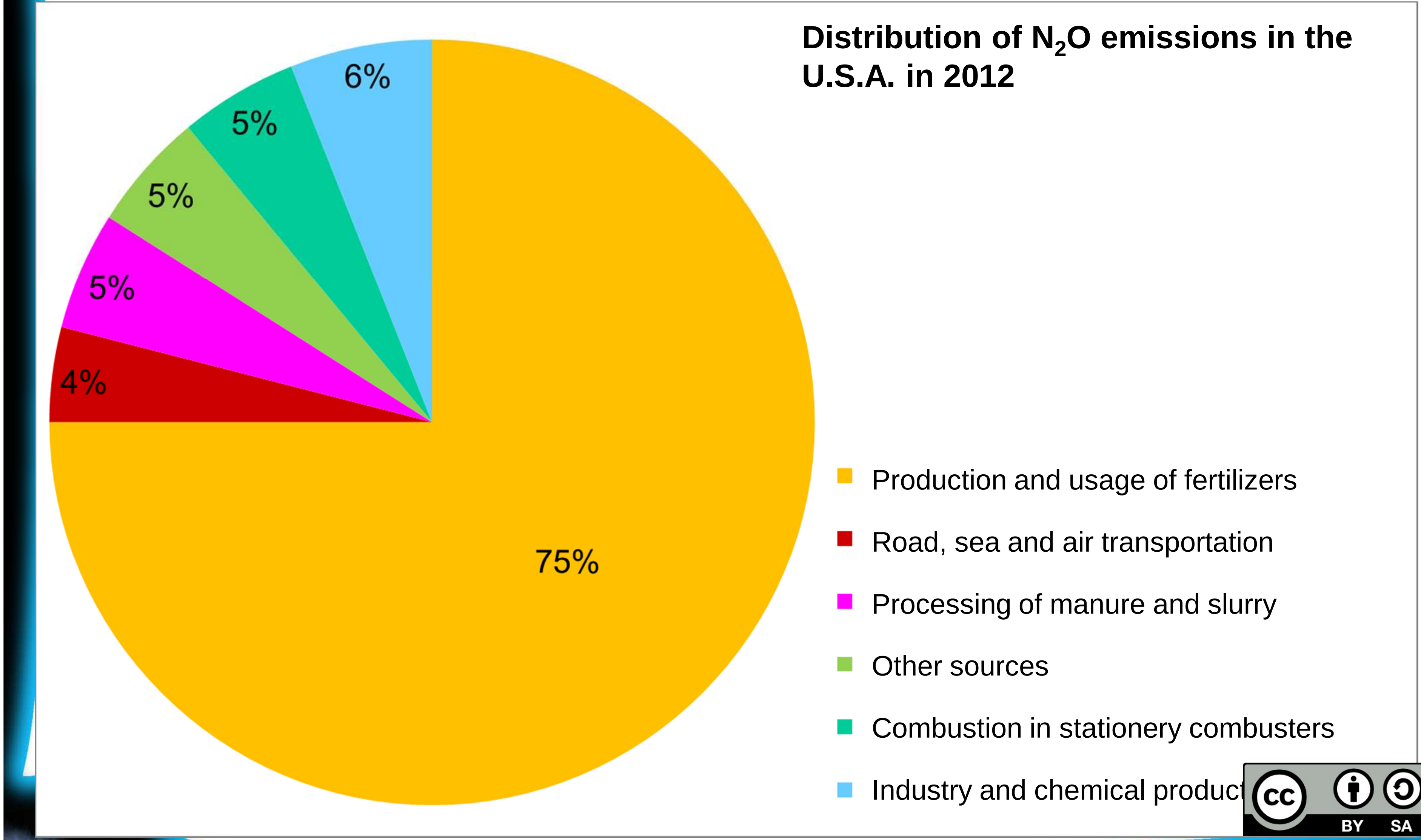
Environmental issues of N_2O

- **Formation of N_2O** (Source: EPA)
  - 40 % of N_2O emissions are anthropogenic;
  - Agriculture: Major source – production and utilisation of nitrogen-based synthetic fertilizers;

    Decomposition of natural manure, slurry and urea;
  - Transport: Combustion of gasoline and diesel in car engines;
  - Agriculture: Manufacture of adipic acid and following production of polyamides, e.g. Nylon (note: HNO_3 included above among synthetic fertilizers);
  - Natural emissions of N_2O: bacterial decomposition of nitrogen based compounds in soil and oceans;
  - Natural decomposition of released N_2O: metabolized by some species of specialized bacteria, photochemical decomposition under UV radiation.

Environmental issues of N_2O

- **Formation of N_2O** (Source: EPA)



Environmental issues of N_2O

- Formation of N_2O beyond combustion processes (Source: W.C.Heraeus, GmbH)
- Production of nitric acid and subsequent products ⇒ the biggest source of nitrous oxide emissions;
- Problematics of HNO_3 production;
  - In the world, there are continuously (not by fits and starts) operated:

    600 nitric acid production units

    Overall N_2O emission estimated at $1,2.10^6$ t/year

    With GWP 310 times higher than CO_2 ⇒ comparable with operation of 80.10^6 personal cars!

Environmental issues of N_2O

- **Principle of nitric acid manufacture**
  - Incineration of mixture ammonia-air at higher pressure on Platinum catalyst;
  - Released heat is utilised in production of process steam in boiler;
  - Subsequent absorption of nitrose gases in demineralised water (counterflow absorber);
  - Overpressure released by the two ways: older installations have gas turbine for common incineration with methane, recent installations equipped with expansion turbine;
  - Possibility of optional installation of 3 levels of catalysts:

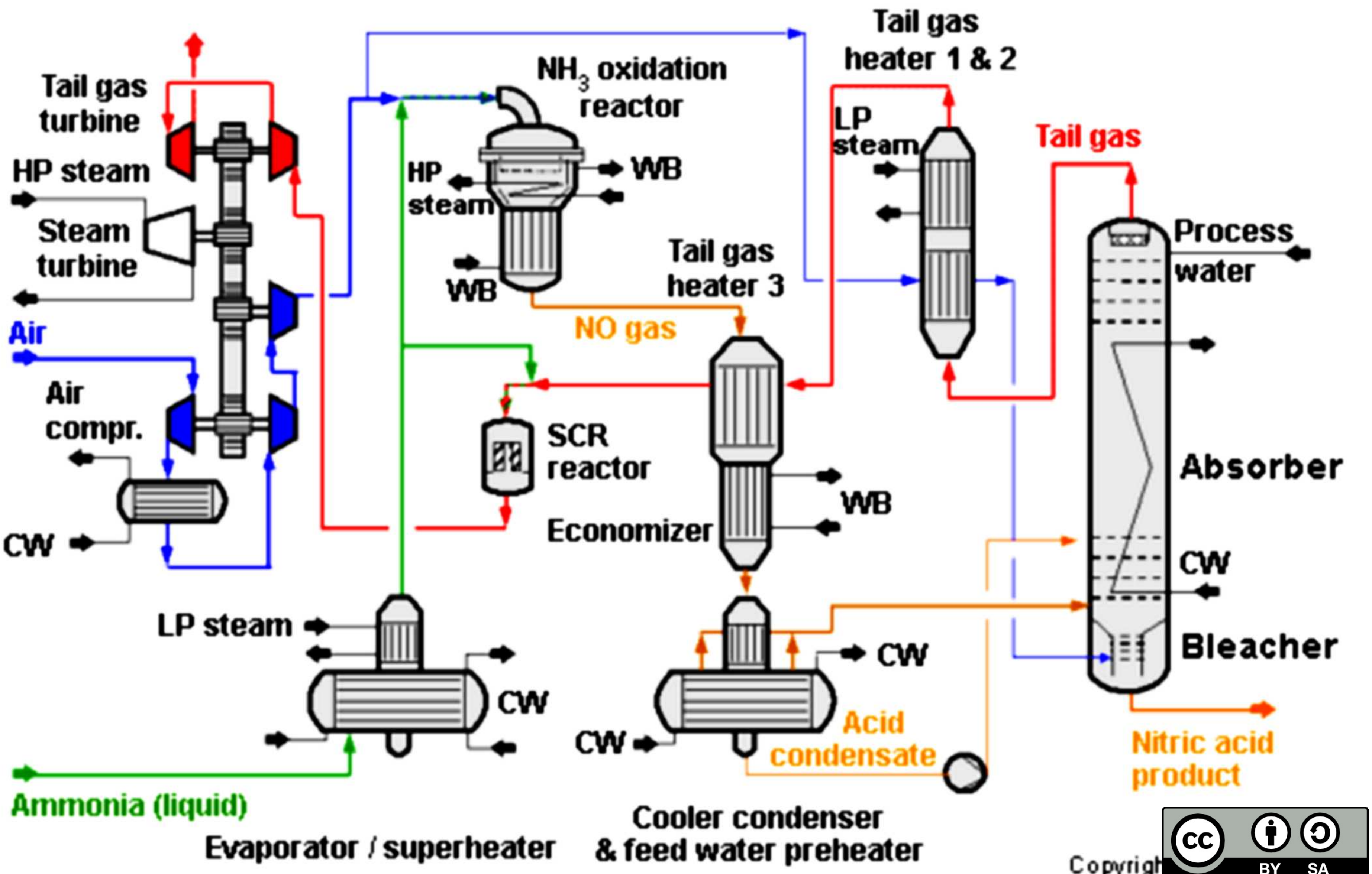
Primary catalyst – oxidation of NH_3
Secondary catalyst – high temperature decomposition of N_2O
Tail gas reduction catalyst

Environmental issues of N_2O

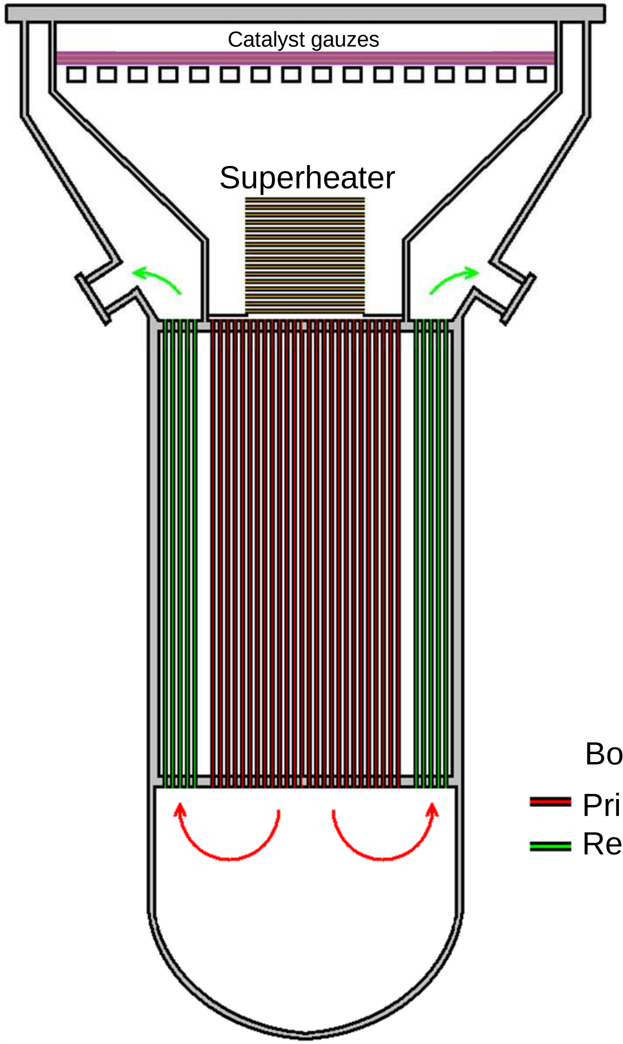
- **Main emissions source – nitric acid manufacture**
- **Czech constructor of NA plants – Chemoprojekt, a.s.**
- **Typical parameters of recent installations:**

– Nominal production capacity	660 – 1 500 $t_{100\%\ HNO3}$/day;
– Adjustable performance scale	70 – 110 % of nominal capacity
– Concentration of produced HNO_3	60 – 68 %;
– Unit consumption of NH_3	282 – 284 kg/t_{HNO3};
– Unit steam production	600 – 700 kg/t_{HNO3};
– Content of NO_x and N_2O in tail gas	< 100 ppmv;
– Conversion efficiency NH_3 to HNO_3	95 – 97 %;
– Combustion temperature (on gases)	890 - 920 °C;
– Pressure in monopressure types	7,8 bar (modern high pressure)
– Pressure in double pressure types	4,5 bar oxidation / 10-12 bar absorption

Environmental issues of N_2O

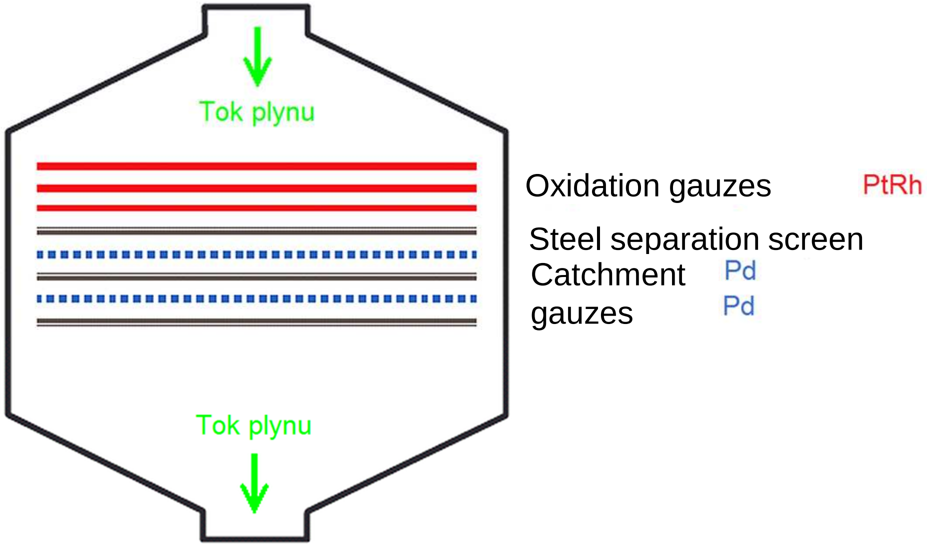


Environmental issues of N_2O



Boiler:

🟥 Primary gas flow
🟩 Reverse flow



So called Ostwald principle of nitric acid synthesis

Efficiency 95 %

Primary emissions of N_2O in stack 1 200 ppm_V

– Ammonia combustor (older conception)

Environmental issues of N_2O

- **Example of installation in the Czech Republic**
  - KD6 Lovosice (Lovochemie, a.s.) – recent system;

Uncovered upper layer of catalyst during maintenance

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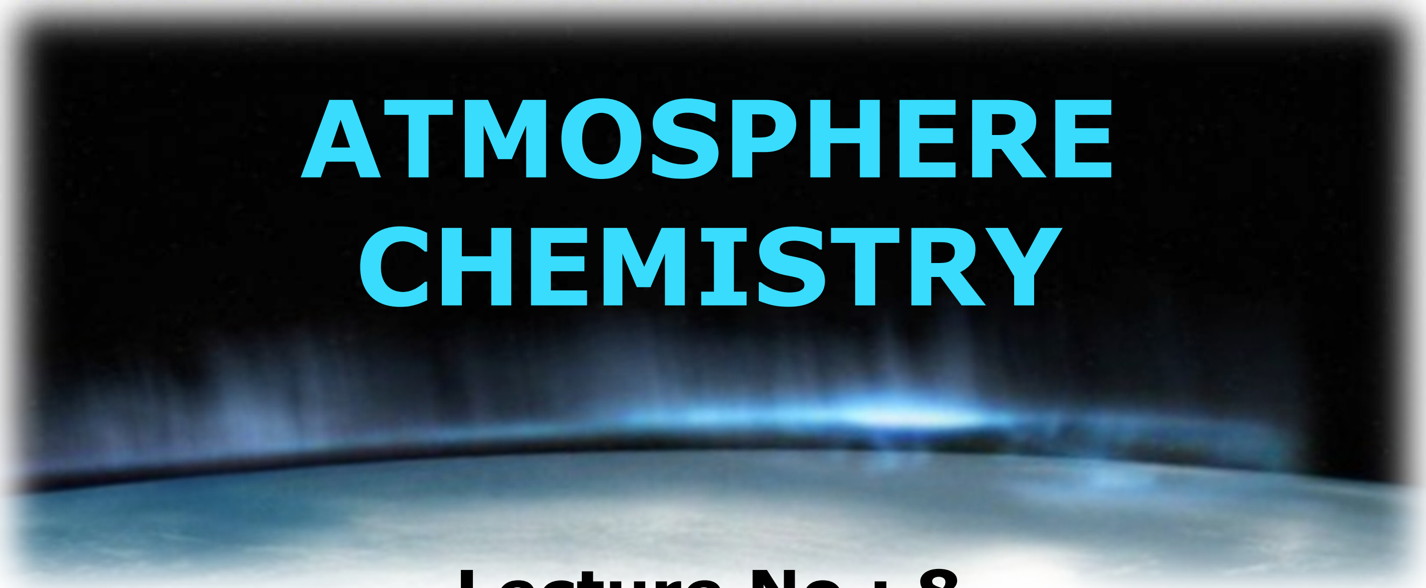

ATMOSPHERE CHEMISTRY

Lecture No.: 8

Organisation of study

- Lecturer: Marek Staf, MSc., Ph.D., phone: +420 220 444 458

  e-mail: marek.staf@vscht.cz,

  web: http://web.vscht.cz/~stafm/

  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 - oral form

- Note:

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Scope of lecture 8

Reactions of selected pollutants and important components in atmosphere – acidic substances

- Distribution of pollutants - review
- Overview of fundamental acidic substances in the atmosphere
- Emissions of sulfur oxides
- Environmental impact and reactions of sulfur oxides
- Emissions of nitrogen oxides
- Environmental impact and reactions of nitrogen oxides

Distribution of pollutants

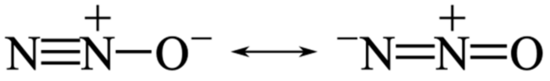
- Pollutants can be divided into following fundamental groups:

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

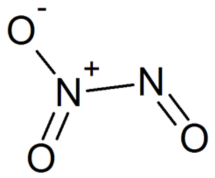
Acidic substances

- The main gases having acidic reaction:
  - Nitrogen oxides (NO_x)

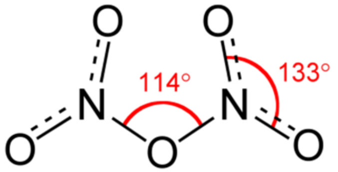
Nitrous oxide	(laughing gas, azoxide)	N_2O



Nitric oxide	(nitrogen monoxide)	NO
Dinitrogen trioxide		N_2O_3



Nitrogen dioxide		NO_2
Dinitrogen pentoxide		N_2O_5



Note 1: Dinitrogen trioxide is formed only at low temperatures (< 21 °C) by reversible reaction $NO + NO_2 \leftrightarrow N_2O_3$.

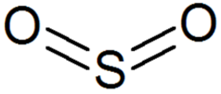
Note 2: Dinitrogen pentoxide is crystallic substance sublimatin t > 30 °C.

Acidic substances

- The main gases having acidic reaction:
  - Sulfur oxides (SO_x)

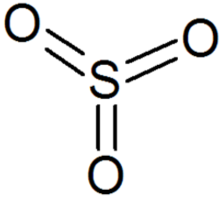
Sulfur dioxide

SO_2



Sulfur trioxide

SO_3



Origin of sulfur oxides emissions

- Natural sources:
  - Volcanic gases
  - In the form of sulfurous acid in mineral springs – releasing of vapors
- Anthropogenic emissions:
  - Combustion processes

    Primarily power industry (combustion of coal; lower emission from crude oil derivatives);
  - Other processes

    Petrochemical industry (crude oil refineries);

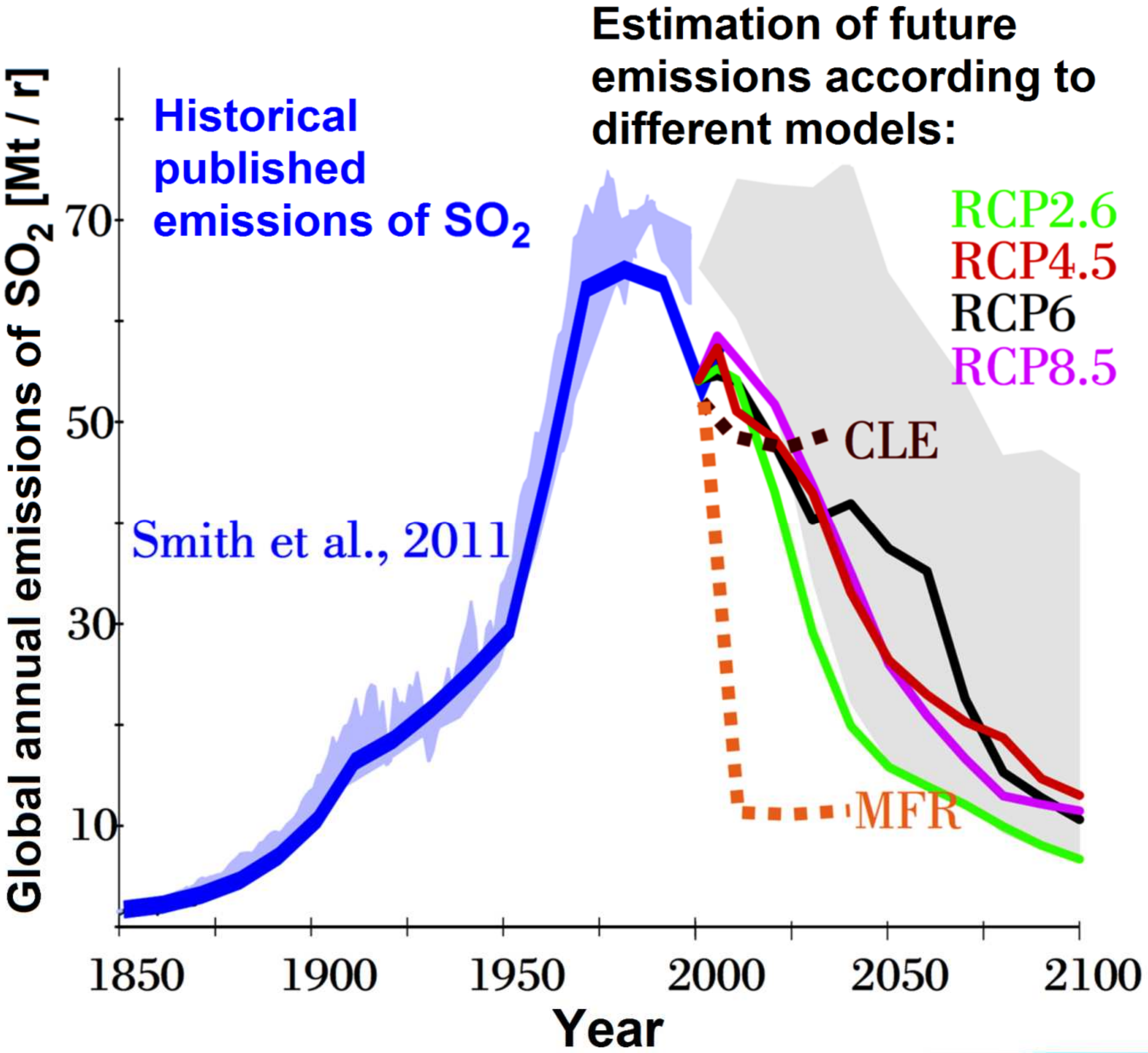
    Metallurgy (melting and sintering of ores, e.g. Production of copper);

    Chemical industry;

    Transportation (combustion of high-sulfur liquid fuels electric locomotives and marine ships and so on).

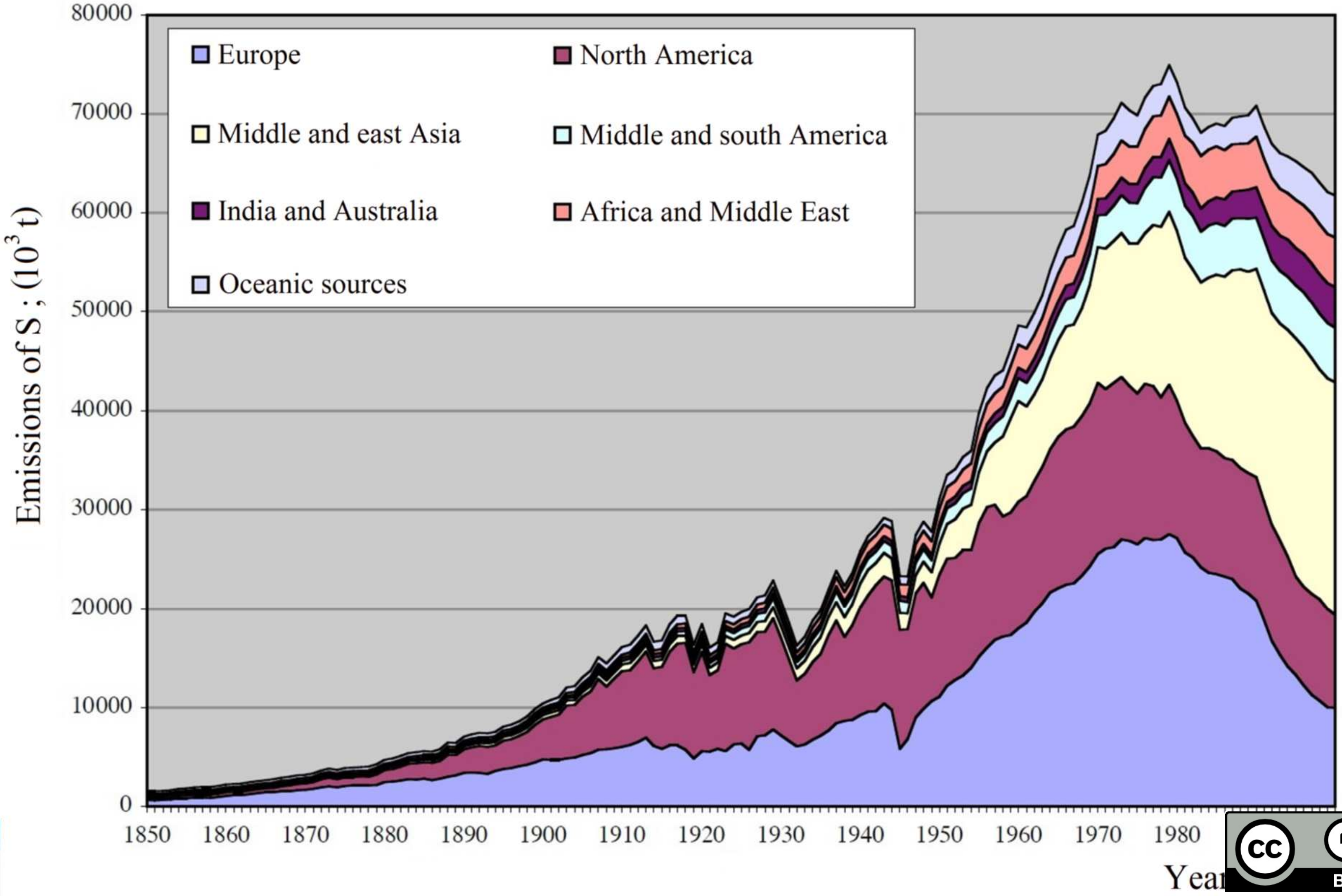
Origin of sulfur oxides emissions

- Estimated evolution of SO_2 emissions – different models (Zdroj: Cofala et al., 2007)



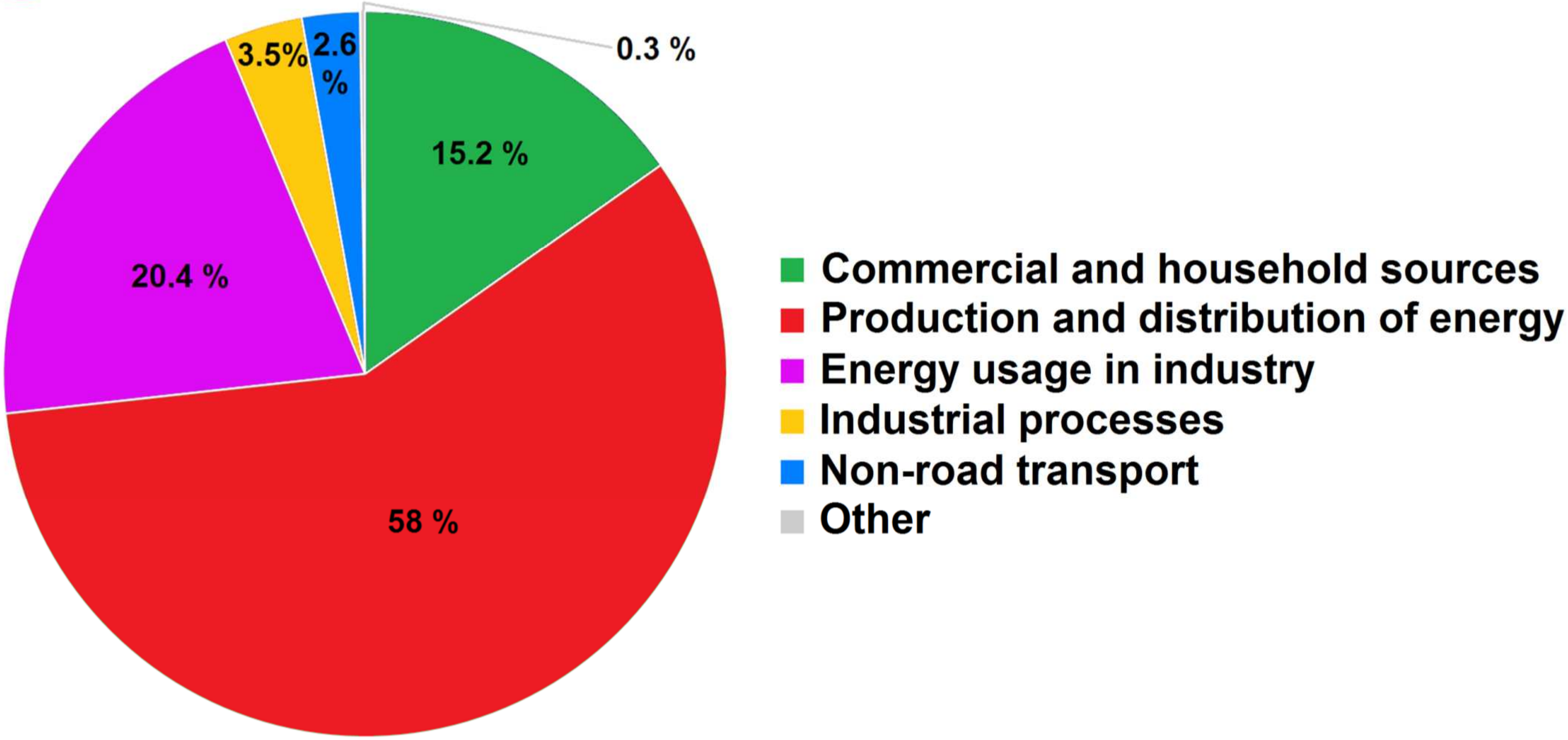
Origin of sulfur oxides emissions

- Time-related evolution of sulfur oxides calculated for S (Source: Pacific Northwest National Laboratory)



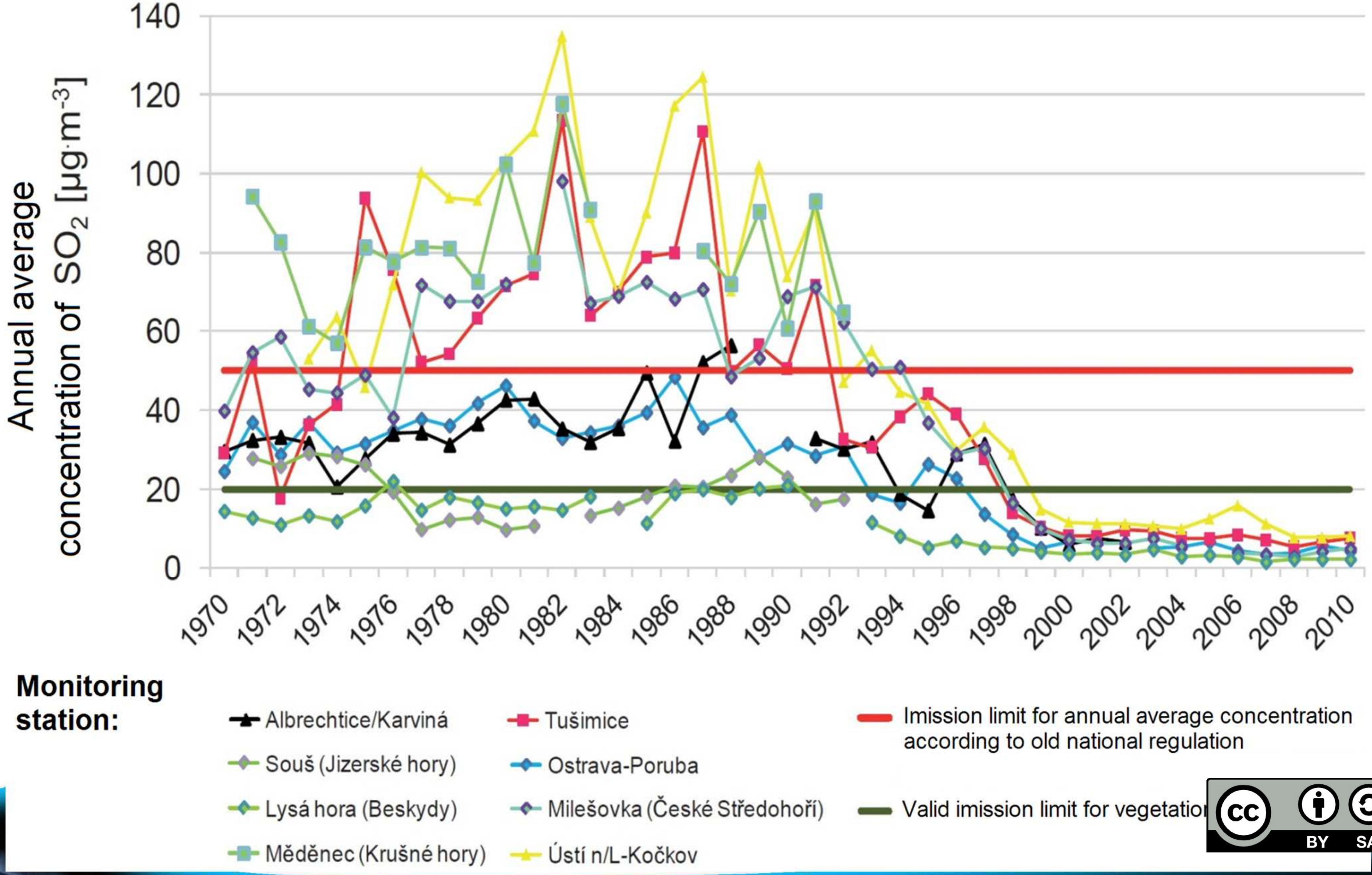
Origin of sulfur oxides emissions

- **Distribution of SO_2 sources in EU in the year 2013** (Source: EEA)



Origin of sulfur oxides emissions

- **SO_2 imissions in Czech rep. between 1971 – 2011** (Source: http://portal.chmi.cz)



Health impact of SO_2

- **Diseases caused by exposition by SO_2** (Source: WHO)
  - Short-term exposure to SO_2 emissions with duration between 5 minutes to 24 hours has a negative effect on the respiratory tract. Acute effects of exposure are: bronchoconstriction (narrowing of bronchi), converting in asthma.
  - Especially affected: people diagnosed as asthma patients, especially during increased physical load requiring increased respiration;
  - Risk groups: children, elderly people, pregnant women, people with chronic respiratory disease (asthma, chronic obstructive pulmonary disease) and circulatory system, and people otherwise weaken (e.g. combination of stress, smoking, impaired immunity, etc.);
  - Studies showed connection between the short-term exposure and increasing frequency of infectious respiratory diseases, esp. within risk groups (see above).
  - Effects of chronic and repeated exposure: emphysema (emphysema pulmonum), hematopoietic disorders, heart damage.

Impact of SO_2 on vegetation

- **Damaging of plants** (Source: Výzkumný ústav rostlinné výroby, v.v.i.)
  - Degradation of plant tissues due to chlorophyll decomposition;
  - Formation of diluted sulfuric acid by reaction with water aerosol;
  - Critical SO_2 concentrations, which exceeding damages plants:

Vegetation type	Critical concentration	Time period
Lichens	10 $\mu g/m^3$	Yearly average
Forest ecosystem*	20 $\mu g/m^3$	Yearly average and months October - March
Native vegetation	20 $\mu g/m^3$	Yearly average and months October - March
Field cultures (crops)	30 $\mu g/m^3$	Yearly average and months October - March

* coniferous forrests more sensitive

Impact of SO_2 on vegetation

- **Damaging of plants** (Source: Výzkumný ústav rostlinné výroby, v.v.i.)

Effects of acidic deposition

- Acidic deposition = wet deposition + dry deposition (gases + aerosol)
- Direct effects
  - Reaction with chlorophyll ⇒ Damaging of photosynthesis ⇒ Defoliation
- Indirect effects
  - Reaction esp. SO_2 with H_2O and reaction SO_3 with H_2O to form acid rains ⇒ acidification of soil, water sources, erosion of building materials (marble, limestone;
- Acid rains = wet deposition after dissolving acidic gases in water:
  - First discovered in 1853 and named in 1872;
  - Generally precipitations with $pH < 5,6$
  - Formed almost by acids of SO_x and NO_x, in minority scale also HCl;
  - Main negative impact on coniferous trees;
  - Weaker effect on south hemisphere.

Effects of acidic deposition

- Water acidification
  - Reducing of pH of the water due to acid deposition and subsequent negative processes affecting the biotope;
  - Degree of acidification is given by amount of deposition, geological structure of surrounding rocks and properties of soils, esp. content of basic cations (Ca^{2+}, Mg^{2+}, Na^{+}, K^{+});
  - Greater content of basic cations supports greater resistance to acidification of the location ⇒ neutralisation of acidic deposition;
  - Bedrock consisting of gneisses and granite ⇒ small resistance to acidification;
  - Land area susceptible to acidification is greater than predicted in the 1990s; actual range: USA, Canada, majority of Europe, large parts of Asia, Africa and South America, consisting of Precambrian and Cambrian rocks with limited capture capacity for SO_4^{2-} a NO_3^{-};
  - Sensitive basin: incomplete neutralization with subsequent transfer of Al^{3+}, Mn^{2+}, Zn^{2+} etc. from the soil into the surface water.

Effects of acidic deposition

- Water acidification
  - Destruction of ecosystem due to:
    - → Decrease of pH value;
    - → Extraction of toxic metals (normally imobilized in rocks): Al, Cd, Pb, Cu;
  - Death of water organisms ⇒ reduction of biodiversity;
  - Dominance of acidophilic species (e.g. sphagnum in wetlands)
  - Disruption of trophic degree ⇒ flushing out the nutrients from water and soil;

  - Paradox! Visually the acidified water seems to be clear and transparent ⇒ due to leak of saprophytic microorganisms phytomass is not decomposed, but it is only accumulated on the bottom.

Effects of acidic deposition

- Sphagnum in wetlands

Acidic deposition – don‘t confuse terms

- Water eutrophication – warning, it is often confused with acidification!
  - Process of enrichment of water by nutrients, especially N and P;

    Natural eutrophication = flushing out the nutrients and decomposition of dead organisms / Unnatural, excessive eutrophication caused by human activity;
  - Nitrogen-based compounds (esp. NO_3^-, NO_2^-) and phosphates (PO_4^{3-}, HPO_4^{2-}, $H_2PO_4^-$, $P_2O_7^{4-}$) cause unnatural eutrophication: origin in synthetic fertilizers + washing agents contained in wastewater;
  - Consequences of eutrophication:

    phase 1 overgrowth of plankton and algae (algal bloom)

    phase 2 mass death of the aforementioned organisms

    phase 3 O_2 drop in the water, esp. at the bottom where decay occurs

    phase 4 extinction of fish and other organisms

    phase 5 extinction of the population esp. at the bottom, (separated by pycnocline – layer separating water wit density and blocking exchange of O_2)

Acidic deposition – don‘t confuse terms

- Algal bloom

Reactions of sulfur oxides

- **Sulfur oxides – mostly anthropogenic / sulfur in reduced form – mostly biogenic**

- **Biogenic forms of sulfur emitted in atmosphere (especially):**

– Carbon disulfide	CS_2
– Hydrogen sulfide	H_2S
– Carbonyl sulfide	COS
– Dimethyl sulfide	$(CH_3)_2S$
– Dimethyl disulfide	$CH_3{-}S{-}S{-}CH_3$

- **Reactions of reduced forms of sulfur**
  - First phase is reaction with $OH^{\bullet}$, following sequence of reaction is not fully mapped, but it leads to oxidation to SO_2
  - SO_2 is either very slowly oxidized: $2SO_2 + O_2 \rightarrow 2SO_3$
  - Or it reacts again with hydroxyl radical, afterwards to H_2SO_4

  Mechanism is demonstrated in following slide.

Reactions of sulfur oxides

- **Oxidation of SO_2 by hydroxyl radical – the most frequent oxidation of sulfur in atmosphere**

$$OH^{\bullet} + SO_2 \longrightarrow HOSO_2^{\bullet}$$

$$HOSO_2^{\bullet} + O_2 \longrightarrow HOO^{\bullet} + SO_3$$

$$SO_3 + H_2O \longrightarrow H_2SO_4$$

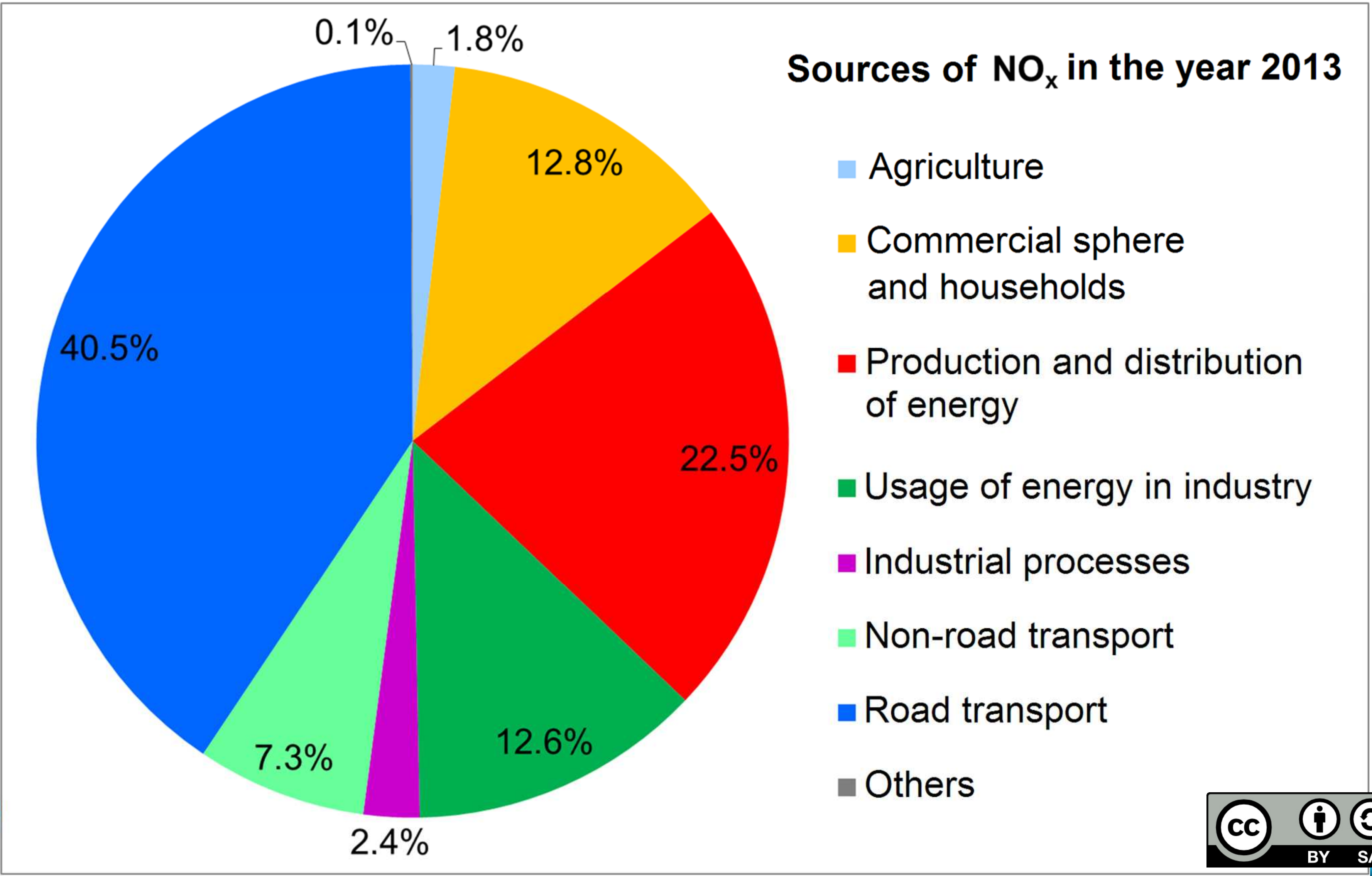
- **Possibility of excitation by UV radiation**
  - SO_2 in lower troposphere is only oxidized and photodissociation does not take part;
  - SO_2^* loses excessive energy by its transfer to inert substances ⇒ SO_2 therefore does not undergo photooxidation.

Origin of nitrogen oxides emissions

- **Origin of NO_x emissions in Europe** (Source: EEA)
- **Main sources of emissions**
  - Land transportation
  - Power industry;
- **Time evolution of NO_x emissions**
  - Within the years 1990 – 2011 decrease of emissions of NO_x by 44 %;
  - Dominating source of emissions during the whole aforementioned period = land transportation;
  - The biggest reduction (1990 – 2011) in the sphere of road transport by 48 % (the decrease rate in average 3 % per year);
  - Warning: concentrations in municipal air decreased more slowly than officially declared progress of emissions reduction in member countries (i.e. the real emissions are higher);
  - In power industry the decrease significant due to introduction of low-emission burners, scrubbers, SCR, SNCR and partial transition from coal to natural gas;

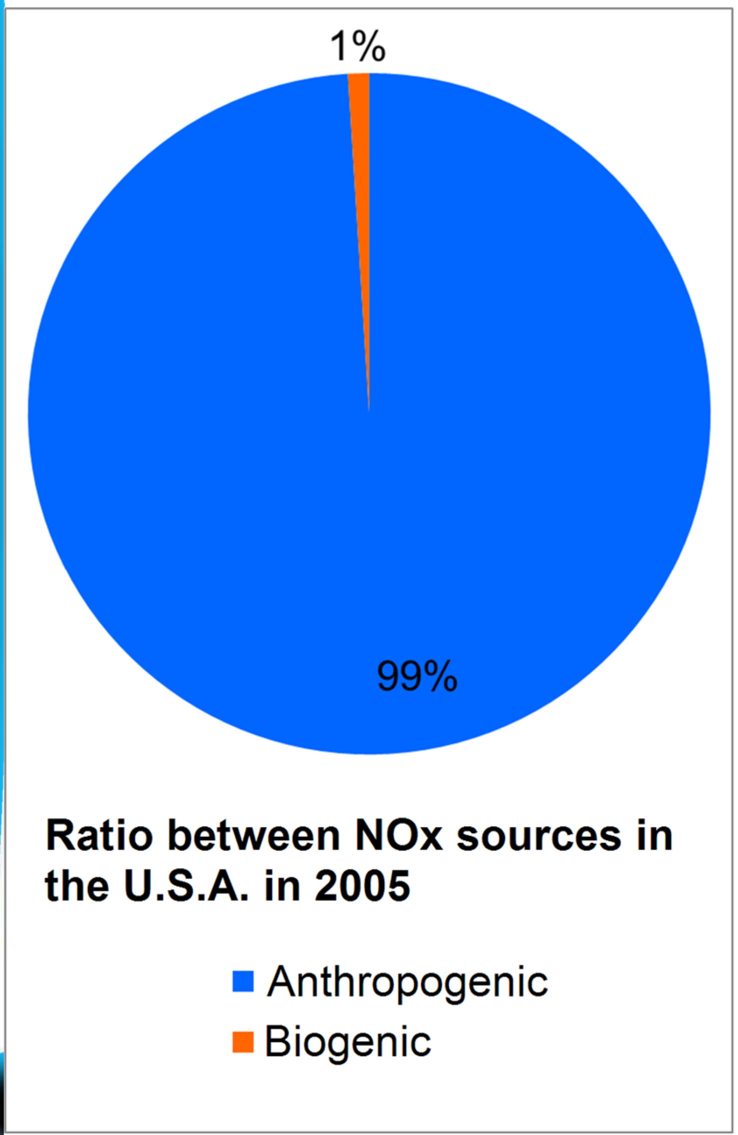
Origin of nitrogen oxides emissions

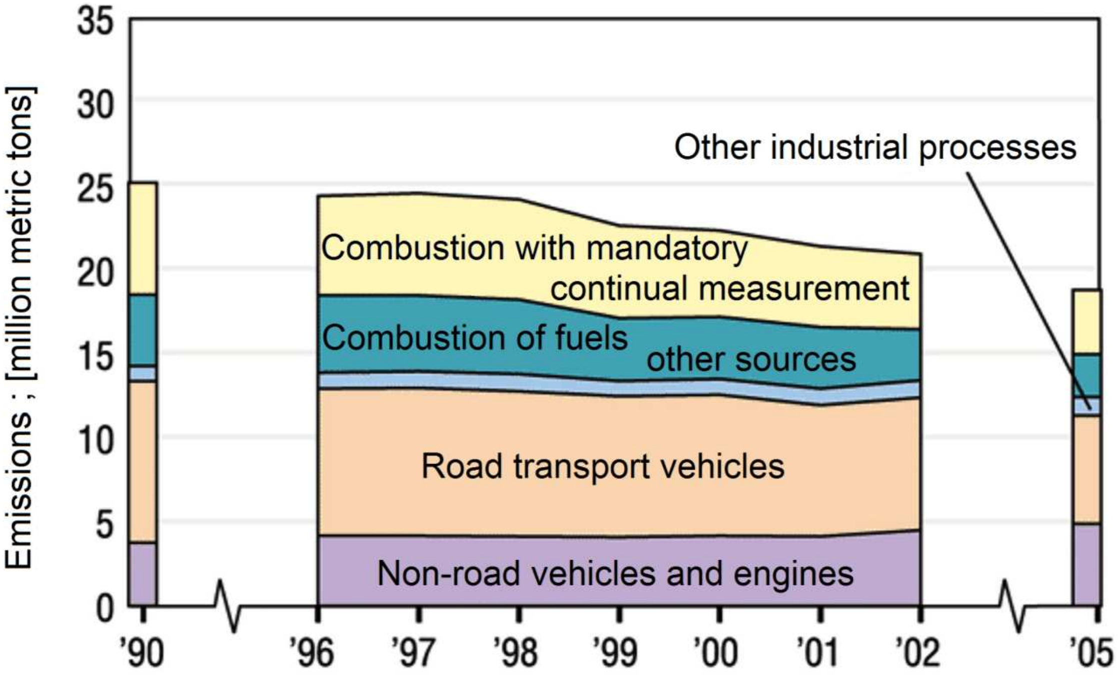
- **Distribution of sources in EU in the year 2011** (Source: EEA)



Origin of nitrogen oxides emissions

- **Distribution of sources in the U.S.A.** (Source: EPA)





Origin of nitrogen oxides emissions

- **Main risks of NO_x emissions from the viewpoint of EU** (Source: EEA)
  - NO_x contributes to acid deposition and eutrophication of soil and water, contributes to the formation of secondary PM aerosols, and tropospheric ozone;
  - Subsequent impacts on aquatic ecosystems in rivers and lakes, damages of forests, field crops and vegetation in general.
  - Eutrophication significantly reduces quality of the water with consequent reduction of biodiversity (incl. changes in the ratio among species);
  - Human health: higher concentrations cause cough, burning, dryness of mucous membranes leading to shortness of breath, inflammation of the air passages, chronic exposure increases susceptibility to respiratory infections;
  - Big NO_2 concentrations cause lethal pulmonary edema with latency up to 72 hours. N_2O reduces hemoglobin concentration in blood.
  - Changes in lung functions due to exposition by NO_2 for healthy persons > 4 mg/m^3, asthmatics ≥ 0.2 , children 0.09 – 0,5 m

Origin of nitrogen oxides emissions

- **Scope of the term NO_x**
  - The term generally includes nitric oxide NO and nitric dioxide NO_2;
  - In the group, there is nitrous oxide N_2O important as greenhouse gas; less important are N_2O_3 and N_2O_5;
  - In the practice the sum is re-calculated to NO_2;
  - The NOx formation especially in energetic processes (combustion), during nitric acid production and during incineration in diesel engines;
  - During combustion processes formation of NO dominates (90 – 99 %), in the second order NO_2 (for liquid fuels 1 – 10 % of total, for solid fuels 1 – 5 % of total).
  - Secondarily in the smoke plume above the stack a part of NO is oxidized to NO_2;
  - During water vapor condensation the mixture of acids HNO_3 and HNO_2, formed from NO_2, represents subsequent acidic deposition to the ecosystem.

Origin of nitrogen oxides emissions

- **Basic mechanisms of NO_x formation**
  - Generating of NO_x is conditioned by high temperatures, with the exception of several industrial chemical processes;
  - 3 mechanisms participate on NO_x formation during incineration of fuels:
    - High-temperature NO_x
    - Fuel NO_x
    - Prompt NOx
  - Among chemical processes the most important role is played by nitric acid manufacture ⇒ see N_2O release in the lecture about GHGs;

Origin of nitrogen oxides emissions

- **High-temperature mechanism**
  - Oxidation of the atmospheric N_2 at high temperatures (especially during combustion of all types of fuels);
  - Reaction rate depends on temperature, concentration of nitrogen, concentration of oxygen and upon the residence time;
  - Necessary condition is reaching the temperature of oxygen dissociation: $O_2 \rightarrow 2O^{\bullet}$;
  - The critical temperature for fast increase of reaction rate is approximately 1200 °C;
  - Mechanism of oxidation is radical-based, however it may vary according to individual concrete conditions;
  - Example: Incineration of coal with excess of air:

$$O_2 \rightarrow 2\,O^{\bullet}$$

$$O^{\bullet} + N_2 \rightarrow NO + N^{\bullet}$$

$$N + O_2 \rightarrow NO + O^{\bullet}$$

Origin of nitrogen oxides emissions

- **High-temperature mechanism**
  - For evaluation of the relative concentration of nitric oxide formed according to high-temperature mechanism Zeldovich proposed formula:

$$[NO] = k_1 \cdot t \cdot e^{\frac{-k_2}{T}} \cdot [N_2] \cdot \sqrt{[O_2]}$$

  - The meaning of symbols are:

k_1	constant characterising the system (related to flow rate) [s^{-1}]
k_2	constant characterising the system (related to temperature distribution) [K]
T	thermodynamic temperature [K]
t	residence time [s]

  - From the aforementioned the possibilities of NO suppression are:

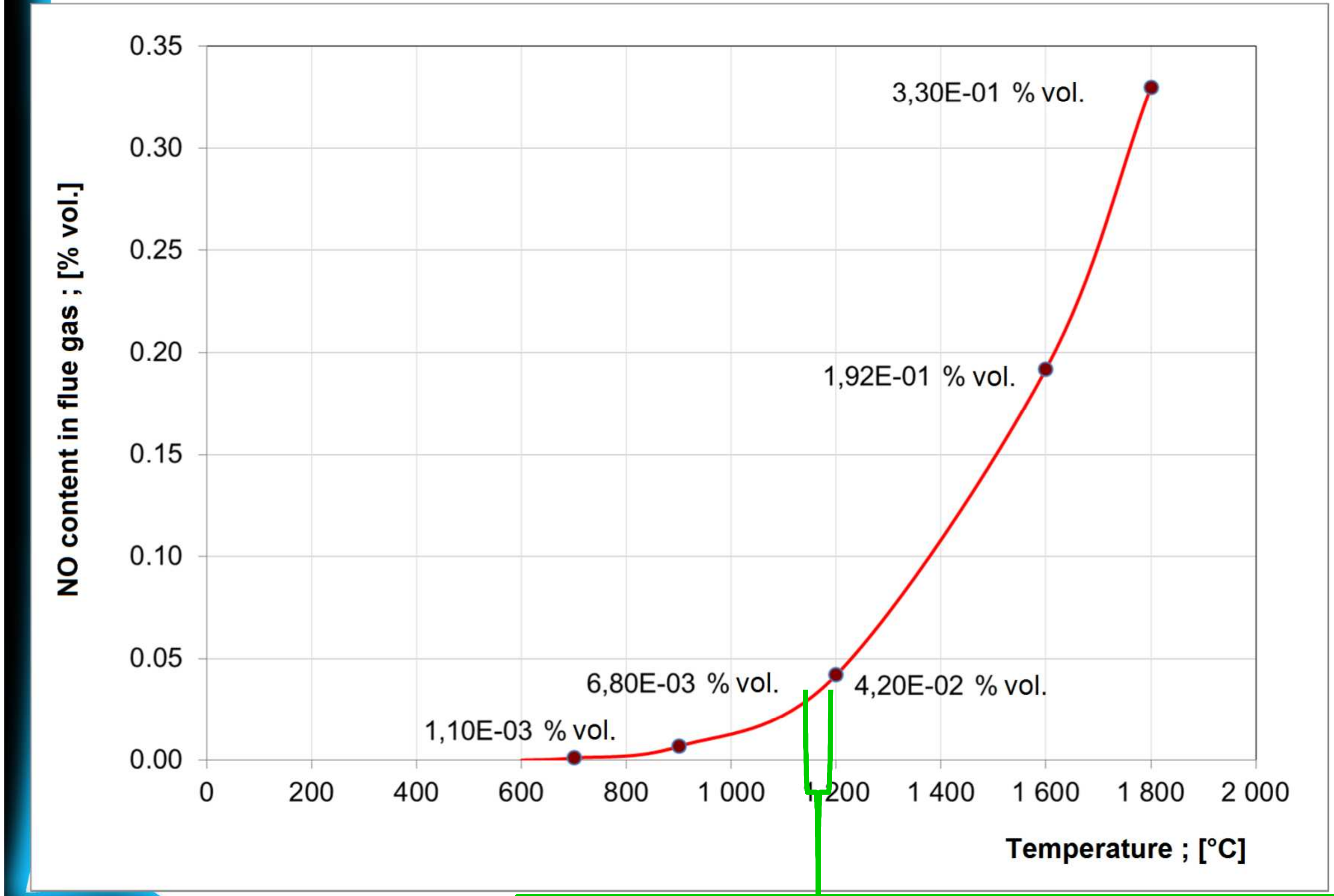
Lowering oxygen concentration (esp. in the high temperature region)

Lowering residence time

Lowering temperature of incineration

Calculation of GHG impact

- **Dependence of NO formation on temperature (combustion of coal)**



1150 – 1200 °C = border of significant contribution of high- ten
mechanism

Origin of nitrogen oxides emissions

- **Fuel nitrogen oxides**
  - Formation from nitrogen contained in the fuel;
  - Reaction requires high temperatures;
  - Only nitrogen bonded within organic molecules undergoes the reaction;
  - Mechanism is determined by three particular actions:
    1. Complicated compounds are decomposed into low-molecular (amines and nitriles), following particles then enter the reaction – N–H, N–C and –C≡N;
    2. Oxidation to NO by oxygen
    3. Reaction with other compounds containing N to form gaseous N_2;
  - Conversion of fuel bonded N to NO is only partial
  - Conversion ratio varies between 0 – 0,85 and depends on the fuel and combustion conditions:

$$\nu = \frac{N_{converted\ \ to\ NO}}{N_{bonded\ \ in\ organics}}$$

Origin of nitrogen oxides emissions

- **Prompt nitrogen oxides**
  - The less frequent mechanism of NO formation;
  - Oxidation of air N_2 inside thin zone at the border of flame;
  - Mechanism is conditioned by presence of gaseous hydrocarbons;
  - The principle discovered by Fenimore:

Initiation creation of hydrocarbons radicals:

$CH^{\bullet}$, $CH_2^{\bullet}$ and so on.

Reaction of radicals with nitrogen:

$$CH^{\bullet} + N_2 \Leftrightarrow HCN + N^{\bullet}$$

$$C + N_2 \Leftrightarrow CN^{\bullet} + N^{\bullet}$$

Transformation of $CN^{\bullet}$

$$CN^{\bullet} + H_2 \Leftrightarrow HCN^{\bullet} + H^{\bullet}$$

$$CN^{\bullet} + H_2O \Leftrightarrow HCN^{\bullet} + OH^{\bullet}$$

Oxidation of $HCN^{\bullet}$ to NO (complicated mechanism depending on conditions).

Origin of nitrogen oxides emissions

- **Primary, secondary and tertiary formation of NO_2**
  - NO_2 is produced by oxidation of NO;
  - In standard burners NO_2, primarily generated inside the combustion chamber, represents max. 10 % of all NO_x;
  - Primary production is determined by shock cooling of the flue gas;
  - The biggest ratio of the primary NO_2 is detected in gas turbines:

    $NO + HO_2^{\bullet} \Leftrightarrow NO_2 + OH^{\bullet}$
  - Secondarily NO is oxidised to NO_2 in the vent and stack at the temperature < 65 °C and excess of air.
  - Tertiary NO is converted into NO_2 in outer environment by photochemical reactions in outer atmosphere and influences formation of tropospheric ozone:

$$NO_2 \xrightarrow{h\nu} NO + O^{\bullet}$$

$$O^{\bullet} + O_2 \rightarrow O_3$$

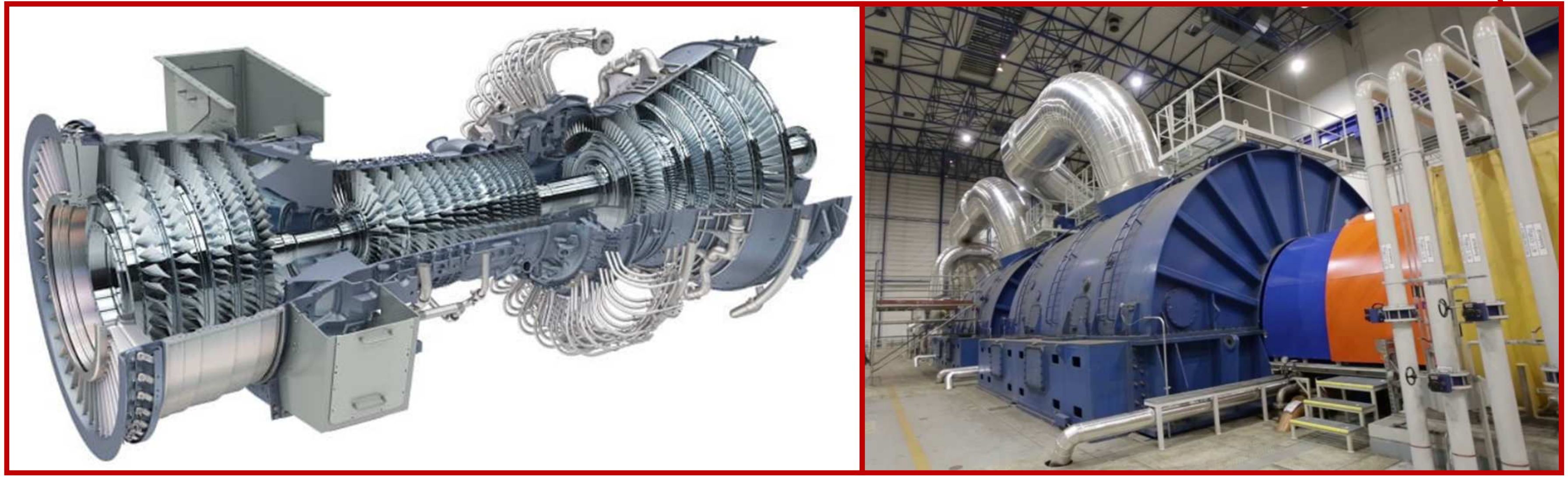
$$O_3 + NO \rightarrow NO_2 + O_2$$

$$H^{\bullet} + O_2 \xrightarrow{M} HOO^{\bullet}$$

$$HOO^{\bullet} + NO \rightarrow OH^{\bullet} + NO_2$$

Origin of nitrogen oxides emissions

- gas turbines:



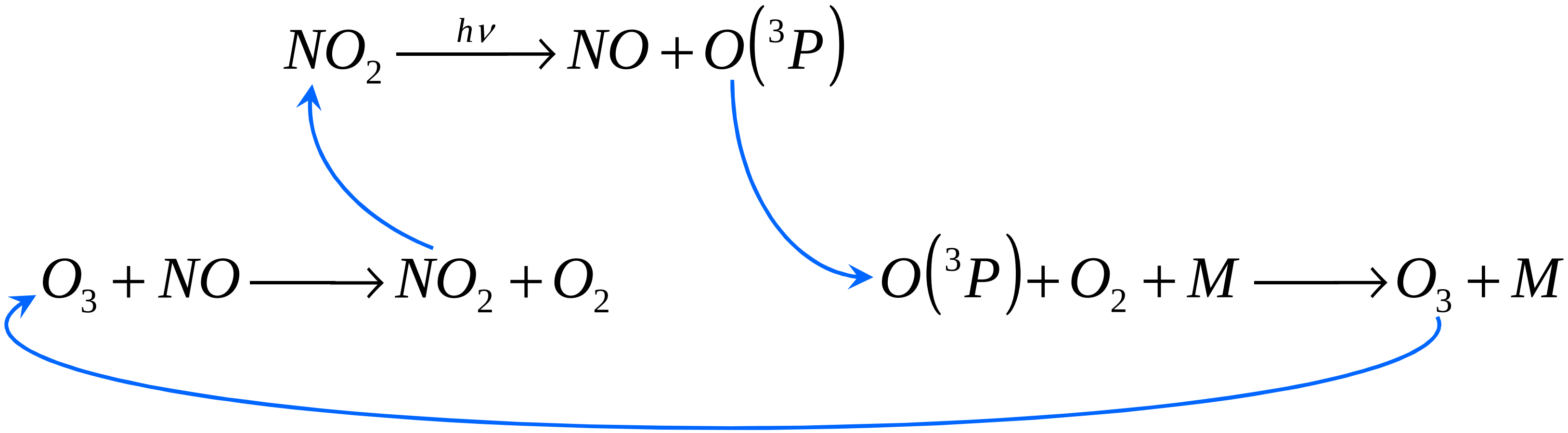
Atmospheric reactions of NO_x

- **Homogenous reactions – reactions of the system NO-NO_2-O_3**
  - The fundament of all tropospheric reactions occurring at daylight;
  - Whereas in the flue gas vents oxidation takes part:

    $2NO + O_2 \rightarrow 2NO_2$ (see above)

    in the free atmosphere reaction with ozone is kinetically preferred:

    $NO + O_3 \rightarrow NO_2 + O_2$
  - Under being exposed by the sunlight following cycle occurs:



$$NO_2 \xrightarrow{h\nu} NO + O\left({}^3P\right)$$

$$O_3 + NO \longrightarrow NO_2 + O_2$$

$$O\left({}^3P\right) + O_2 + M \longrightarrow O_3 + M$$

Note. M is a molecule taking the excessive energy. This is necessary for stabilisation of ozone (see the lecture about reaction mech

Atmospheric reactions of NO_x

- **Homogeneous reactions – reactions of system $NO\text{-}NO_2\text{-}O_3$**
  - Photodissociation $NO_2 \xrightarrow{h\nu} NO + O\left({}^3P\right)$ very fast ⇒ under zenith solar radiation 40° a decay halftime of NO_2 < 2 min
  - oxygen atom in base state $O(^3P)$ reacts with molecular oxygen also immediately;
  - Regeneration reaction of a part of NO to NO_2 called ″titration″ also very fast;
  - Result of the above cycle is equilibrium between photodissociation of NO_2 and oxidation of NO by ozone.
  - Photostationery state is established and is defined by the ratio of rate constants of photolysis of NO_2 and oxidation of NO:

$$\frac{k_{photolysis}}{k_{oxidation}} = \frac{[NO]\cdot[O_3]}{[NO_2]} \qquad [O_3] = \frac{k_{photolysis}}{k_{oxidation}} \cdot \frac{[NO_2]}{[NO]}$$

  - Equilibrium concentration of ozone is given by ratio of NO_2 and NO concentrations.
  - At night only oxidation of NO by ozone occurs, without subs photolysis of NO_2. (Details: photochemical smog)

Atmospheric reactions of NO_x

- **Homogeneous reactions – reactions of system CO-NO_x**
  - CO is released to the atmosphere by incomplete incineration and hydrocarbon oxidation;
  - CO is low reactive but it can form hydroperoxyle radical by reaction with hydroxyle radical:

$$CO + OH^{\bullet} \longrightarrow CO_2 + H^{\bullet}$$

$$H^{\bullet} + O_2 \xrightarrow{M} HOO^{\bullet}$$

  - Hydroperoxyle radical reacts subsequently with NO (see tertiary formation of NO_2) and regenerates hydroxyle radical.

$$HOO^{\bullet} + NO \longrightarrow NO_2 + OH^{\bullet}$$

  - During a day NO_2 undergoes photodissociation as described in previous slides
  - Termination reaction of all cycles above is:

$$OH^{\bullet} + NO_2 \longrightarrow HNO_3$$

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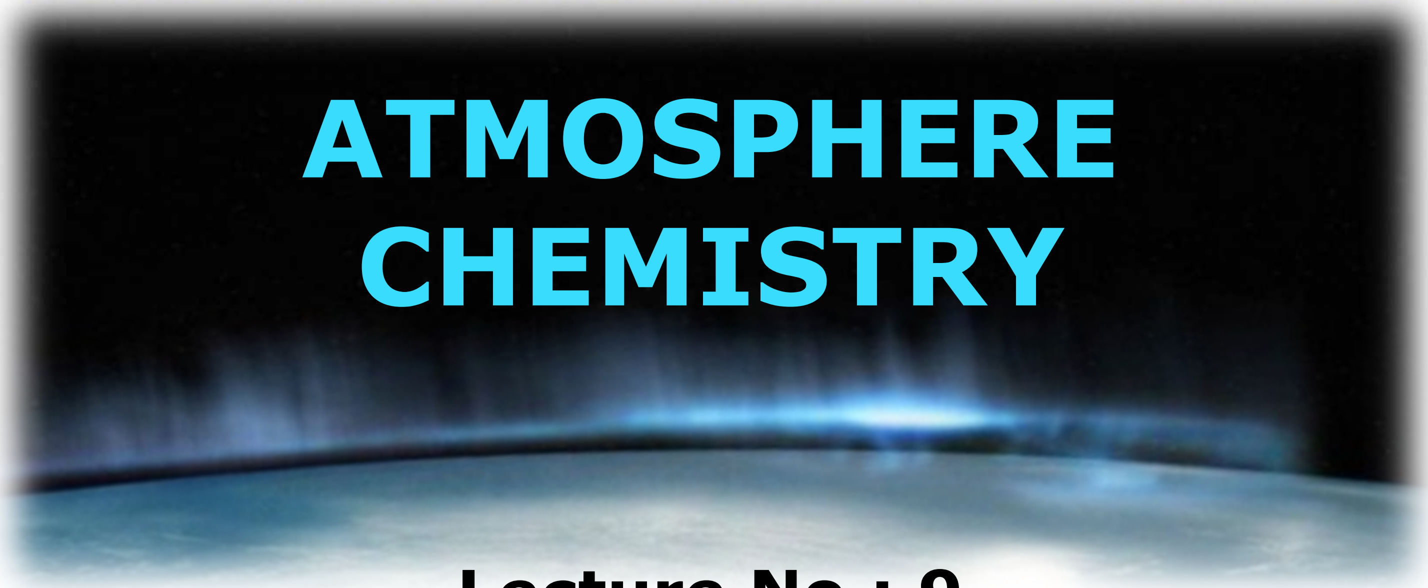


ATMOSPHERE CHEMISTRY

Lecture No.: 9

Organisation of study

- Lecturer: Marek Staf, MSc., Ph.D., phone: +420 220 444 458

  e-mail: marek.staf@vscht.cz,

  web: http://web.vscht.cz/~stafm/

  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 - oral form

- Note:

Scope of lecture 9

Reactions of selected pollutants and important components in atmosphere – toxic substances

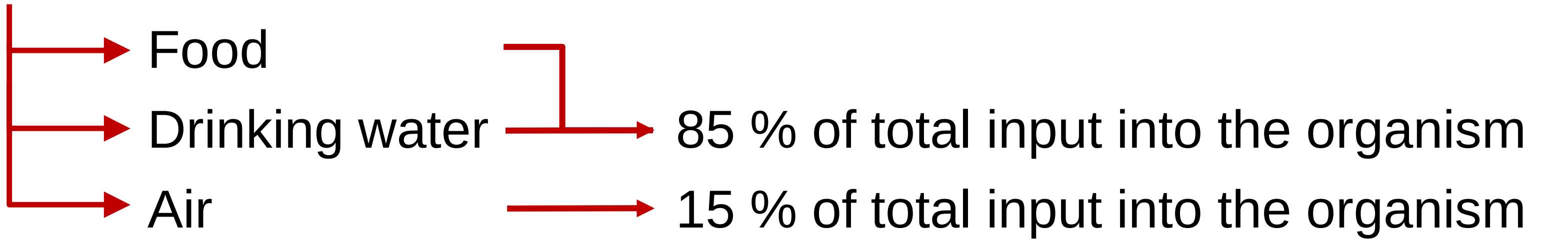
- Toxic substances in atmosphere: definition, distribution, state of aggregation
- Legal definition of heavy metals and volatile organic compounds
- Persistent organic pollutants: compounds classified within POPs and their common properties
- Polychlorinated biphenyls, their congeners, history of the manufacture and utilisation, atmospheric transport
- Organic chlorinated pesticides and polycyclic aromatic compounds
- Polychlorinated dibenzo dioxins and dibenzo furans: their synthesis, health and environmental effects, accidental release
- Chemical weapons: distribution into categories, history of their production and use, examples of health effects

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 - chemically, physically or due to their radioactivity damage health of plants and animals;
  - Substances damaging O_3 - decompose stratospheric ozone layer;
  - Greenhouse gases - change a balance between heat absorption and radiation from the atmosphere;
  - Precursors - in their initial form show no dangerous properties, but undergoes changes resulting in above mentioned properties, or they allow other compounds transformed into dangerous.

Toxic substances generally

- **The largest group of toxic substances present in the air – organic compounds**
- **Presence of toxic compounds in atmosphere – big risk for health**
  - 3 main environmental factors of toxic substances for health:



Food

Drinking water → 85 % of total input into the organism

Air → 15 % of total input into the organism

  - Problem: Food + drinks can be chosen, air is respired spontaneously and inevitably in the volume of 15 – 20 m³/day (= 18 – 24 kg/day);
- **Regarding organic substances, following terms are frequently used:**

– Persistent organic pollutants	POPs;
– Persistent, bioaccumulative and toxic substances	PBT;
– Very persistent and very bioaccumulative substances	vPvB;
– Polyaromatic Hydrocarbons	PAHs;
– Volatile Organic Compounds	VOC:

Toxic substances generally

- **Forms of appearance of toxic substances in nature:**
  - Homogeneous system
    - gases (above critical point)
    - vapors (under critical point)
  - Heterogeneous system
    - liquid aerosols
    - solid aerosols

- **The biggest latent danger = liquids and solid compounds adsorbed onto particulate matter (aerosols)**
  - Carrier = whichever dusty particles: soot, pollen grains, spores, and crystals, salt crystals etc.;
  - Toxic substance itself, especially: POPs, heavy metals, asb radionuclides etc.

Toxic substances generally

- **Definition of toxic substance – complicated**
  - **Paracelsus (1493 – 1541):**

„All things are poison and nothing is without poison; only the dose makes a thing not a poison.“

General definition:

any substance that can impair function, cause structural damage, or otherwise injure the body, or destroys life when absorbed into the system.

  - **Legal definition:**

see for example European Regulation 1272/2008 on classification, labelling and packaging (CLP) of substances and mixtures

GHS06 – Toxic substances

Note. Hazard symbols according to GHS
(Globally Harmonized System
of Classification And Labeling of Chemicals;
Introduced by UN)

GHS08 –
Substances
for h

Toxic substances – heavy metals

- **Definition – heavy metals (in atmosphere especially as aerosols)**
  - Ambiguous definition rather historical indication (in fact all toxic metals)
  - Older definition: All metals, which density is higher than Fe (it means > 7,86 g/cm³) ⇒ valid for Cd, Hg or Pb, not applicable for Se, Al, moreover As is not metal but semimetal;
  - Alternative definition: classification criterium is density > 5 g/cm^3;
  - Universal definition: Heavy metals are all metals or semimetals, which represent any risk for environment;
  - The most discussed heavy metals: Ag, As, Cd, Co, Cr, Cu, Hg, Pb, Ni, Sb, Se, Tl, Zn.

Toxic substances – VOC

- **Definition – Volatile Organic Compounds, VOC**
  - More than one acceptable definitions
  - **Definition according to the method ASTM D3960-90**

    Organic compounds having at 25 °C their vapour pressure (tension) > 13,3 Pa

  - **According to European directive 1999/13/EC** „VOC Solvents Directive“

    Organic compounds having at 20 °C their vapour pressure > 10 Pa

  - **According to UN ECE (United Nations Economic Commission for Europe)**

    All organic compounds with anthropogenic origin, other than methane, which are able to form photochemical oxidants by reaction with NO_x at presence of solar radiation. (the same according to directive 2001/81/EC or 2002/3/EC)

Toxic substances – VOC

- **Definition – Volatile Organic Compounds VOC**
  - Other definitions (continuing from previous slide)
  - **Definition according to directive 2004/42/EC** on the limitation of emissions of volatile organic compounds due to the use of organic solvents in decorative paints and varnishes and vehicle refinishing products and amending (so called Deco Paints Directive)

    Organic substances having at normal pressure 101,3 kPa their boiling point lower or equal to 250 °C.

Toxic substances – VOC

- **Emissions from industry**
  - Especially hydrocarbon solvents (varnishes, paints, glues etc.)
  - Emissions from high number of industrial processes – even unexpected
  - Example: offset printing of newspapers, journals, books, leaflets etc.

Dampening system in offset printing:

aqueous solution with conent of 2 – 12 % vol. of isopropyl alcohol

Cleaning of the printing (ink) rollers:

mixture of aliphatic hydrocarbons with flash point 40 – 60 °C

Toxic substances – POPs

- **Definition – Persistent organic pollutants POPs**

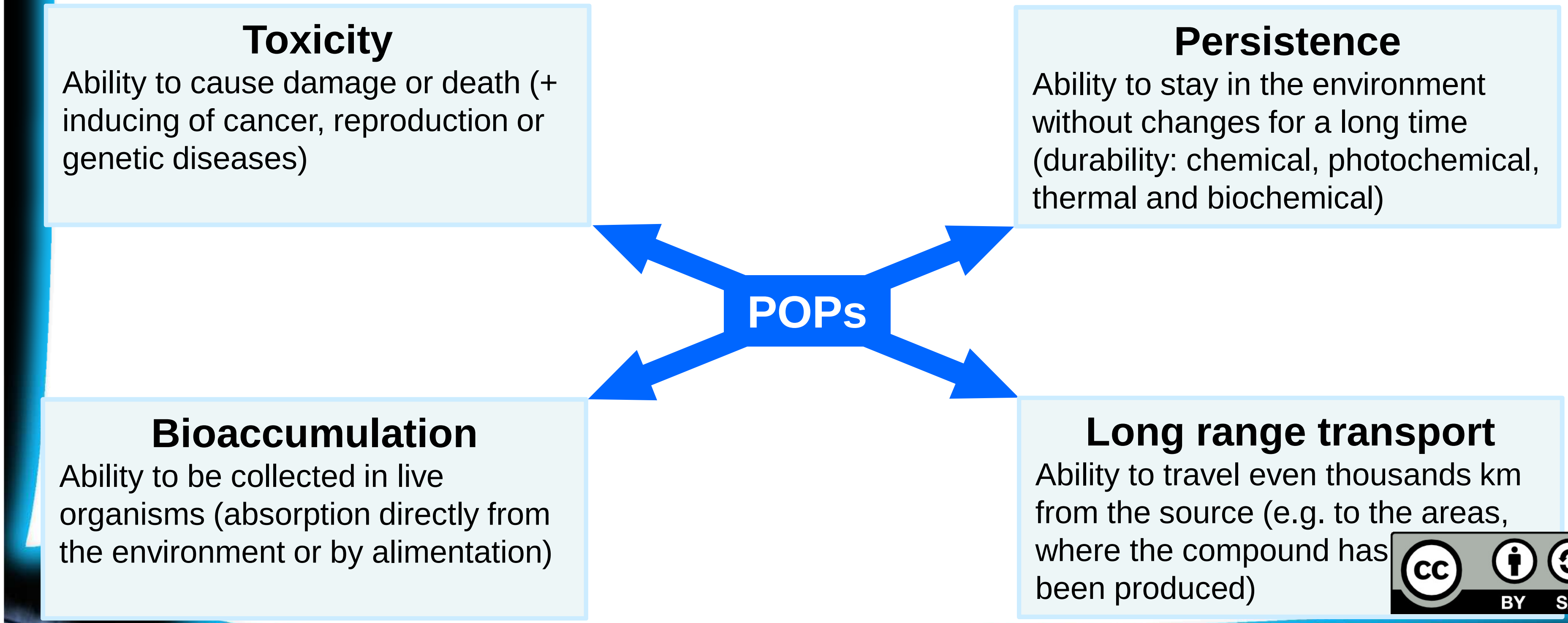
  according to Protocol on POPs, agreed in Aarhus in the year 1998 and according to the Stockholm Convention on POPs from 2001:

  (Source: www.recetox.muni.cz)

  - Persistent organic pollutants are such organic compounds, which:
    - show any toxic properties,
    - are persistent (degradation rate in the environment is slow),
    - are bioaccumulated,
    - undergo long range transport in the air, crossing state borders, and allow depositions,
    - have probable significant negative effect on human health or adverse effects on the environment.

Toxic substances – POPs

- **Completion of definition of POPs** (Source: www.recetox.muni.cz)
  - They are present as chemical individual or as the mixture, forming specific group. Compounds in the group:
    - have similar properties and are released to the environment together;
    - mixture is available only as certain preparation.



Toxicity
Ability to cause damage or death (+ inducing of cancer, reproduction or genetic diseases)

Persistence
Ability to stay in the environment without changes for a long time (durability: chemical, photochemical, thermal and biochemical)

POPs

Bioaccumulation
Ability to be collected in live organisms (absorption directly from the environment or by alimentation)

Long range transport
Ability to travel even thousands km from the source (e.g. to the areas, where the compound has been produced)

Toxic substances – POPs

- **Distribution of persistent organic pollutants – according to the composition**
  - Polychlorinated biphenyls (PCB);
  - Pesticides, mainly organic chlorinated pesticides (OCP);
    e.g. Chlorinated insecticides
  - Polycyclic aromatic hydrocarbons (PAHs);
    sometimes called polyaromatic hydrocarbons
  - Polychlorinated dibenzo dioxins dibenzo furans (PCDD);
    and polychlorinated dibenzo furans (PCDF);
  - Other persistent, bioaccumulative and toxic substances (PBT);
    Note: Usually second generation, i.e. substitutes of the older types of highly toxic POPs.

Toxic substances – POPs

- **Distribution of persistent organic pollutants – according to origin**
  - Compounds, which were wilfully manufactured for certain purpose; Especially:

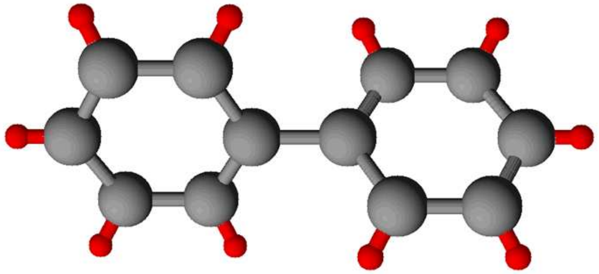
Polychlorinated biphenyls	PCB
Polychlorinated benzenes (solvents)	PCBz
Polychlorinated naphthalenes	PCN
Polychlorinated phenols	PCP
(pentachlorphenol – wood impregnation)	
Polybrominated diphenyl ethers	PBDE
(so called brominated flame retardants)	
Chlorinated paraffins	CP
(lubricants, solvents etc.)	

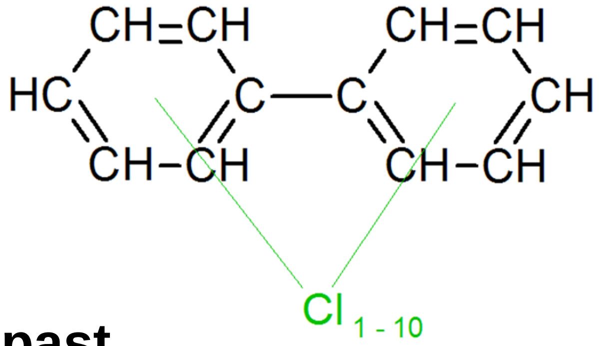
  - Compounds, which are formed as by-products of other processes; Especially:

Polychlorinated dibenzo dioxins and furans

Polychlorinated biphenyls

- **General characteristics**
  - Number of chlorine atoms in the biphenyl molecule is 1 – 10;
  - Molecules can be differently substituted, in total 209 congeners were identified;
  - The biggest toxicity – in so called coplanar arrangement

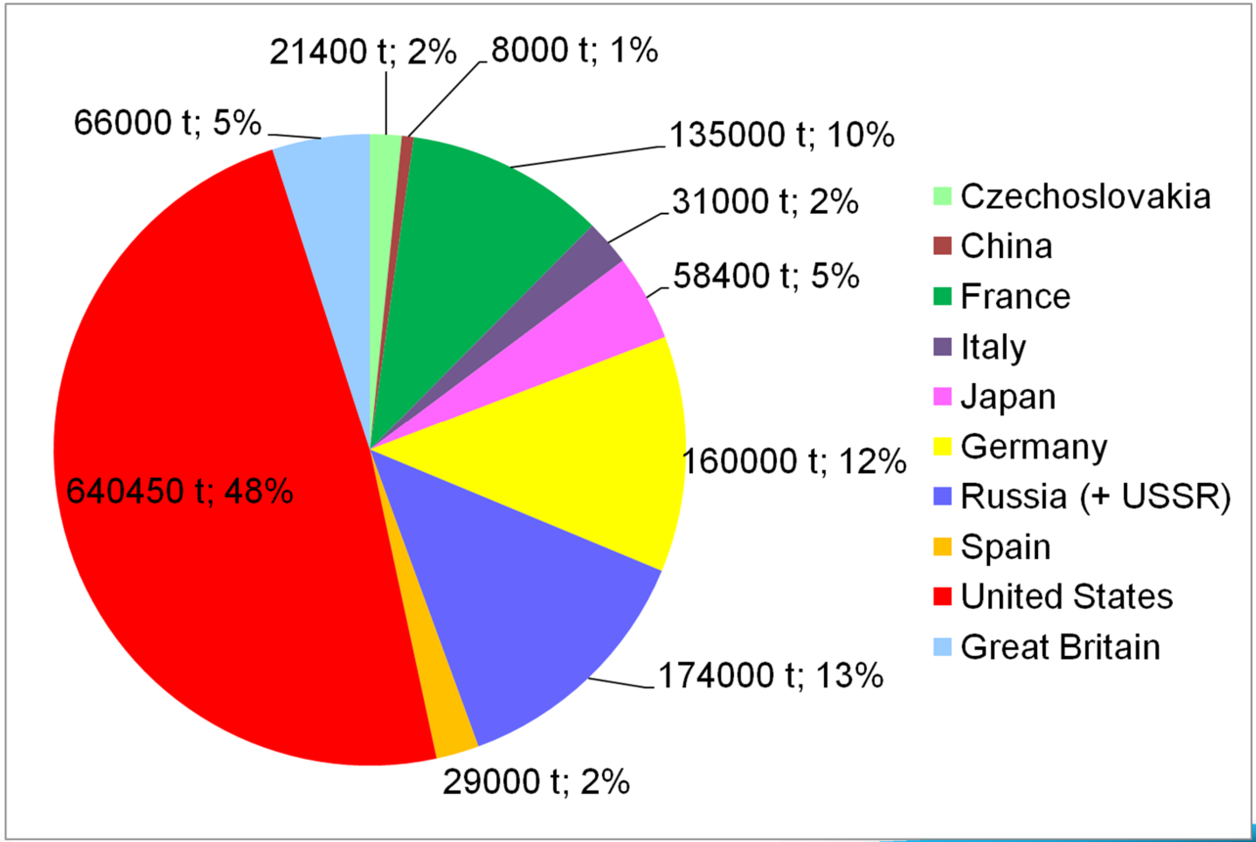




- **Production – massive manufacture in the past**
  - At present their production (with some exceptions) stopped;
  - Basic historical applications: heat exchanging media;
    hydraulic liquids (vacuum pumps, drilling systems);
    cooling liquid in transformers;
    dielectric liquid in capacitors.

Polychlorinated biphenyls

- **Production**
  - Totally produced ca. 1,7.10^6 metric tons
- **Transport in atmosphere**
  - high boiling point ⇒ particularly aerosol in the air, e.g. PCB sorbed on dusty particles.



Organic chlorinated pesticides

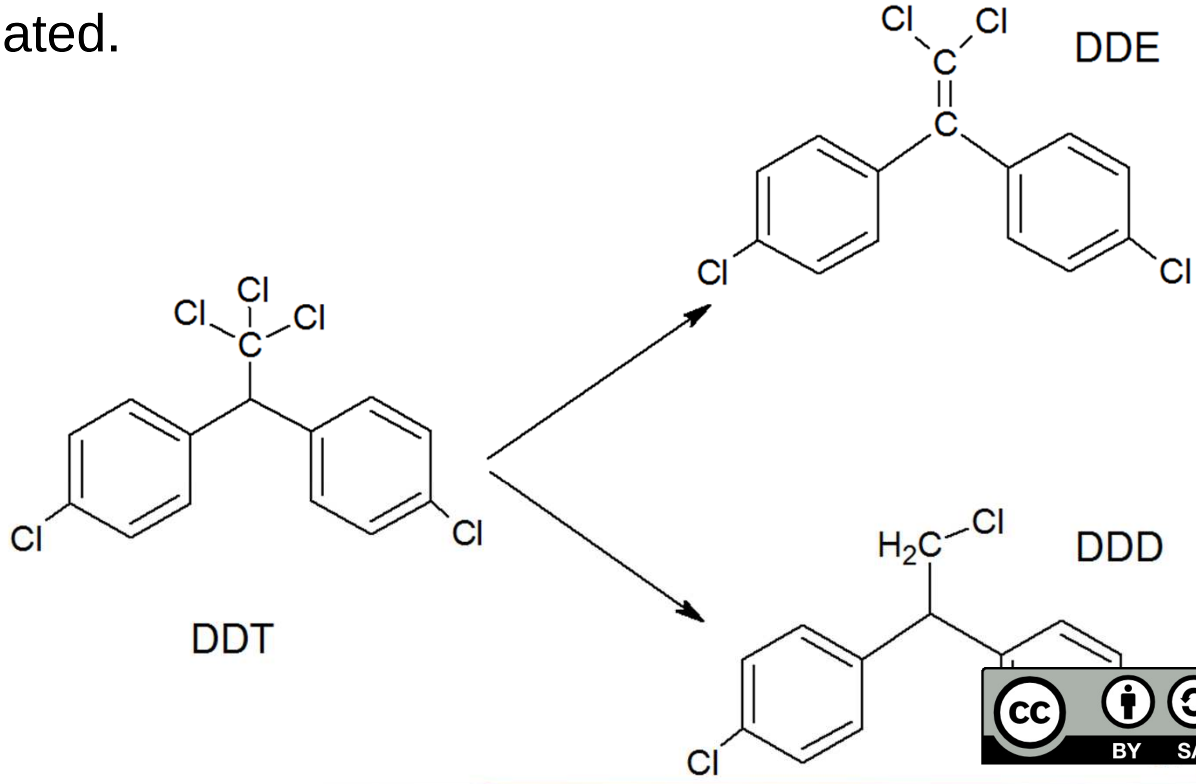
- **Characterization of OCP**
  - almost without exceptions: persistent, bioaccumulative and toxic;
  - majority of OCP belongs to organochlorinated insecticides;
  - production and selling is generally banned.
- **Atmospheric appearance**
  - usually present in soil and water ⇒ in the air they are present as aerosol (and on the surface of dusty particles etc.).
- **Historically most produced OCP**
  - DDT 1,1,1-trichloro-2,2-bis(4-chlorphenyl)ethane
  - γ-HCH 1,2,3,4,5,6-hexachlorocyclohexane lindane

    (totally 5 stereoisomers, which the most important α-HCH +β-HCH)
  - CHL cis/trans-1,2,4,5,6,7,8,8-octachloro-2,3,3a,4,7,7a-hexahydro-4,7-methano-1H-indene chlordane
  - Aldrine

    Dieldrine } chlorinated cyclodiene-based insecticides na famous chemists Diels and Alder.

Organic chlorinated pesticides

- **DDT – possibilities of natural decomposition**
  - very slow process (e.g. In Czechoslovakia DDT production stopped in 1974, in Russia in 1993), however significant concentrations still detected in the environment;
  - natural decay possible by dehydrogenchlorination and dechlorination
  - from the concentrations ratio (DDE + DDD)/DDT the biodegradation rate can be calculated.



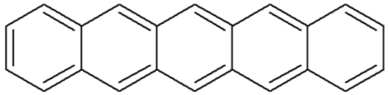
Organic chlorinated pesticides

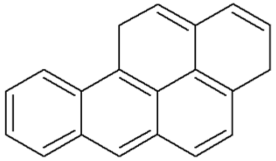
- **DDT**

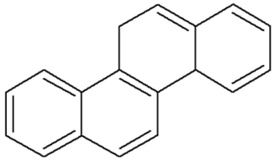
Shortly after its invention in 1939, DDT was promoted as a miricle pesticide all around the world.

Polycyclic aromatic hydrocarbons

- **PAHs**
  - less frequent synonym is also PAC polycyclic aromatic compounds
  - or, sometimes PNA polynuclear aromatics
  - they are formed by two or more benzene cores, arranged:
    - linear arrangement
    - cluster arrangement
    - angular arrangement


Pentacen
Pentacene


Benzo(a)pyren
Benzo(a)pyrene


Chrysen
Chrysene

  - Also their following derivatives are PAHs too: alkyl-, halogen-, nitro-, amino-, hydroxy-
  - Extraordinary toxic compound: benzo(a)pyrene – strongly carcinogenic and mutagenic:

    formed by incomplete combustion (300 up to 600 °C)

    discovered in 1933 in black coal tar (one of the first carcinogenes)

Polycyclic aromatic hydrocarbons

- **PAHs – Emissions into the air:**

  Combustion processes – present in tar and soot (carbon black) e.g. from steelworks and heat plants

  Combustion engines - especially diesel

  Household sources (danger for homes candles, grilled and fried food, fireplaces and so on).

PCDDs and PCDFs

- **Polychlorinated dibenzo-p-dioxins and polychlorinated dibenzo furans**
  - Example tetrachlorodibenzoparadioxin ($LD_{50} = 10^{-9}$ x body weight)
  - Illustrative example of accidental leakage to the atmosphere:

Seveso 1976 – accident in the premises of the company Givaudan (part of concern Hoffmann-La Roche)

Manufacture of herbicide TCP (trichlorophenol) ⇒ failure in production process with accumulation of TCDD in the reactor and subsequent release of 2 kg TCDD into the air via security valve;

Error repaired within 20 minutes, but the leakage officially confessed after 17 days ⇒

Transfer of TCDD to soil by the rain

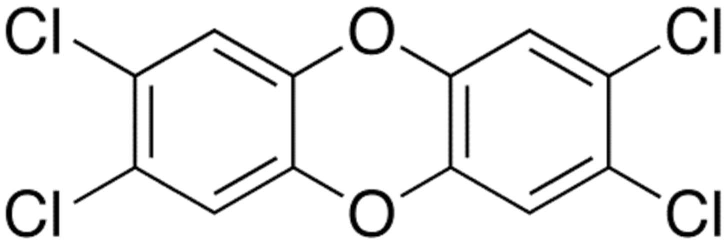
Contamination of wide area

250 people hospitalized

Evacuation of 600 persons + subsequent health damages

PCDDs and PCDFs

- **Polychlorinated dibenzo dioxins and polychlorinated dibenzo furans**
- **Course of the accident:**
  - Production of the herbicide TCP (2,4,5 – trichloro phenol) for wood knapweed control
  - 2,3,7,8-tetrachloro dibenzo dioxin (TCDD) is a by-product of the TCP synthesis



  - Production reactor must be stirred permanently to avoid overheating
  - Saturday, 10th July, 1976: weekend shutdown ordered according to Italian law.
  - Staff did not accomplish the prescribed correct shut down sequence - stirrer disabled before the tank was cooled down completely
  - In the tank a mixture TCP + NaOH started to react exothermally = raising of pressure

PCDDs and PCDFs

- **Polychlorinated dibenzo dioxins and polychlorinated dibenzo furans**
- **Course of the accident:**
  - Pressure exceeded the value set up on the safety valve = emergency opening
  - Leakage of up to 6 tons of the mixture containing ca. 1 – 2 kg TCDD
  - Dispersion of the hot aerosol over the area of 18 km^2
  - Due to adverse wind conditions the toxic cloud was transferred near the city.
  - The malfunction in the factory was removed until 20 – 30 minutes.
  - Legal authorities were not informed about TCDD content in the released aerosol by the management = no immediate measures were adopted.
  - Only after health problems reported by the inhabitants (14 days after the accident) the government established a committee and evacuated all the people living within 4 km around the factory.
  - 1000 ha of the fields contaminated, factory closed and after demolished

PCDDs and PCDFs

- **Seveso – the city located in the north Italy: Givaudan company**

14,000 inhabitants

Location:

20 km north of Milan

CC BY SA

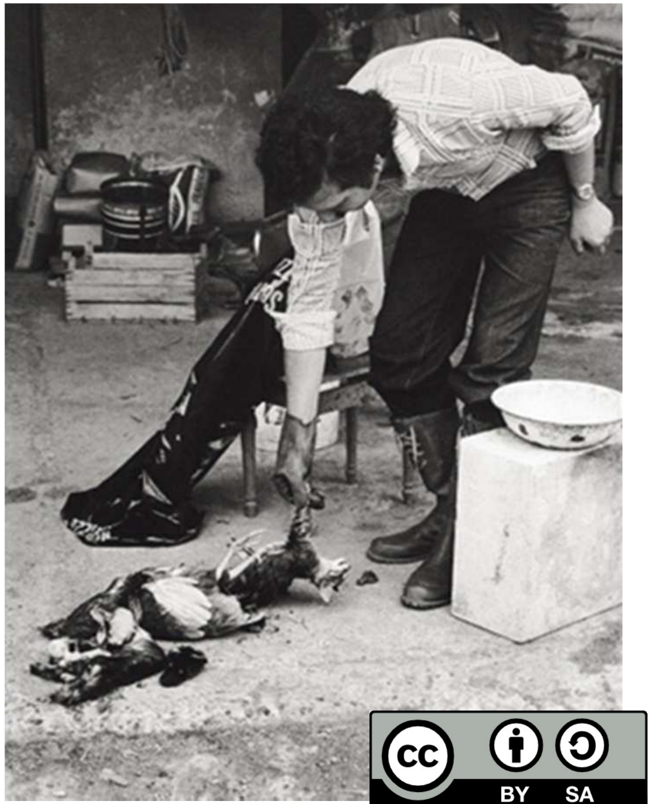
PCDDs and PCDFs

- **PCDD – consequences of the Seveso accident**

  Immediate decease of birds exposed by the aerosol during their flight!

  Within the are of 5 x 0.7 km decease of 3,000 animals (especially sheep)

  Subsequently 80,000 exposed farm animals were euthanized.



PCDDs and PCDFs

- **PCDD – illustrative photos from Seveso accident**

Typical skin injury, caused byPCDD

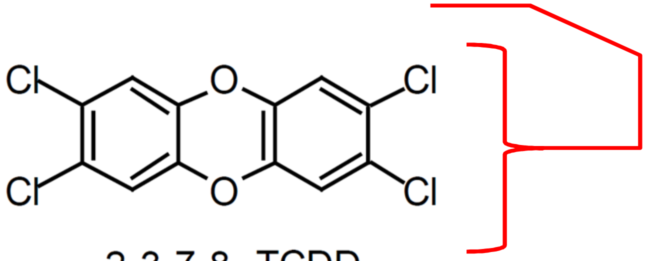
– expansion of chloracne

PCDDs and PCDFs

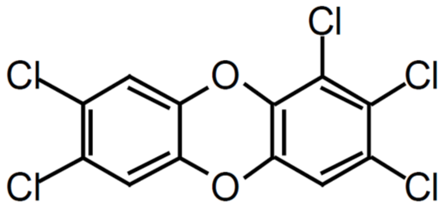
- **PCDD – consequences of the Seveso accident**
  - Exposed inhabitants suffered by the acute intoxication: headache, respiratory difficulties and skin itching
  - Later symptoms: severe rash and blistering - development of chloracne in several hundred people, after a certain time about 200 people suffered from severe hepatic and renal damage (cirrhosis, liver cancer)
  - 600 people sterile permanently, tens of pregnant women must undergo interruption due to seriously damaged foetus.

PCDDs and PCDFs

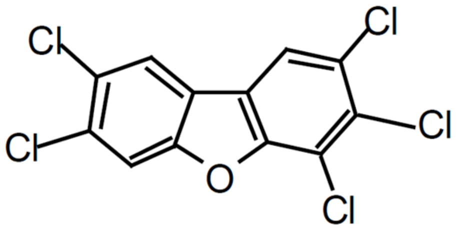
- **Generation of PCDD a PCDF during incineration (esp. wastes)**
  - Highly toxic, carcinogenic, mutagenic and teratogenic compounds ⇒ very low imission limit 0.1 ng.m_n^{-3} TEQ (3 the most toxic depicted):



2,3,7,8,-TCDD



1,2,3,7,8,-pentaCDD



2,3,4,7,8,-pentaCDF

  - During combustion decomposition of halogen derivatives and subsequent synthesis of PCDD/F during cooling down the flue gas ⇒ temperature window 200 – ca. 450°C (sometimes up to 6

PCDDs and PCDFs

- **Generation of PCDD and PCDF during combustion** (Source: Konduri & Altwicker 1994)
  - Formed both in gaseous phase or catalytically on solid surfaces.
  - Reaction on the surfaces considered as main source for combustion processes.
  - For catalytic surface process two mechanisms were proposed:
    - Mechanism through precursors;
    - Synthesis de novo;
  - Precursor mechanism is based on reaction of chlorinated hydrocarbons (chlorobenzenes and chlorophenols).
  - De novo synthesis estimates recombination of carbon, oxygen, hydrogen and chlorine.
  - Ratio of pyrosynthetic mechanism in gas, precursor mecha de novo synthesis is not accurately defined.

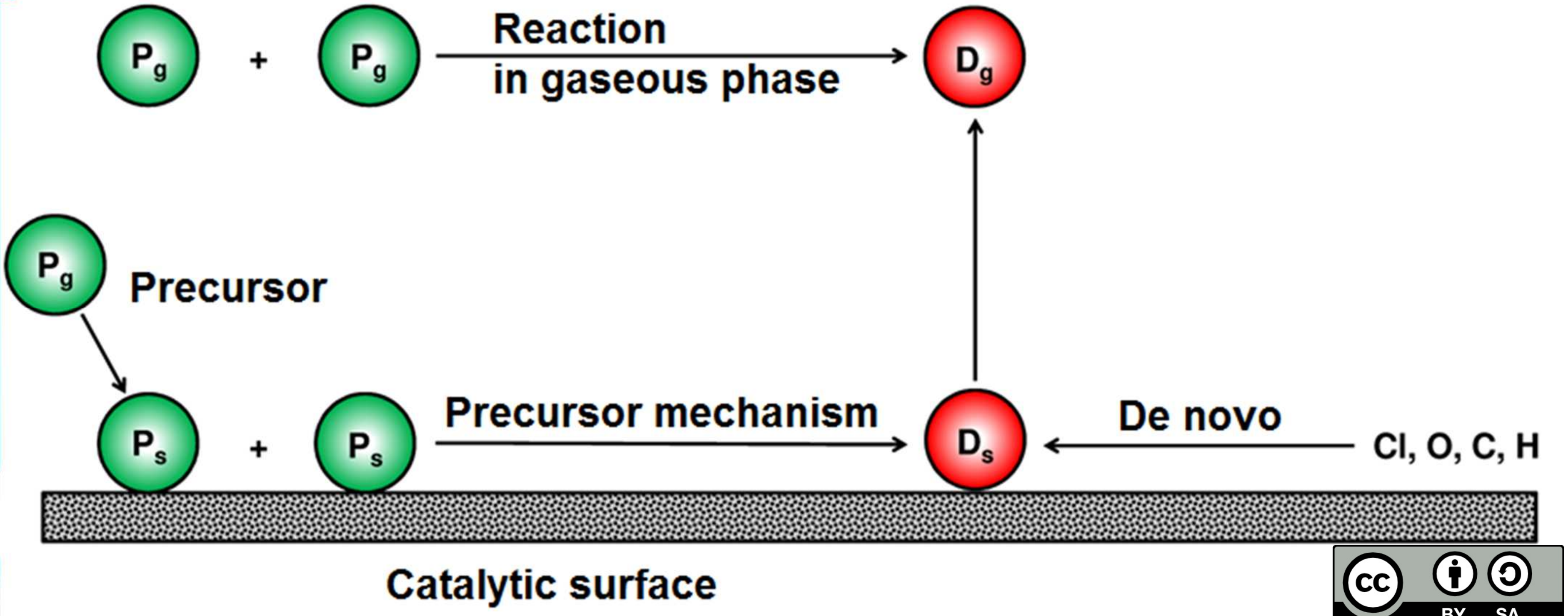
PCDDs and PCDFs

- **Formation of PCDD and PCDF during incineration**

  (Source: Konduri & Altwicker 1994)

  - General rules: Precursor mechanism is primary and runs at higher temperatures.

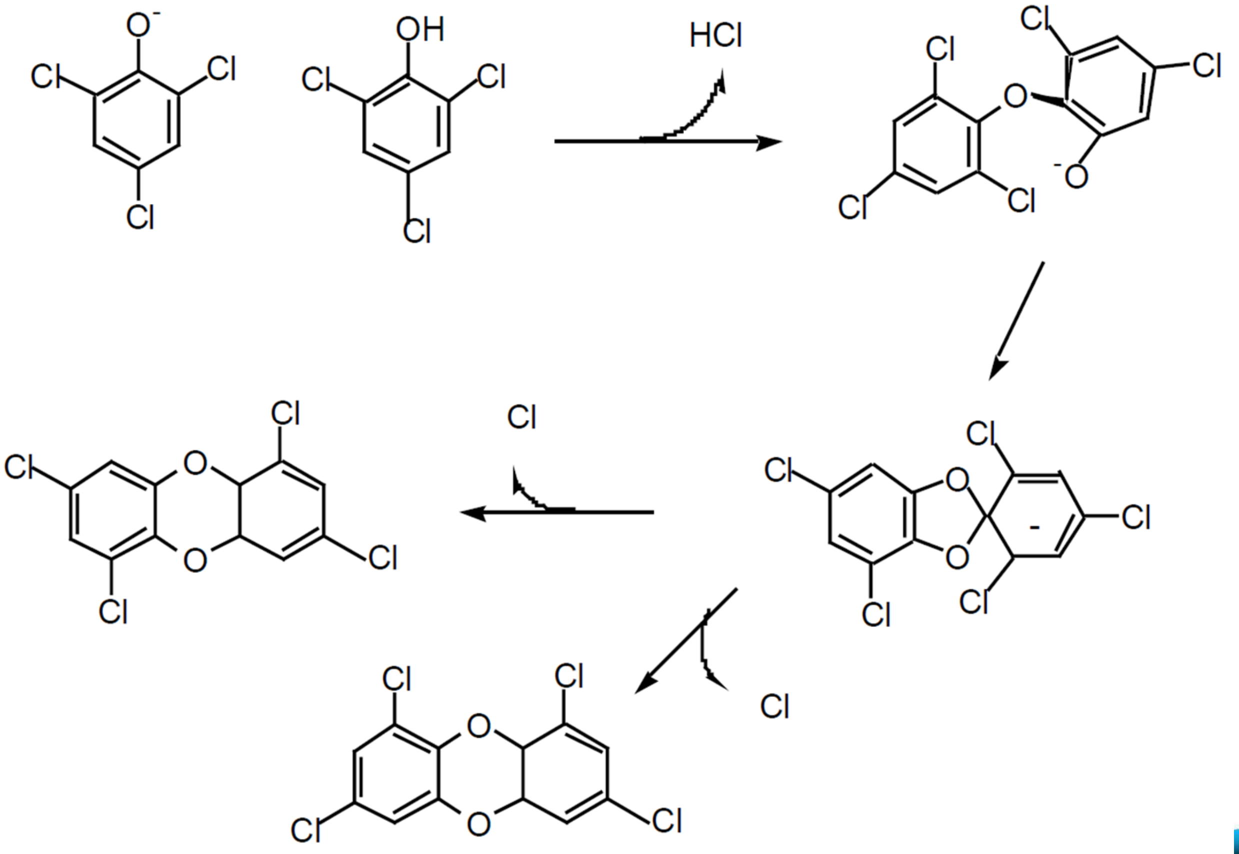
    Synthesis de novo continues at lower temperatures.



PCDDs and PCDFs

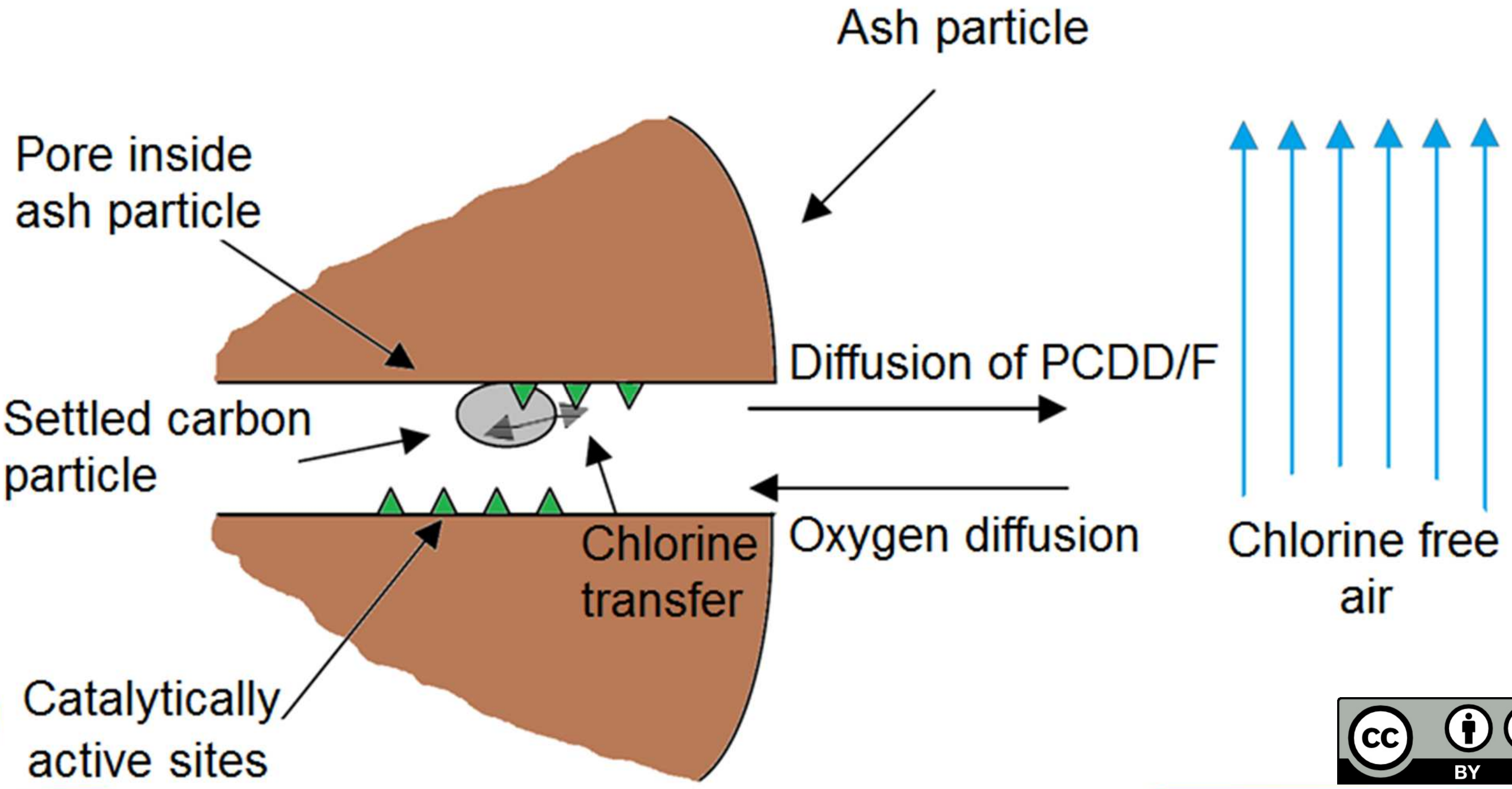
- **Formation of PCDD and PCDF during incineration**
  - Precursor mechanism includes more alternatives.
  - Reaction runs via chlorinated phenolate intermediate (Source: Tuppurainen et al 1998):

Note. PCDDs are formed also during some chemical processes like pentachlorphenol production etc.



PCDDs and PCDFs

- **Formation of PCDD and PCDF during incineration**
  - De novo synthesis;
  - Strong catalytic activity of Cu
  - Maximum reaction yield at 325 °C (Source: Milligan and Altwicker 1995):



Chemical weapons - introduction

- **History of chemical warfare**
  - Written sources available from antiquity (Source: www.population-protection.eu)

    Example: In 178 A. D. suppression the rebellion of peasants in China using unspecified arsenic-containing mist (As_2O_3);
  - Massive application during WW1 (Source: www.valka.cz)

    Estimative number of exposed people is 1,297,000, where 91,200 soldiers died

    Totally applied:

Germany	68 000 tons
France	36 000 tons
Great Britain	25 000 tons

  - Ban of chemical weapons: Geneva protocol (1925) and sub international agreement (1993).

Chemical weapons - overview

Group	Examples		
Tear-forming	bromobenzylcyanide (BA) chloropicrin (PS) 2-chloro-benzalmalononitrile (CS)		chloroacetophenone (CN) 1-bromo-2-propanone (BA) dibenz[b,f][1,4]oxazepine (CR)
Causing vomiting	adamsit diphenylcyanoarsane		diphenylchloroarsane
damaging haematopoiesis	arsane (AsH_3) hydrogen chloride		cyanogen chloride hydrogen cyanide
Causing respiratory damages	chlorine diphosgene nitrogen dioxide perfluoroisobutylene		phosgene red phosphorus chlorosulphonic acid $TiCl_4$ ZnO_2
Oxygen transport inhibitors	hydrogen cyanide		sulphane
Blistering agents	yperite lewisite phosgene	ethyl dichloroarsane nitrogen yperite phosgene oxim	methyl dichloroarsane phenodichloroarsane sesquiyperite
Neurotoxic	sarin soman	cyklohexylsarin tabun	diisopropyl-phospho GE, VE, VG, V-Gas,

Chemical weapons – production

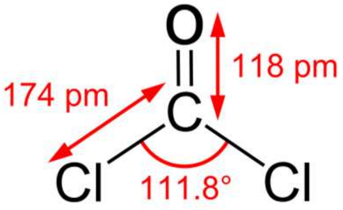
Period		Compound
WW1	1915	chlorine, phosgene, benzylbromide
	1916	diphosgene, dibromo methyl-ethylketone, chloropicrine, yperite
	1917	diphenyl chloroarsane
	1918	diphenyl-cyanoarsane, ethyl-dichloroarsane, dichloromethyl ether
Betwen wars	1930	First nervously paralytic agents (Germany)
WW2	1941 – 1945	CO, HCN concentration camps
	1942 – 1945	produced 12,000 tons of tabun, not used
	1944 – 1945	sarin, soman + 200 other organophosphates, not used
After WW2	1955	group of compounds type agent V (USA)
	1958	VX (USA)
	1979 - 1988	yperite, Iran vs. Iraq
	2013 (?)	yperite, sarin Syria (?)

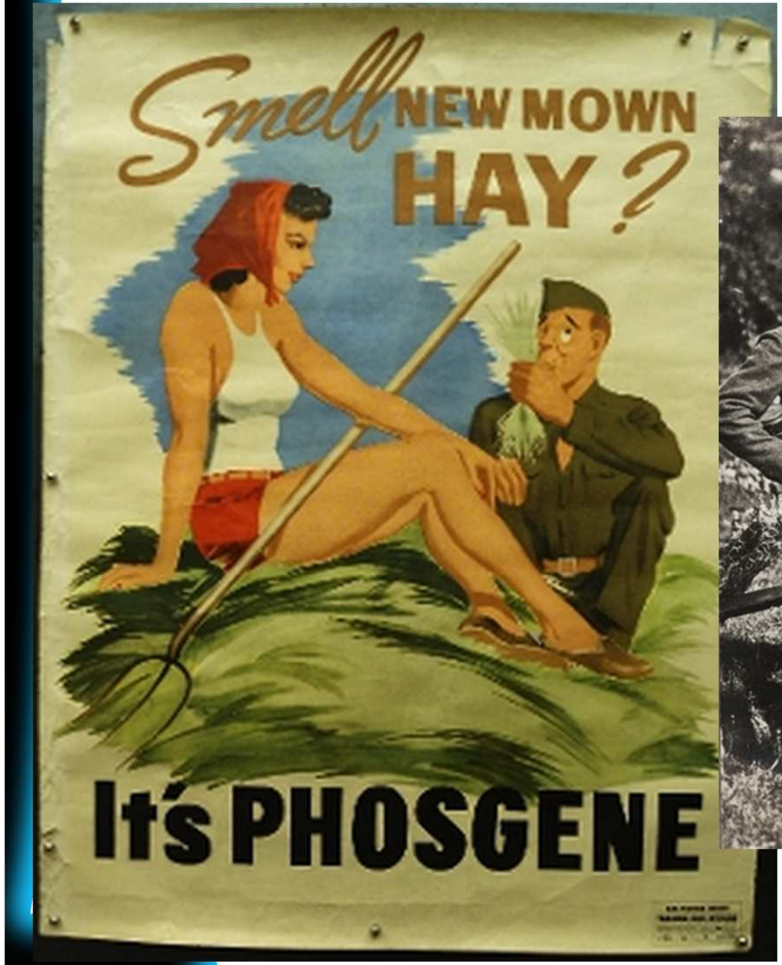
Chemical weapons - examples

- **Phosgene (carbonyl dichloride)**
  - Suffocating and toxic colourless gas;
  - After high dilution the smell of hay or rotten potatoes;
  - Manufacture via direct synthesis $CO + Cl_2$ at 130 – 150 °C and catalysis by active coal or Pt sponge;
  - Atmospheric formation by photolysis of chlorinated hydrocarbons (CH_2Cl_2, CCl_4 and so on);
  - Mechanism of intoxication: hydrolysis in lungs to $H_2CO_3 + HCl \Rightarrow$ subsequently damaging membranes of lung alveoli and progression of oedema;
  - Immediately life endangering concentrations > 50 ppm_V, where the content of 500 – 800 ppm is lethal during exposition < 1 min.
  - Civil utilisation: raw material for organic syntheses;
  - Military application: WW1, especially cannon ammunition filled with the compound.

Chemical weapons - examples

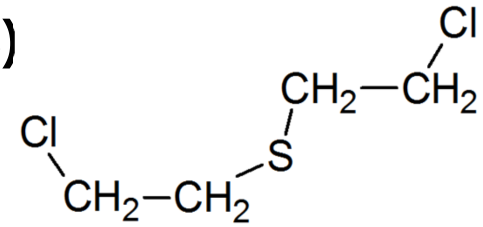
- **Phosgene (carbonyl dichloride)**
  - Contemporary pictures:





Chemical weapons - examples

- **Yperite; bis(2-chloroethyl)sulphide (mustard gas)**
  - At 20 °C colourless oily liquid without smell (characteristic mustard odour due to insufficient purity during production)



  - Mechanism of intoxication: penetration into organism through skin, respiratory tract or other mucous membranes; exposed surface shows morphological changes, inflammation and necrosis;
  - Symptoms: does not irritate immediately

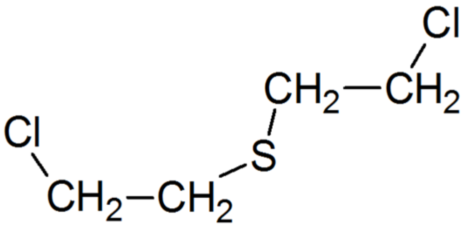
    The effect comes after a latency time; depression, headache, weakness, raised temperature, fluctuating blood pressure and pulse;

    After certain time skin is reddish and swelling is visible; within 24 hours blisters appear with subsequent development during up to 6 days (risk of infection);

    In case of intrusion into eyes large swelling of the eyelids, damage to the cornea.
  - War application: dispersion of aerosol by grenade explosion etc.
  - Civil application: not manufactured or used.

Chemical weapons - examples

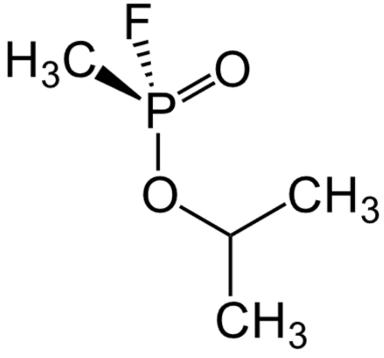
- **Yperite; bis(2-chloroethyl)sulphide (mustard gas)**
  - Contemporary pictures:



Affected skin

protective cl

Chemical weapons - examples

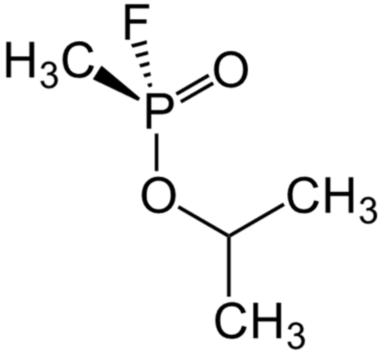


- **Sarin; O-isopropylmethyl fluorophosphonate**
  - organophosphates-based neurotoxin
  - At 20 °C colourless volatile liquid with fruity scent
  - Synthesised in Germany in 1939 by the team: **S**chrader, **A**mbros, **R**itter, Van der L**in**de.
  - Production: synthesis of isopropanol with methyl difluorophosphate (CH_3POF_2).
  - Mechanism of intoxication: penetration into organism through skin, respiratory tract or other mucous membranes; exposed surface without local symptoms; subsequently inhibition of choline esterase causing accumulation of acetyl choline ⇒ interruption of signal transfer via neurons;
  - Symptoms: headache, then salivation and respiratory insufficiency, convulsions, in the last stage loss of consciousness, vomiting, defecation, polio of respiratory muscles and death
  - War application: dispersion of aerosol (possible synthesis in
  - Civil application: not produced or used

Chemical weapons - examples

- **Sarin; O-isopropylmethyl fluorophosphonate**

Contemporary footage: (1995, Tokyo attacked by the sect Aum Shinrikyo)



Shoko Asahara (leader)

first aid for victims (12 people died 5,500 poisoned)

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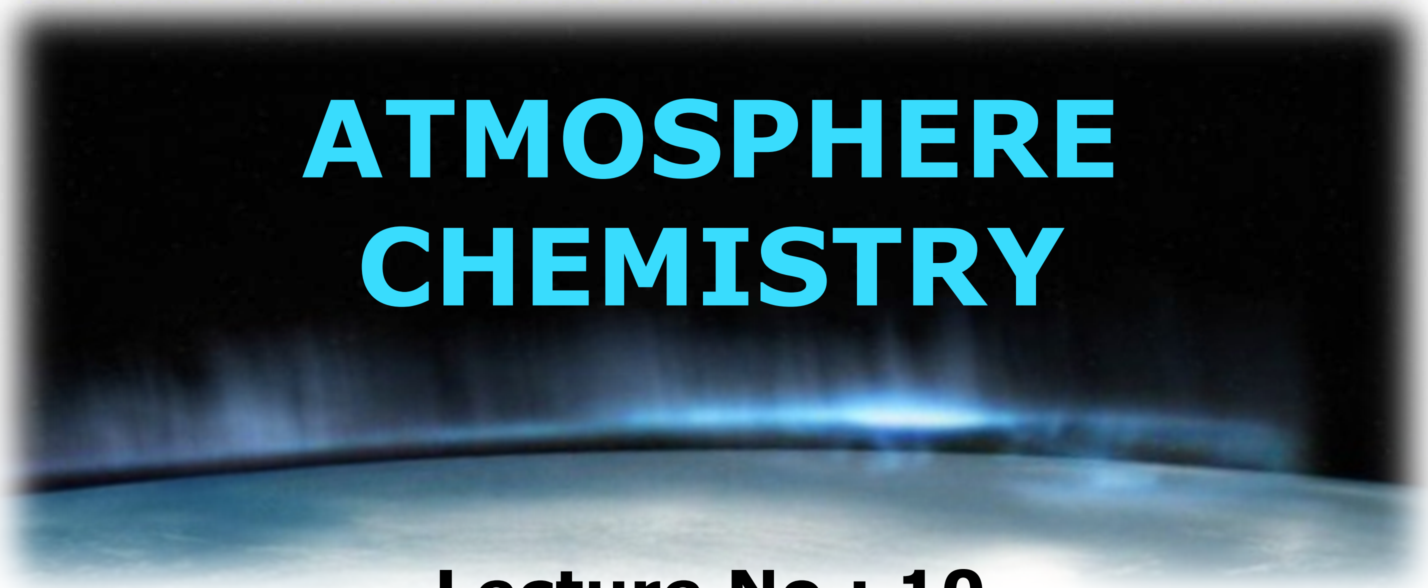

ATMOSPHERE CHEMISTRY

Lecture No.: 10

Organisation of study

- Lecturer: Marek Staf, MSc., Ph.D., phone: +420 220 444 458

  e-mail: marek.staf@vscht.cz,

  web: http://web.vscht.cz/~stafm/

  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 - oral form
- Note:

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Scope of lecture 10

Reactions of oxygen and water, formation of clouds and precipitations

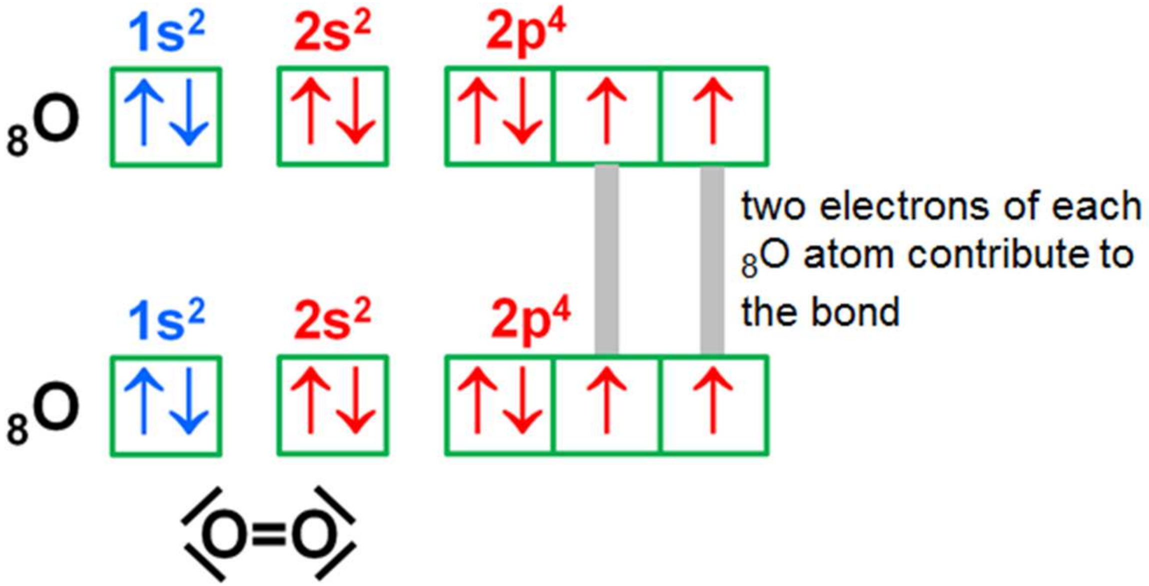
- Oxygen, its electron configuration in the base and excited state and possible ways of excitation
- Concentration of different forms of oxygen in atmosphere, generation of atomic oxygen and its ions
- Origin of water in the troposphere and stratosphere
- Importance of cloud cover for energetic balance of the planet
- Mechanism of rainfalls and their annual volumes
- Morphology of clouds

Reactions of oxygen in atmosphere

- **Configuration of oxygen**
  - Electron configuration: [He] $2s^2\ 2p^4$
  - Molecular oxygen:

Base state triplet (parallel spin) with two unpaired e^-

$^{3P}O_2$



Excited states: singlet (antiparallel) $^{1D}\Delta g$ or $^{1D}\Sigma g^+$ without unpaired electrons

$^{1D}O_2$ highly reactive ⇒ significantl

responsible for polymers photode

Reactions of oxygen in atmosphere

- **Configuration of oxygen**
  - Molecular oxygen – excited singlet states $^{1D}\Delta g$ or $^{1D}\Sigma g^{+}$:

    Excitation via 3 processes

    - direct photochemical excitation
    - adopting energy from other excited particles
    - photolysis of ozone
    - high energy reactions generating oxygen

  - Atomic oxygen

Base state	triplet	^{3P}O
Excited state	singlet	^{1D}O

Reactions of oxygen in atmosphere

- **Occurence of oxygen**
  - The most frequent biogenic element on the Earth
  - Sum of free + bonded O_2 (hydrosphere + lithosphere + atmosphere) = 45.5 weight %;
  - Content in atmosphere = 20.95 vol. % ≅ 23 weight %;
  - Content in hydrosphere (in H_2O molecules + dissolved) = 85 wt. %
  - Note: Even on the Moon surface there is elevated concentration present (oxide minerals), namely 44.6 wt. %.
  - Free oxygen in fact by 100 % generated biochemically ⇒ photosynthesis:

$$H_2O + CO_2 + h\nu \xrightarrow{chlorophyl,\,enzymes} O_2 + CH_2O\,(saccharides)$$

In total photosynthesis is strongly endothermal sequence of processes

Energy supplied by solar radiation $$\sum_i \Delta H0_i = 469\,kJ \quad {}^{-1}$$

Reactions of oxygen in atmosphere

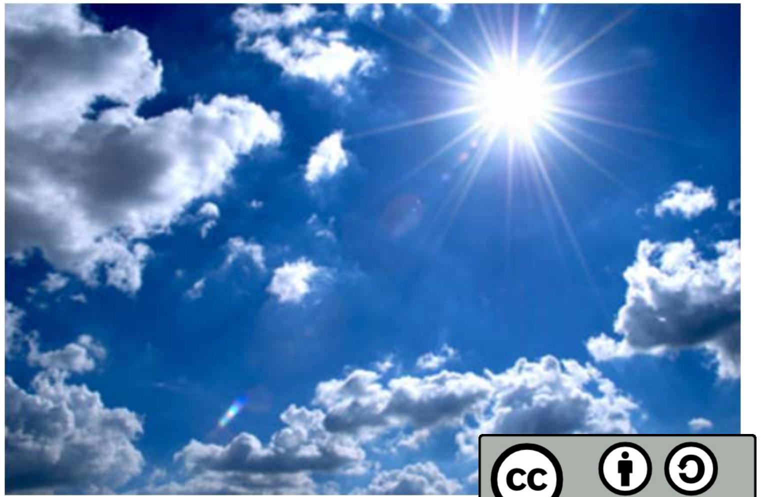
- **Appearance of oxygen**
  - Free molecular O_2 on Earth is always gaseous

    ⇒ melting point = −218,8 °C
    ⇒ boiling point = −182,97 °C
  - Beware of mistake:

    In gaseous phase O_2 is fully transparent and colourless.

    In liquid and solid state it is light blue, however (!) blue sky is not caused by oxygen but due to Raleigh dispersion of light.

≠



Reactions of oxygen in atmosphere

- **Occurrence of oxygen**
  - Content of O_2 in water – limited solubility

At 0 °C	49 $cm^3.l^{-1}$
At 20 °C	31 $cm^3.l^{-1}$

Note: in some organic solvents the oxygen solubility is by ca. 10 times higher!

- Natural oxygen = mixture of three isotopes (superscript = nucleon number):

^{16}O	(99,76 %)
^{17}O	(0,04 %)
^{18}O	(0,2 %).

Reactions of oxygen in atmosphere

- **Creation of atomic oxygen**
  - Stability of atomic O is generally low but increases in thermosphere (80 – 700 km);

    Reason: very low pressure ⇒ low number of collisions with a particle M, taking the excessive energy during synthesis O + O = O_2 and stabilising O_2 molecule:

    Thermosphere:

    $$\xcancel{O+O+M \longrightarrow O_2+M}$$

    Decrease of molecular O_2 with rising altitude occurs in so called heterosphere: 400 km above the sea level … only 10 %;
  - Formation of atomic oxygen:

    photolysis of O_2 by UV radiation in the range of 135 – 176 nm or 240 – 260 nm

    photolysis of ozone (O_3 less stable ⇒ easier cleavag

    $$O_3 + h\nu \xrightarrow{\lambda < 308\,nm} O^* + O_2$$

Reactions of oxygen in atmosphere

- **Generation of atomic oxygen**
  - Besides O_3 photolysis excited O* is formed by high energy reactions, like:

$$3O \longrightarrow O^* + O_2$$

- **Properties and extinction of atomic oxygen and generation of ions**
  - Excited O* emits radiation within visible part of spectrum with maximum λ = 636, 630 and 558 nm
  - This visible radiation is permanently emitted by the atmosphere as so called airglow;
  - Atomic oxygen in ionosphere products cations O^+, contributing to formation of other cations:

$$O + h\nu \xrightarrow{UV} O^+ + e^-$$

$$O^+ + O_2 \longrightarrow O_2^+ + O$$

$$O^+ + N_2 \longrightarrow NO^+ +$$

Appearance of water in atmosphere

- **Tropospheric and stratospheric water**
  - Water in troposphere – evapotranspiration from surface (hereinafter described within the chapter about cloud cover);
  - Water in stratosphere – vapour is blocked by tropopause ⇒ another origin of H_2O molecules: photochemical oxidation of methane (see the lecture about GHG – reactions of methane);
  - Water in stratosphere = source of hydroxyle radicals:

$$CH_4 + 2O_2 \xrightarrow{h\nu;\ several\ steps} CO_2 + 2H_2O$$

$$H_2O + h\nu \longrightarrow HO^{\bullet} + H$$

Atmospheric moisture

- Importance of cloud cover
    - Cloud cover = ratio of square covering of the visible sky by clouds
    - Important factor for energetic balance of the planet (due to albedo = reflection coefficient)

albedo of clouds	up to 75 %
albedo of continents	up to 30 %
albedo of oceans	up to 2 – 7 %

    - global value of cloud cover ca. 54 %
- Generation of cloud cover
    - evapotranspiration from the surface (continents + oceans)
    - maximum saturation of air by water 4 % vol.
    - vapor carried by ascending (convectional) flows with speed between 20 and 80 km/hour ⇒ decrease of pressure and temperature occurs.

Atmospheric moisture

- Generation of cloud cover
  - Due to temperature drop below dew point condensation or desublimation may occur alternatively (desublimation takes place if T < 0°C);
  - Liquid aerosol or aerosol consisting of ice crystals is generated;
  - Height of condensation level depends on season and region; average value is ca. 1 km;
  - Height of desublimation level in summer season 5 – 6 km, in winter season 1 – 2 km;
- Characterisation of cloud cover
  - cloud cover = all types of clouds without respect to their shape, height and so on;
  - cloud = visible conglomeration of particles of liquid water or ice (+ anthropogenic or natural pollutants in aerosol);
  - diameter of condensed or desublimated particles ca.

Mechanism of rainfalls

- **Rainfalls are generated solely by tropospheric water**
  - Evapotranspiration → generation of clouds → long range transport → precipitations;
  - Formation of raindrops: mechanism of coalescence = clustering

    Primary condensation on condensation cores (dust particles, ice or salt crystals); primary droplets are very small and kept hovering by vertical flows.

    Coalescence occurs by joining droplets in liquid phase (so called warm rain) or by growth of ice crystal from overcooled water (-10 to -30 °C, so called cool rain) followed by melting during fall ⇒ Bergeron‘s process;

    Falling velocity is directly proportional to droplet diameter: after reaching the equilibrium between air resistance and friction against gravity the velocity becomes constant;
  - Final raindrop diameter 0,1 – 5 mm, seldom up to 8 mm and exceptionally (especially in tropics) up to 10 mm.

Rainfall volumes

- Annual rainfalls
  - Extremely low volumes: Aswan (Egypt) 0,5 mm.year^{-1}
  - Extremely high volumes: Kauai (Hawai) 12 090 mm.year^{-1}
  - Czech Rep., normalized values 1981-2010: 686 mm.year^{-1}
- Basic tools – manual or automated rain gauges
  - recording rain gauge called ombrograph (older type with writing on paper)
  - recording tipping bucket

    rain gauge with datalogger and

    online connection

Morphology of clouds

- Clouds are divided into 10 basic types according to their shape (Source: http://www.ok1jfh.net/oblaka/oblaka.htm#Ac)
  - Specific altitude range – height level – is typical for each of the types.
  - Low, middle and high level clouds can be recognised.
  - Borders between the levels are not defined precisely, there are differences during calendar year due to seasons. See examples:

Winter: cirrus-like clouds (normally in high level) descend below 5 km

Summer: altocumulus (normally in middle level) rises up to 6 km

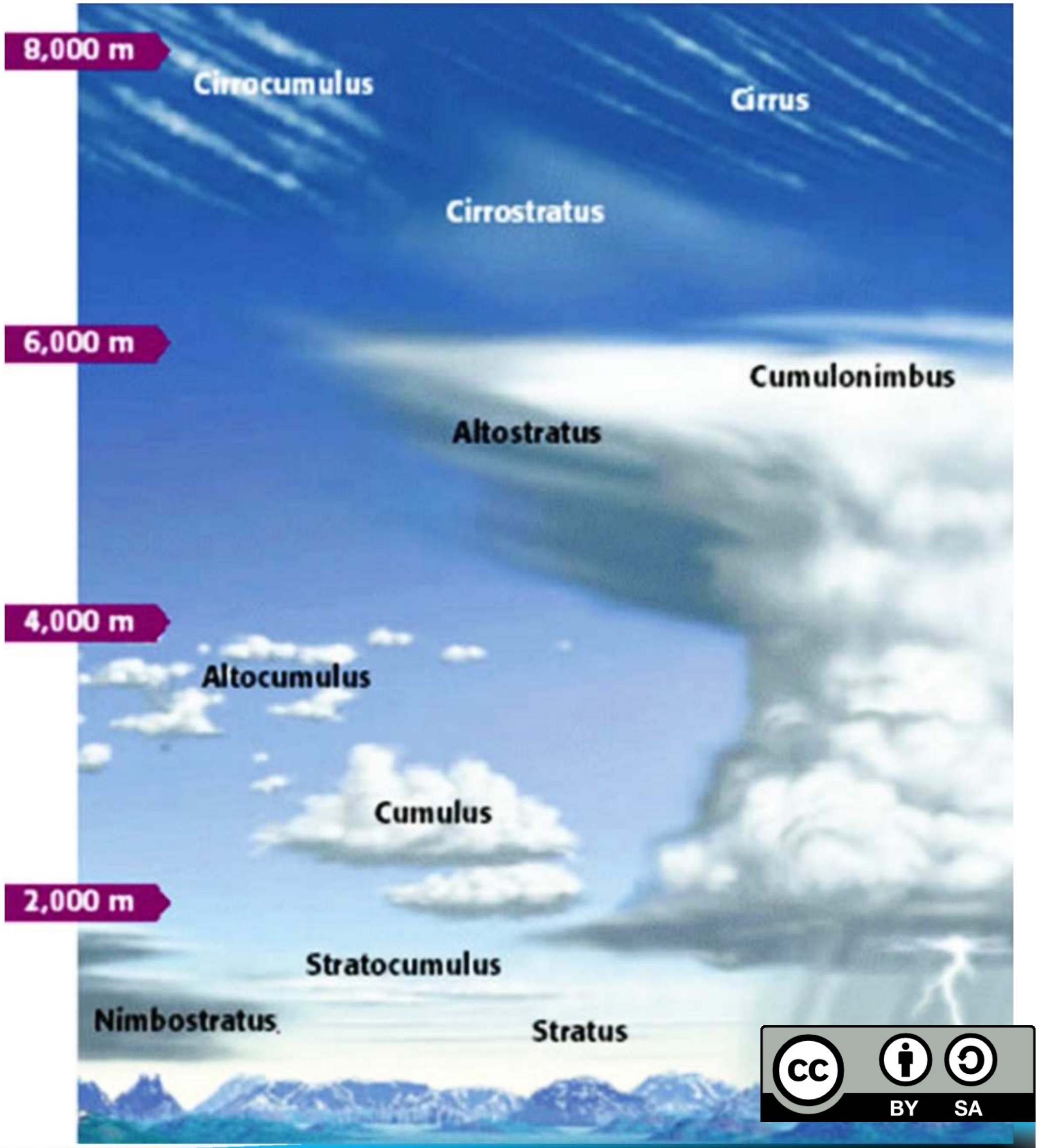
- List of basic types of clouds:

1. Altocumulus	**6. Cumulus**
2. Altostratus	**7. Cumulonimbus**
3. Cirrus	**8. Nimbostratus**
4. Cirrocumulus	**9. Stratus**
5. Cirrostratus	**10. Stratocumulus**

Morphology of clouds

- Height distribution of cloud cover (Source: http://altamontanha.com)

Warning: This is schematic drawing only.
In real state the clouds are not present
in more levels at once!

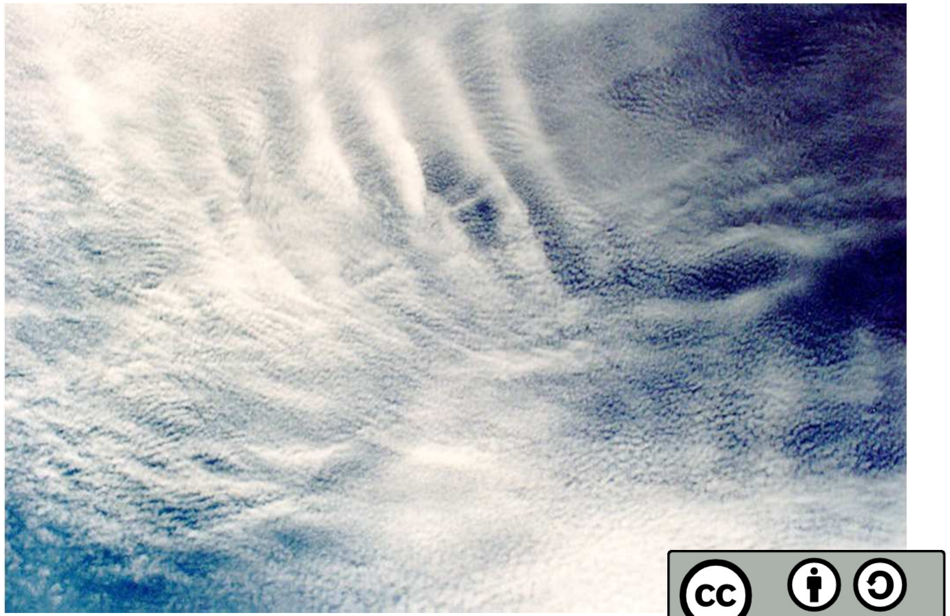


Morphology of clouds

- Characteristics of cloud types (Source: http://www.ok1jfh.net/oblaka/oblaka.htm#Ac)
- Cirrus (Ci) = so called „mares' tails“
  - Localisation: high level; 7 – 10 km
  - Description: separated clouds, having a form of white fine fibers, white stripes and so on. Ci has often fiber-like appearance and silk gloss. Ci is composed of ice particles ⇒ it does not form any rainfalls, but it can be a symptom of incoming front or high pressure ridge.

Morphology of clouds

- Characteristics of cloud types (Source: http://www.ok1jfh.net/oblaka/oblaka.htm#Ac)
- Cirrocumulus (Cc)
  - Localisation: high level; 7 – 10 km
  - Description: smaller or larger groupings of white clouds, sometimes having ribbon structure. Its appearance is possible as separated clouds as well as regular ordered conglomerates.

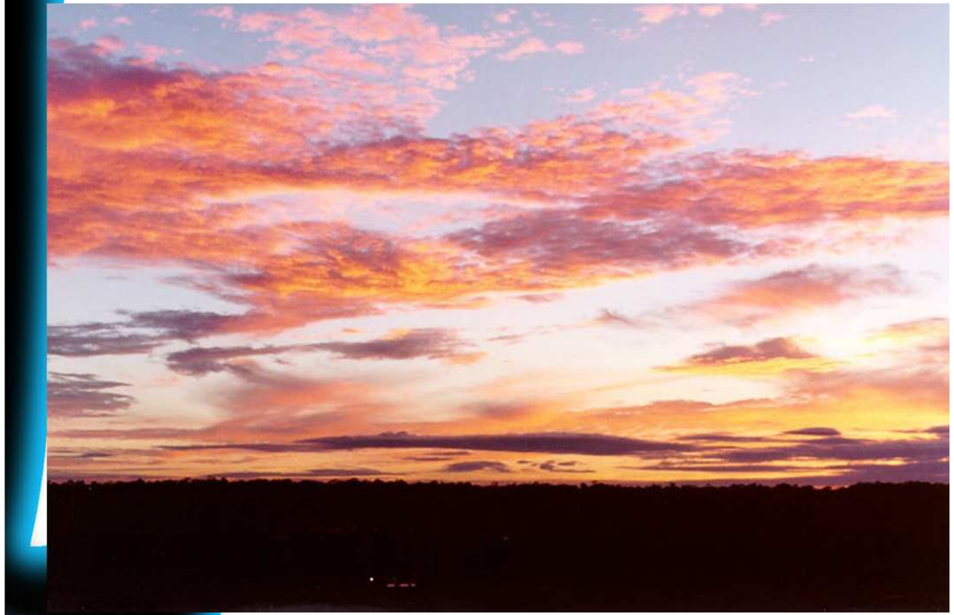


Morphology of clouds

- Characteristics of cloud types (Source: http://www.ok1jfh.net/oblaka/oblaka.htm#Ac)
- Cirrostratus (Cs)
  - Localisation: high level; 7 – 10 km
  - Description: translucent whitish haze, with fiber appearance and covering partly or completely the sky. In some cases it is formed by increasing number of cirrus clouds till the moment, when they join together to form the uniform layer.

Morphology of clouds

- Characteristics of cloud types (Source: http://www.ok1jfh.net/oblaka/oblaka.htm#Ac)
- Altocumulus (Ac)
  - Localisation: middle level; max. ca. 5 km
  - Description: grouping of white or grey cloud, consisting mainly of water droplets; unlike the cirrus-like clouds Ac drops its own shadow. Ac may exist also as entire cloud cover, but with visible division into particular clouds.



Morphology of clouds

- Characteristics of cloud types (Source: http://www.ok1jfh.net/oblaka/oblaka.htm#Ac)
- Altostratus (As)
  - Localisation: middle level; ca. 5 km, sometimes high 8 km
  - Description: greyish layer with smooth, uniform appearance, sometimes with fiber or ribbon structure. In the thinnest parts it can be slightly permeable for sunshine. Rainfalls produced by As in some cases reach the surface.

Morphology of clouds

- Characteristics of cloud types (Source: http://www.ok1jfh.net/oblaka/oblaka.htm#Ac)
- Nimbostratus (Ns)
  - Localisation: middle level, extended into low and high levels
  - Description: grey or dark grey uniform cloud cover. Rainfalls caused by Ns usually reach the surface (soil) and are long lasting and intensive. Under the low basement of NS, there is sometimes low cloudy haze present.

Morphology of clouds

- Characteristics of cloud types (Source: http://www.ok1jfh.net/oblaka/oblaka.htm#Ac)
- Stratocumulus (Sc)
  - Localisation: low and middle level 1,5 – 3 km
  - Description: grey and whitish conglomerates of clouds, which are formed by parts looking like spherical stones or fluffs. Sc has no fiber-like appearance. It may cause rainfalls with low intensity.

Morphology of clouds

- Characteristics of cloud types (Source: http://www.ok1jfh.net/oblaka/oblaka.htm#Ac)
- Stratus (St)
  - Localisation: low or middle layer 0,3 – 2 km
  - Description: grey, continuous cloudy layer with uniform and low basement; It often covers top of the hills. St is partially transparent for sunshine. St is quite often formed only as a local cloud and it may cause low intensity rain showers.

Morphology of clouds

- Characteristics of cloud types (Source: http://www.ok1jfh.net/oblaka/oblaka.htm#Ac)
- Cumulus (Cu)
  - Localisation: low or middle level 0,5 – 3 km
  - Description: Solitary bright white or greyish cloud with „mound“ shape and sharp edges. It undergoes time disintegration with several stages of the process (Cu humilis, Cu mediocris, in case of sufficient humidity it forms Cu congestus). Cu is composed of water aerosol, with ice crystals in the middle level; It can be a source of short rain showers.

Morphology of clouds

- Characteristics of cloud types (Source: http://www.ok1jfh.net/oblaka/oblaka.htm#Ac)
- Cumulonimbus (Cb)
  - Localisation: basement 0,2 km, top 7 – 9 km
  - Description: huge, opaque, storm cloud, with cone shape, from the basement to the top it sometimes forms flat discoid or „anvil“ shape; the basement is very dark colored.

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YOUTH AND SPORTS

ATMOSPHERE CHEMISTRY

Lecture No.: 11

Organisation of study

- Lecturer: Marek Staf, MSc., Ph.D., phone: +420 220 444 458
  e-mail: marek.staf@vscht.cz,
  web: http://web.vscht.cz/~stafm/
  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 - oral form
- Note:

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Scope of lecture 11

Reactions of ozone, chemistry of the background troposphere, hydroxyl radical, hydroperoxyl radical

- Chemical and physical properties of ozone and its importance
- Mechanism of ozone decomposition, nitrogen cycle and chlorine cycle
- Consequences of damaging the ozonosphere for fauna, flora and human health
- Meaning of the terms „clean troposphere“ and „background troposphere“
- Reactions in the background troposphere, hydroxyl radical and hydroperoxyl radical and the cycles of their formation and extinction
- Characteristics of the day and night phases of tropospheric reactions
- Natural sources of reactants for tropospheric reactions

Chemistry of ozone in atmosphere

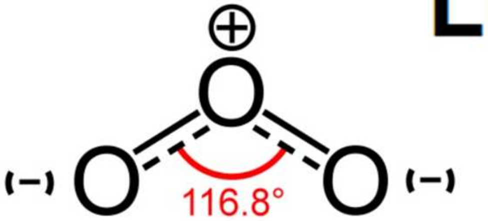
- **Ozone – trioxygen**
  - Compared to O_2 it has characteristic odour (ozein = to smell);
  - Detectable by the sense of smell from 0,01 ppm above;
  - Unlike O_2 gaseous ozone in thick layer is has blue colour.
  - Ozone is strongly oxidizing, reactive and in concentrations above 70 % vol. it is explosive.
  - O_3 is significantly more stable in acidic solutions than in alkali.
  - Compared to O_2 ozone is well soluble in water:
    at 20 °C 494 $cm^3.l^{-1}$;
  - O_3 is toxic ⇒ e.g. at workplaces in the Czech Rep. its permissible exposure limit (PEL) is 100 $\mu g.m^{-3}$ as average value not exceeded within a shift, while Maximum permissible concentration (MPC) 200 $\mu g.m^{-3}$ must not be exceeded never;
  - Ozone O_3 on Earth is always gaseous ⇒ melting point =
    ⇒ boiling point =

Chemistry of ozone in atmosphere

- **Ozone – trioxygen**
  - Unlike O_2 ozone is blue both in liquid and gaseous states.

Liquid O_3

Liquid O_2



Sourcec: http://sciencemadness.wikia.com, http://www.eielson.af.mil

Chemistry of ozone in atmosphere

- **Formation and extinction of ozone**
  - Ozone formation in stratosphere:

    Photolysis of molecular oxygen with subsequent termolecular synthesis – excessive energy is removed by a third particle (other molecule of O_2, N_2):

$$O_2 + h\nu \xrightarrow{\lambda<242{,}4\,nm} O + O$$

$$O + O_2 + M \longrightarrow O_3 + M$$

  - Extinction of ozone:

    Ozone is unstable molecule – being exposed to radiation willingly decomposes: $2O_3 \rightarrow 3O_2$ or $O_3 + O \rightarrow O_2 + O_2$

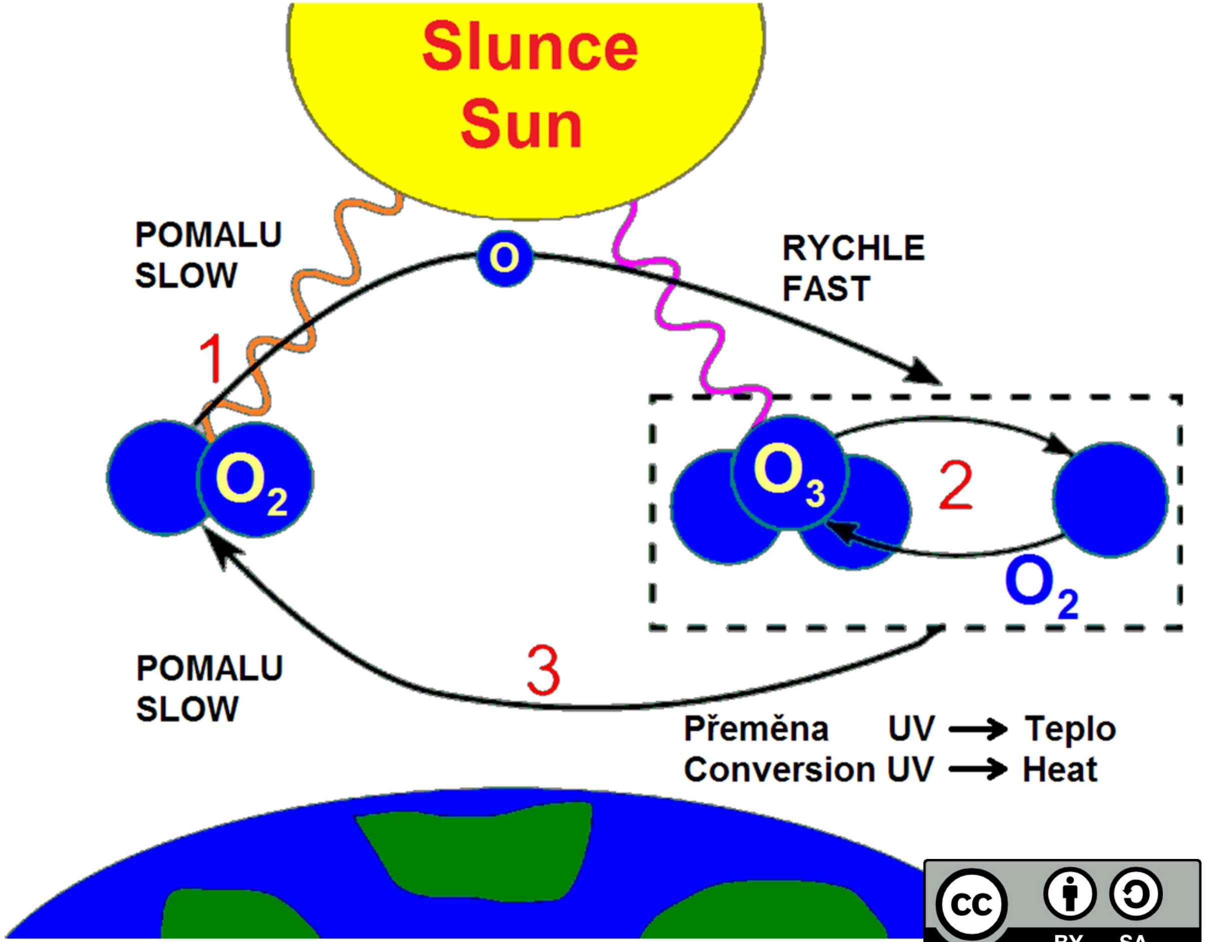
    Decomposition catalysed by biogenic or anthropogenic substances:

nitrogen oxides	NO, NO_2
hydrogen containing particles	$H^{\bullet}$, $HO^{\bullet}$,$HOO^{\bullet}$
halogen derivative residues	$ClO^{\bullet}$, Cl, Br, BrO

Chemistry of ozone in atmosphere

- **Natural generation and decay of ozone**
  - Chapman cycle (majority of reactions runs within Shumann-Runge interval λ = 175-200 nm and within so called Hertzberg continuum up to 242.4 nm)

1. O_2 molecules undergo photolysis into 2 atoms O
2. O_3 and atoms O converts cyclically (UV radiation splits O_3 and atoms O react with another O_2 molecule
3. Ozone is decomposed by reaction with atom O, with another O_3 molecule or with other gas (e.g. Cl etc.)



Chemistry of ozone in atmosphere

- **Importance of ozone**
  - Importance of stratospheric ozone – absorption of UV radiation;
  - Ozonosphere (15 – 35 km); maximum concentration O_3 between 25 – 30 km;
  - Ozone absorbs UV radiation with maximum 220 – 330 nm. During absorption UV radiation is transformed to heat.
  - Temperature maximum, caused by UV absorption by O_3 molecules, was measured in altitude of 50 km – ozone is able to absorb effectively even at its low concentrations.
  - The ozonosphere itself remains cold, but essential for terrestrial life.
  - In the altitudes below **30 km** gradual decrease of O_3 concentration because:

    photodissociation of O_2 essential for O_3 synthesis runs up to 242.4 nm, while O_3 decomposition continues up to 1,200 nm

    $\Rightarrow$ decomposition of O_3 dominates

Chemistry of ozone in atmosphere

- **Destruction of ozonosphere**
  - The lowest O_3 concentrations are measured in Antarctica;
  - According to the Montreal Protocol (from 1987) the majority of chlorofluorinated hydrocarbons is banned;
  - Due to long lasting persistence high CFC concentrations are still present in the atmosphere;
  - Diameter of the „ozone hole“ depends on weather:

During the winter on the south hemisphere (summer on the north) the atmosphere upon Antarctica is isolated due to polar atmospheric vortex and mass exchange is therefore limited;

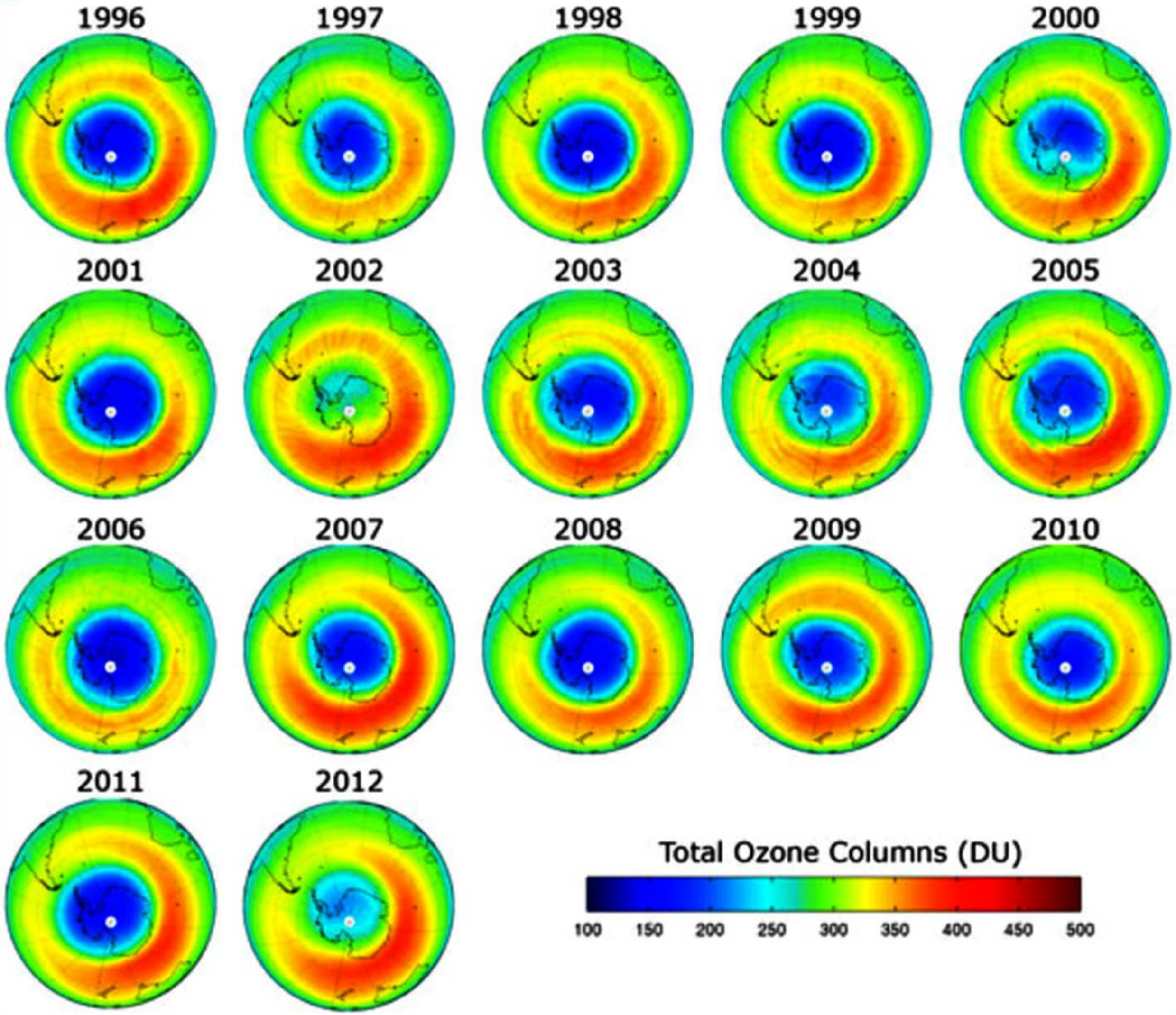
Formation of stratospheric clouds wit very low temperature;

In the polar stratospheric clouds (PSC) maximum O_3 occurs;

During September + October (spring in Antarctica) ⇒ more intensive sunshine + presence of PSC = activation of radicals ⇒ intensive decay of O_3.

Chemistry of ozone in atmosphere

- **Destruction of ozonosphere** (Source: Deutsches Zentrum für Luft- und Raumfahrt e.V.)
  - Proven CFCs decrease in atmosphere – better for O_3 restoration:



DU = Dobson Unit = 2.69 × 10^{20} molecules O_3 per m^2

1 DU = layer of pure O_3 having the height 10 μm

(at normal conditions).

Chemistry of ozone in atmosphere

- **Destruction of ozonosphere**
  - General mechanism:

$$O_3 + X \longrightarrow O_2 + OX$$

$$OX + O \longrightarrow X + O_2$$

  - X is in fact a catalyst;
  - 3 main cycles of O_3 decomposition:
    - HO_x cycle
    - Nitrogen cycle
    - Chlorine cycle
  - HO_x cycle:

Radicals $H^{\bullet}$, $HO^{\bullet}$,$HOO^{\bullet}$ are generated naturally from water vapour, methane and molecular hydrogen;

Radical $HO^{\bullet}$ contributes to the O_3 decomposition in the lower stratosphere (16 – 20 km) by up to 50 %, but it is predominating in the altitudes above 40 km.

Chemistry of ozone in atmosphere

- **Destruction of ozone layer**
  - Nitrogen cycle (discovered in 1970):

    Catalysts X can be NO or NO_2, generated in the stratosphere due to oxidation of N_2O (unlike the troposphere – see the lecture about acidic gases) or they are generated by photodissociation of N_2 and subsequent oxidation:

$$\text{above 30 km: } N_2O + h\nu \xrightarrow{UV} N_2 + O^*$$

$$O^* + N_2O \longrightarrow NO + NO$$

$$\text{above 80 km: } N_2 + h\nu \xrightarrow{UV} N + N$$

$$N + O_2 \longrightarrow NO + O$$

NO_x react with radicals $HO^\bullet$ and $ClO^\bullet$ ⇒ creating collectors of ozone destructive agents having the form of $ClNO_3$ and HNO_3:

$$ClO^\bullet + NO_2 \longrightarrow ClONO_2$$

$$ClONO_2 + h\nu \xrightarrow{UV} Cl$$

Chemistry of ozone in atmosphere

- **Destruction of ozone layer**
  - Chlorine cycle (predicted in 1974, confirmed later):

    Catalysts X are: ClO•, Cl

    The sources of Cl can be alternatively chlorinated or chlorofluorinated hydrocarbons (CFC). Mechanism is following:

    Reservoir compounds are accumulated in the stratosphere (HCl, $ClONO_2$)

    On the active surface of aerosol (see PSC clouds) crystals of H_2O + $HNO_3.3H_2O$ are formed with H_2SO_4 on the top together with thin layer of water condensate, where reactions take place

$$ClONO_2\,(g) + H_2O\,(l) \longrightarrow HClO\,(l) + HNO_3\,(l)$$

$$HCl\,(g) \xrightarrow{\text{dissociation in } H_2O\,(l)} H^+ + Cl^-$$

$$Cl^- + HClO\,(l) \longrightarrow Cl_2\,(g) + OH^-$$

$$OH^- + H^+ \longrightarrow H_2O$$

Chemistry of ozone in atmosphere

- **Destruction of ozone layer**
  - Chlorine cycle – next step:

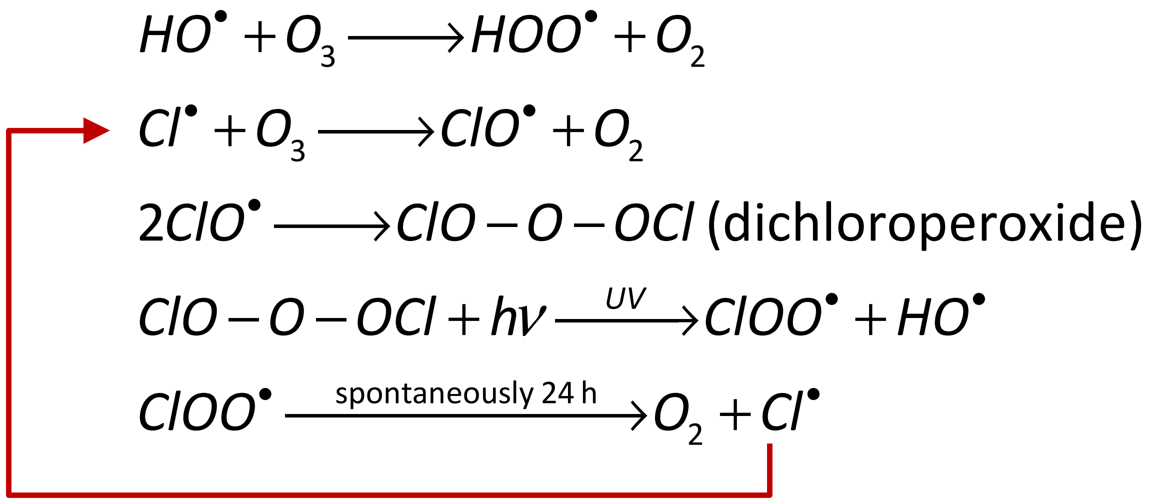
    During polar night accumulation of HClO and Cl_2 occurs;

    When the sunrise begins photolysis starts:

$$Cl_2\,(g) + h\nu \longrightarrow 2Cl^{\bullet}$$

$$HClO\,(g) + h\nu \longrightarrow Cl^{\bullet} + HO^{\bullet}$$

Initiation of ozone destruction follows:



$$HO^{\bullet} + O_3 \longrightarrow HOO^{\bullet} + O_2$$

$$Cl^{\bullet} + O_3 \longrightarrow ClO^{\bullet} + O_2$$

$$2ClO^{\bullet} \longrightarrow ClO-O-OCl \text{ (dichloroperoxide)}$$

$$ClO-O-OCl + h\nu \xrightarrow{UV} ClOO^{\bullet} + HO^{\bullet}$$

$$ClOO^{\bullet} \xrightarrow{\text{spontaneously 24 h}} O_2 + Cl^{\bullet}$$

Chemistry of ozone in atmosphere

- **Destruction of ozone layer**
  - Chlorine cycle – temporary deactivation:

Main process of Cl radicals deactivation is reaction with NO_2;

Until PSC is present deactivation does not occur – NO_2 is bonded in the PCS crystals as HNO_3;

When PSC disappears deactivation starts:

$$HNO_3 + h\nu \longrightarrow NO_2 + HO^{\bullet}$$

$$ClO^{\bullet} + NO_2 \longrightarrow ClONO_2$$

At the moment when PSC is formed again, the process of $ClNO_3$ cleavage starts again: $ClONO_2 \rightarrow HClO \rightarrow Cl_2 \rightarrow Cl^{\bullet}$ and so on!

Warning! Persistence of chlorine reservoirs is roughly 100 years!

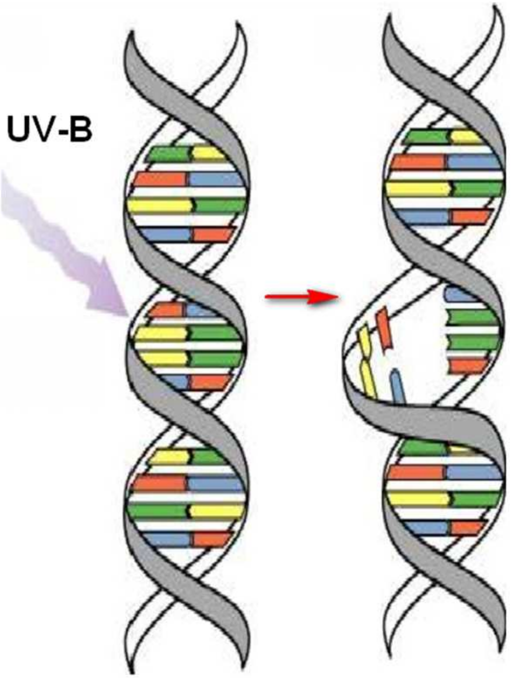
Chemistry of ozone in atmosphere

- **Consequences of ozone layer damaging**
  - Penetration of UV-B radiation on the Earth‘s surface has negative impact on animals and plants.
  - Impact to skin ⇒ tumours (e.g. melanoma);
  - Impact to eye cornea ⇒ eye tumours + cataract;
  - Impact to plants ⇒ inhibition of photosynthesis
  - Impact to immunity ⇒ decrease of resistance against infections;
  - Influencing aquatic organisms ⇒ extinction of small species living in the surface layers = damaging the trophic chains.
  - Damaging material property ⇒ accelerated degradation of lacquers, varnishes, plastics and wood.
  - Influencing climate ⇒ changes in structures of temperature distribution in atmosphere and changes in circulation flows.

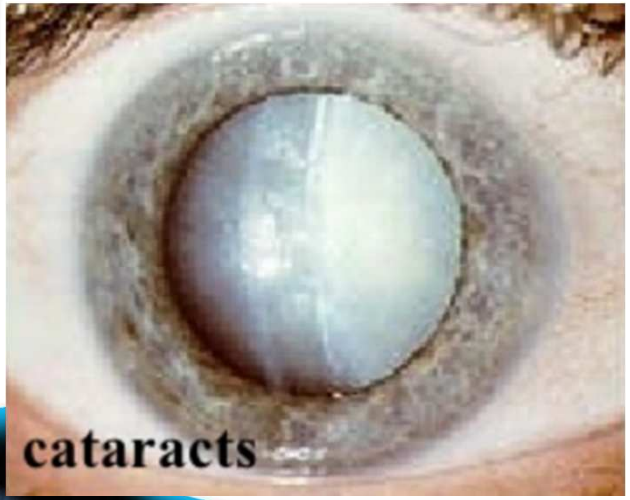
Chemistry of ozone in atmosphere

- **Consequences of ozone layer damaging – exposition to UV-B light**

Extinction of krill



Damaging DNA



Damaging eyes

Background troposphere

- **General rules**
  - Background troposphere = clean troposphere
  - 2 possible meaning of the term „clean troposphere“
  - Mechanistic definition:

    Clean troposphere = part of the troposphere, where concentration of non-methane hydrocarbons is so low that it does not influence formation and decay of HO• radical

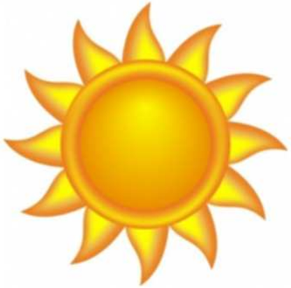
    HO• radical is then created only by reaction of excited singlet ^{1D}O with water vapour and is decomposed by reaction with CH_4 and CO.
  - Environmentalistic definition:

    Clean troposphere = troposphere without anthropogenic pollutants.
  - Different reactions runs per day (photochemical) and other per night:

Background troposphere (HO•)

- **Synthesis of hydroxyl radical (lifetime ca. 1 second)**
  - Photolysis of ozone (UV radiation 290 – 360 nm)

    Main mechanism of its formation



$$O_3 + h\nu \xrightarrow{\lambda\, 290-360\, nm} {}^{3P}O + O_2$$

$$O_3 + h\nu \xrightarrow{\lambda\, 319\, nm} {}^{1D}O + O_2$$

$${}^{1D}O + H_2O \longrightarrow 2HO^\bullet$$

^{1D}O very unstable ⇒ at relative air humidity 50 % only 4,5 % atoms of ^{1D}O are converted to HO•

  - Photolysis of nitrous acid (UV radiation < 400 nm)

    Minority mechanism

$$HNO_2 + h\nu \xrightarrow{\lambda < 400\, nm} HO^\bullet + NO$$

  - Photolysis of hydrogen peroxide (UV radiation < 370 nm)

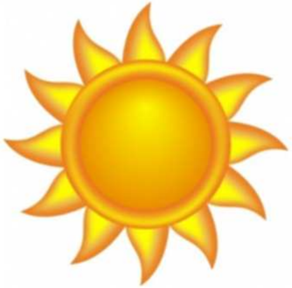
    Minority mechanism

$$H_2O_2 + h\nu \xrightarrow{\lambda < 370\, nm} 2HO^\bullet$$

Background troposphere (HO•)

- **Decomposition of hydroxyl radical (lifetime ca. 1 second)**
  - Reaction with methane or CO

    Dominating mechanism of decomposition



$$HO^{\bullet} + CH_4 \longrightarrow H_3C^{\bullet} + H_2O$$

$$HO^{\bullet} + CO \longrightarrow CO_2 + H^{\bullet}$$

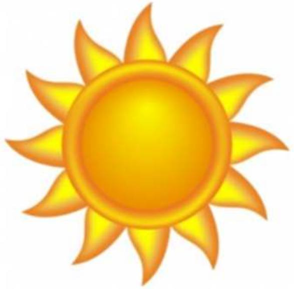
Due to anthropogenic emissions of CO and hydrocarbons ⇒ on the northern hemisphere concentration of HO• radicals is by 20 % lower;

- **Regeneration of hydroxyl radical**
  - Reaction of hydroperoxyl radical with nitrogen monoxide

    Dominating mechanism

$$HOO^{\bullet} + NO \longrightarrow NO_2 + HO^{\bullet}$$

Background troposphere (HOO•)



- **Synthesis of hydroperoxyl radical**
  - Reaction of hydrogen radical with oxygen

    (second phase of HO• decomposition)

    Main mechanism

$$HO^{\bullet} + CO \longrightarrow CO_2 + H^{\bullet}$$

$$H^{\bullet} + O_2 \longrightarrow HOO^{\bullet}$$

  - Photolysis of aldehydes (as the intermediates of hydrocarbon oxidation)

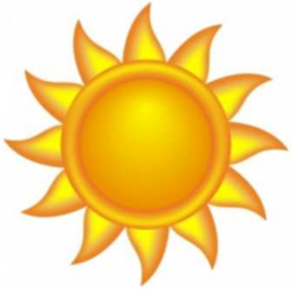
    Main mechanism

$$HCHO + h\nu \longrightarrow H^{\bullet} + HCO^{\bullet}$$

$$HCO^{\bullet} + O_2 \longrightarrow HOO^{\bullet} + CO$$

$$H^{\bullet} + O_2 \longrightarrow HOO^{\bullet}$$

Background troposphere (HOO•)



- **Decomposition of hydroperoxyl radical**
  - Reaction with hydroxyl radical

$$HOO^{\bullet} + HO^{\bullet} \longrightarrow H_2O + O_2$$

  - Reaction with another hydroperoxyl radical

$$HOO^{\bullet} + HOO^{\bullet} \longrightarrow H_2O_2 + O_2$$

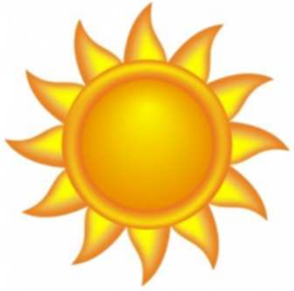
  - Reaction with nitrogen monoxide (see regeneration of hydroxyl radical)

$$HOO^{\bullet} + NO \longrightarrow NO_2 + HO^{\bullet}$$

  - Reaction with ozone (also regeneration of hydroxyl radical)

$$HOO^{\bullet} + O_3 \longrightarrow 2O_2 + HO^{\bullet}$$

Background troposphere



- **Characteristics of day phase of tropospheric reactions**
  - In the clean troposphere low temperature, multiphase oxidation of admixtures, released due to natural processes from the Earth surface in their reduced form.
  - Ozone represents the initial oxidation agent, secondary it is hydroxyl radical.
  - Following compounds undergo the oxidation:

Methane	CH_4
Carbon monoxide	CO
Formaldehyde	$HCHO$
Nitrogen monoxide and dioxide	NO and NO_2

Background troposphere

- **Natural sources of reactants for tropospheric reactions**
  - Sources of methane

    Biogenic sources (anaerobic fermentation)

    Leakages from lithosphere
  - Sources of carbon monoxide

    Oxidation of methane by HO• (50 % of the overall CO concentration is generated this way)

    Oxidation of natural terpenes

    Incineration processes

Big emissions of methane – wetlands in Siberia

Coniferous forests – source of natu

Background troposphere

- **Natural sources of reactants for tropospheric reactions**
  - Sources of nitrogen oxides

    Soil and oceanic processes

    Combustion processes

    Electric discharges

  - Sources of ozone (tropospheric)

    Photochemical reactions

    Transfer from stratosphere

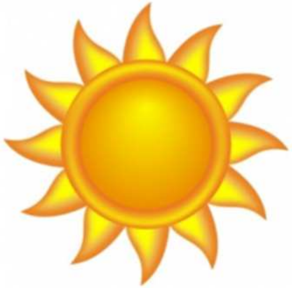
    (only ca. ¼ of the total conc.)

Flash – source of NO_x (and minority of O_3)

Forest fires – source of NO_x

Background troposphere

- **Day tropospheric reactions**
  - Reaction of hydroxyl radical with methane



$$CH_4 + HO^\bullet \longrightarrow H_3C^\bullet + H_2O$$

$$H_3C^\bullet + O_2 + M \longrightarrow CH_3OO^\bullet + M$$

subsequent reaction of methylperoxyl radical with nitrogen monoxide

$$CH_3OO^\bullet + NO \longrightarrow NO_2 + CH_3O^\bullet$$

$$CH_3O^\bullet + O_2 \longrightarrow HCHO + HOO^\bullet$$

  - Reaction of hydroxyl radical with carbon monoxide

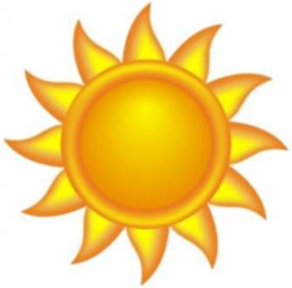
$$HO^\bullet + CO \longrightarrow CO_2 + H^\bullet$$

$$H^\bullet + O_2 + M \longrightarrow HOO^\bullet + M$$

subsequent reaction of hydroperoxyl radical with nitrogen monoxide

$$HOO^\bullet + NO \longrightarrow NO_2 + HO^\bullet$$

Background troposphere



- **Day tropospheric reactions**
  - Reaction of hydroxyl radical with formaldehyde

$$HCHO + HO^{\bullet} \longrightarrow CHO^{\bullet} + H_2O$$

$$CHO^{\bullet} + O_2 \longrightarrow CO + HOO^{\bullet}$$

- **Termination reactions of hydroxyl and hydroperoxyl radical**
  - Reaction of hydroxyl radical with nitrogen dioxide

$$HO^{\bullet} + NO_2 \longrightarrow HNO_3$$

  - Reaction of hydroperoxyl radical with another hydroperoxyl

$$HOO^{\bullet} + HOO^{\bullet} \longrightarrow H_2O_2 + O_2$$

$$H_2O_2 + h\nu \longrightarrow 2HO^{\bullet} \quad \text{(only small part)}$$

Hydrogen peroxide represents temporary collector (reservoir) of hydroxyl radicals.

Background troposphere

- **Night tropospheric reactions**
  - All nitrogen oxides are converted to NO_2, which reacts with ozone.
    Nitrate radical reacts with another nitrogen dioxide.
    Subsequently dinitrogen pentoxide is formed and converted to the acid:

$$NO_2 + O_3 \longrightarrow NO_3^{\bullet} + O_2$$

$$NO_3^{\bullet} + NO_2 + M \longrightarrow N_2O_5 + M$$

$$N_2O_5\,(g) + H_2O\,(l) \longrightarrow 2HNO_3\,(l)$$

  - Nitrate radical is unstable during a day (photolysis to NO or NO_2 depends on λ).
  - During a night $NO_3^{\bullet}$ stable ⇒ reaction with hydrocarbons (mostly alkenes) and forming alky peroxynitrates.

    Alkyl peroxynitrates react with oxygen to alkylperoxy radicals or they stay unchanged till morning when their photolysis occurs.

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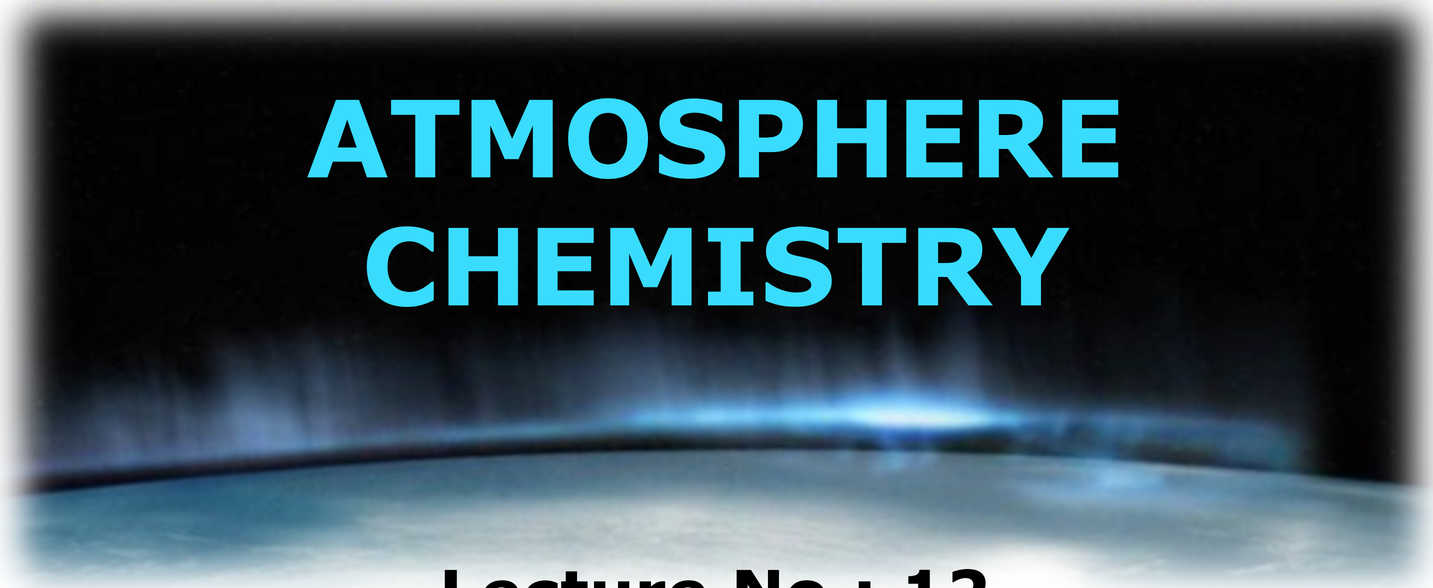

ATMOSPHERE CHEMISTRY

Lecture No.: 12

Organisation of study

- Lecturer: Marek Staf, MSc., Ph.D., phone: +420 220 444 458

  e-mail: marek.staf@vscht.cz,

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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 - oral form

- Note:

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Scope of lecture 12

Worldwide evolution in the field of air protection and important international agreements

- Milestones of anthropogenic pollution in pre-industrial and industrial era
- Industrial revolution and emissions from coal combustion
- Progress in legislation limiting air pollution in the U.S.A. and Europe
- The most important international agreements related to air protection
- Evolution in the international activities leading to mitigation of the GHG emissions
- The basic protocols binding the signatories to decrease GHG emissions – Kyoto protocol etc.
- The legislation process following the Kyoto protocol

Phases of air pollution

- **Main milestones of anthropogenic pollution** (Source: Encyclopedia of Life Support Systems EOLSS)
  - till half of. 18th century = Pre-industrial era
    - in households heavy pollution by burning oil and wood in domestic furnaces (pulmonary anthracosis + pneumoconiosis)
    - external atmosphere polluted by the combustion of mainly wood in the cities and due to the mining and processing of metals (Athens ca. 200,000 inhabitants in 430 b.c., Rome ca. 1 mil. in 150 a.d., example: 535 a.d. Emperor Justinian issues decrees where the importance of breathing fresh air is mentioned)
  - ca. 1780 – 1950 pollution mostly from combustion of black coal and brown coal (emissions of SO_2, PM etc.)
  - 1950 – present new sources (tropospheric O_3, CFCs, V

Phases of air pollution

- **Pre-industrial epoch – beginnings of coal usage**
  - První použití v Římské říši, rozvoj ve Velké Británii ve středověku;
  - End of 11th century — Evidence of expanded coal burning, the oldest deposits on the Church soil at the Tyne River
  - 11th – 13th century — využívání uhlí pouze v kovárnách a vápenkách
  - Edward I., „Longshanks“ (1239 – 1307) – dekret o zákazu spalování uhlí v Londýně z důvodu zápachu a dýmu: dokumentován případ jednoho trestu smrti za nedodržení;
  - End of 11th century — deforestation of England, expansion of coal for heating
  - Elisabeth the 1st (1533 – 1603) — coal domination for household heating

Phases of air pollution

- **Industrial revolution – roughly between 1750 – 1900**
  - Gradual transition to industrial production with the beginning in England
  - The massive use of coal: from 1709 introduction of coke in iron metallurgy, the gradual replacement of water, wind and animal propulsion by steam machinery;
  - James Watt (1736 – 1819):

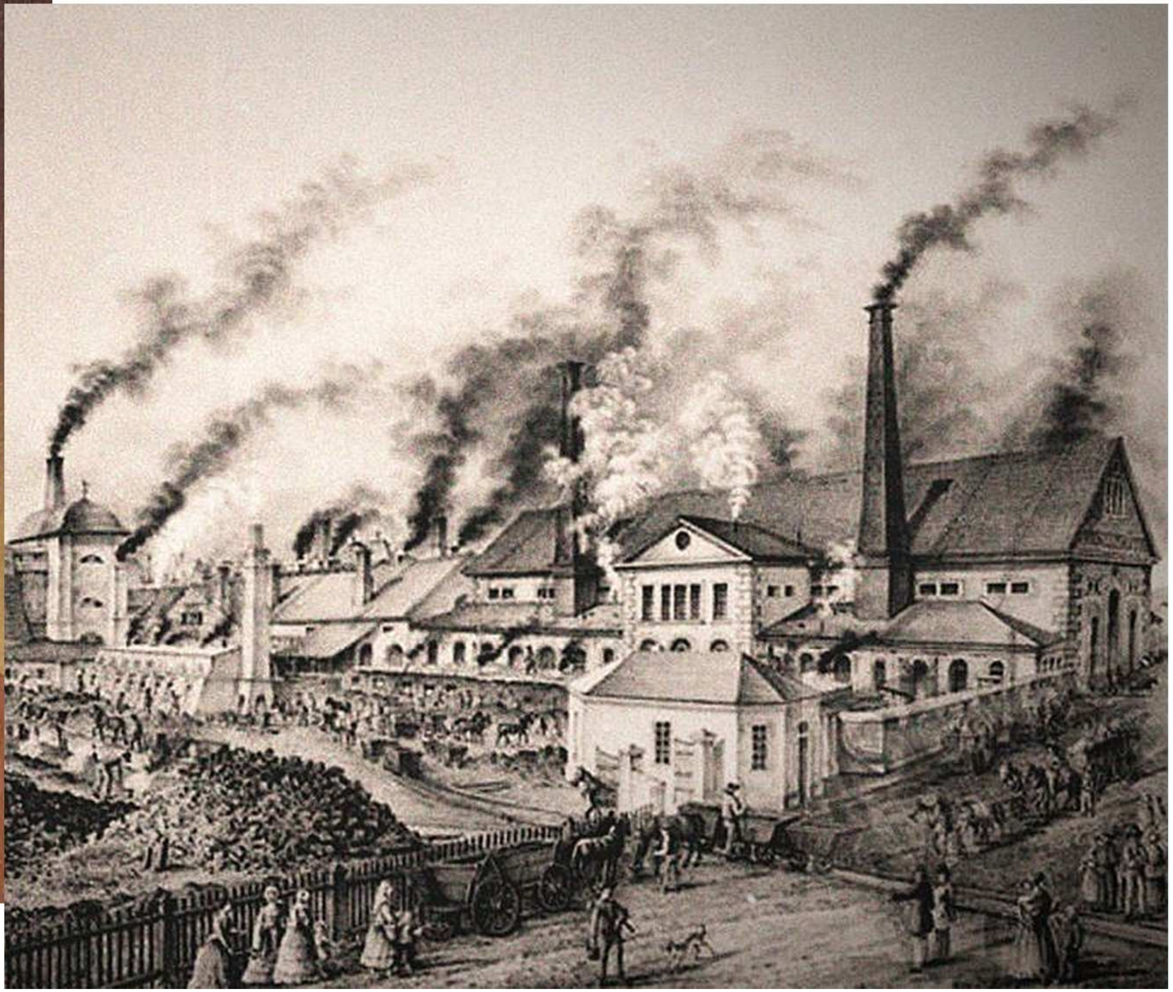
    1763 started improvement of the Newcomen's steam engine;

    1769 patented separate steam condenser = increased machine efficiency
  - 1775 – 1800 ca. 500 engines produced (textiles, metallurgy, mills)
  - 1800 patent expiration, then rapid development and transition to high pressure machines ⇒ deployment in transportation;

Phases of air pollution

- **Industrial revolution – roughly between 1750 – 1900**

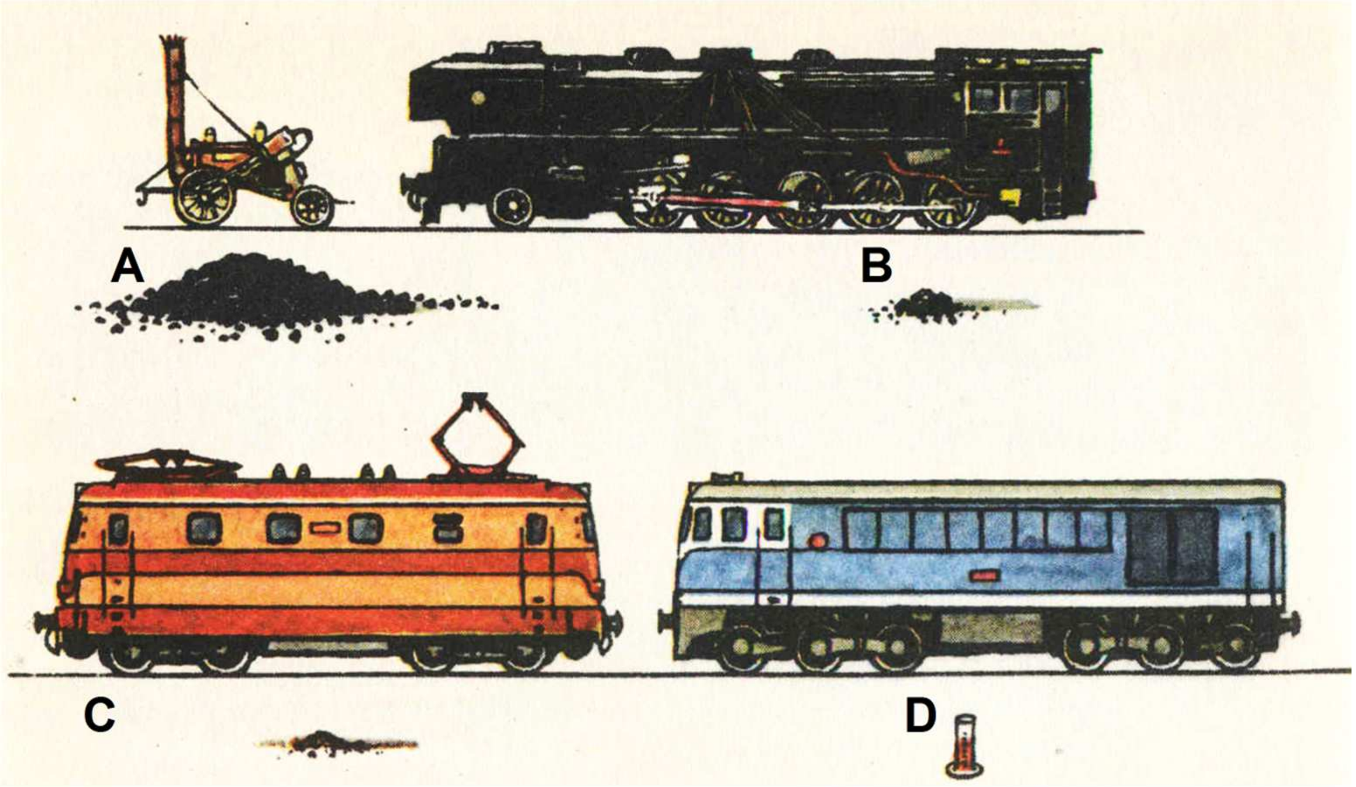
James Watt (1736 – 1819)



Factory at the turn of 18th and 19th

Phases of air pollution

- **Pollution from transport - low efficiency of old steam engines**



Fuel consumption per 1 HP (0.735 kW):

A) Stephenson's „The Rocket"	5,2 kg of coal
B) 1930's Czechoslovakia type 556.0	0,8 kg of coal
C) 1960's electric (incl. power station)	0,4 - 0,7 of coal
D) 1970's diesel-electrical	0,17 kg of c

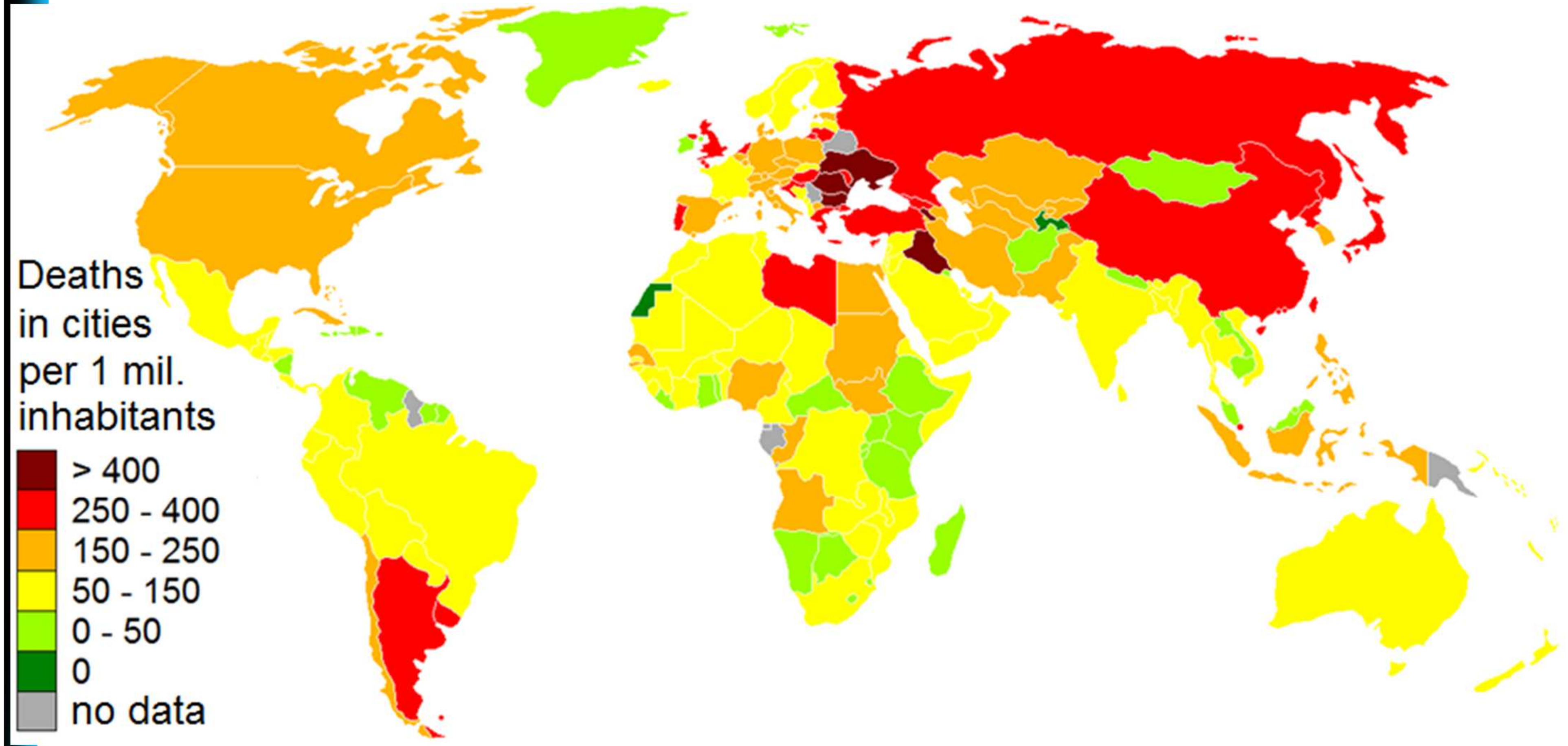
Phases of air pollution

- London - A symbol of air pollution in the cities in the mid-20th century.
- The so-called Great Smog in London - December 1952 to March 1953

immediate extinction of 4,000 persons!!!

Phases of air pollution

- Deaths due to air pollution in cities in 2004 (Source: EEA)



History of environmental law

- **Air protection in Europe** (Source: Hanibal, J., Raab, P. Problematika kvality ovzduší, Praha, 1979 a EEA)
  - beginning of 19th century
    Germany and Austria enacted the possibility of recovering compensation for damage to health and property from the company;
  - beginning of 20th century
    Italy issues the law determining dislocation of selected technologies from settlements;
  - 1956 The UK issued law on the protection of the air against "black smoke„ (due to „big smog“);
  - 1970 and 1972 two EEC Directives on the harmonization of motor vehicle emissions legislation;
  - 1973 the first environmental action program, which prefers prevention of pollution before solving the impacts;

History of environmental law

- **Evolution of air protection in Europe** (Source: EEA)

1978	Council Directive 78/176 / EEC on wastes from the titanium dioxide industry (replaced by the Industrial Emissions Directive since 2014);
1987	Unified European act in which the Environmental Protection Act was implemented into the EC legal system;
1999	Council Directive 1999/13 / EC on the limitation of emissions of VOCs (replaced by the Industrial Emissions Directive since 2014);
2001	Directive 2001/8 / EC of the European Parliament and of the Council on the limitation of emissions of certain pollutants into the air from large combustion plants;

- Note: The list is far from complete, only examples were presented

History of environmental law

- **Evolution of air protection in the U.S.A.** (Source: CCPS: Safe Design and Operation of Process Vents and Emission Control Systems, 2006, Wiley)
  - End of 19th century – local regulation directives in the big cities;

1881	Chicago and Cincinnati adopted a local law on the limitation of smoke and fly ash from factories, railways and inland waterways;
1928	initiation of the air pollution monitoring in the eastern cities through the US Public Health Service;
1939	due to the extreme smog situation St. Luis permanently limited burning of low-grade brown coal;
1955	adoption of the first nationwide Air Pollution Control Act;

History of environmental law

- **Evolution of air protection in the U.S.A.** (Source: CCPS: Safe Design and Operation of Process Vents and Emission Control Systems, 2006, Wiley)

– 1967	adopting the nationwide Clean Air Act (or Air Quality Control Act) to create emission limits for stationary sources;
– 1970	novelization where the maximum level of pollution was defined for PM, SO_x, CO, NO_x, O_3, Pb; EPA agency was established to set imission thresholds and regulatory measures (among other things);
– 1970 – 1990	EPA began regulating emissions of asbestos, benzene, Be, As, Hg, radionuclides and vinyl chloride;
– 1990	tightening requirements for concentrations of NOx, ozone precursors, and VOCs;

- The US refused to ratify the Kyoto Protocol.

International environmental acts

- **Geneva convention**
  - 1979 Geneva: Convention on Long-Range Transboundary Air Pollution (Convention on Acid Rains)

- There are eight Implementing Protocols to this General Convention
- Unlike the Framework Convention, the Protocols are much more specific.

International environmental acts

- **Geneva convention – 8 follow-up protocols**
  - 1987 Helsinki Protocol on the Reduction of transboundary Sulfur Emissions by at least 30 %; (1987 = coming into force)
  - 1988 Protocol on Long-Term Financing of the Cooperative Programme for Monitoring and Evaluation of the Long-range Transmission of Air Pollutants in Europe (EMEP);
  - 1988 Nitrogen Oxide Protocol (emissions or their flows across the state borders);
  - 1997 Volatile Organic Compounds Protocol;
  - 1998 Oslo Protocol on Further Reduction of Sulfur Emissions;
  - 2003 Protocol on Heavy Metals;
  - 2003 Aarhus Protocol on Persistent Organic Pollutants;
  - 2005 Gothenburg Protocol to Abate Acidification, Eutrophication and Ground-level Ozone;

International environmental acts

- **Other important agreements from 1980's**
  - 1981 Montreal: Environmental Protection: Aircraft Engine Emissions;
  - 1985 Vienna: Vienna Convention for the Protection of the Ozone Layer;
  - 1986 (signed 91): Air Quality Agreement (bilateral agreement between US and Canada on acid rains);
  - 1987 Montreal: Montreal Protocol on Substances that Deplete the Ozone Layer (follow-up protocol to Vienna Convention);
  - 1988: IPCC panel was founded by UN WMO + UNEP
  - 1992 Rio de Janeiro: (or New York respectively, as the seat of UN)

    UN Framework Convention on Climate Change (UNFCCC)

International environmental acts

- **Montreal Protocol on Substances that Deplete the Ozone Layer (follow-up protocol to Vienna Convention)**
  - Czechoslovakia ratified the Vienna Convention on December 30, 1990. (Czech Rep. as successor country is automatically party too);
  - More than 190 states joined the Montreal Protocol.
  - Objective: To exclude production and consumption of 96 controlled ozone-depleting substances;
  - Included are fully halogenated chlorofluorocarbons (CFCs), bromofluorocarbons, and partially halogenated chlorofluorocarbons (HCFCs)
  - By the year 1987, yearly around 1.1 million tonnes CFCs were consumed worldwide (ca. 5,500 t accounted for today's Czech Rep.)
  - Production and usage of these compounds by 98 % stopped;
  - If the Protocol is applied in its entirety, the ozone layer will return to the pre-1980 status by 2050.

International environmental acts

- **UN Framework Convention on Climate Change (UNFCCC)**
  - Totally ratified by 196 parties/states
  - Dlouhotrvající proces tvorby UNFCCC (13 years!)
  - The outcome of the first World Climate Conference (Geneva 1979) – the call for industrialized countries to reduce CO_2 emissions by 20% by the year 2005 compared to 1988 was adopted;
  - 1989 45th session of the UN General Assembly - decision on the inclusion of climate change in the program of the UN Conference on the Environment
  - 1992 Rio de Janeiro above mentioned conference – setting up the UNFCCC
  - 1997 Kyoto protocol elaborated on the basis of outcomes from UNFCCC.

International environmental acts

- **UN Framework Convention on Climate Change UNFCCC**

  Note: Al Gore has campaigned in the US for ratification of the Kyoto Protocol. Sometimes there are controversies with links to some companies and problems with financing of the presidential campaign.

General Assembly of the UN

Al Gore (Nobel price winner
together with IP

International environmental acts

- **Kyoto Protocol**
  - 1997 Kyoto: The Protocol was drawn up on the basis of the above-mentioned Framework Convention;
  - Includes 6 substances: CO_2, CH_4, N_2O, HFCs, PFCs, SF_6
  - Agreed: December 1997

    ratified by the EU 2002
  - Confirmed: by December 2004 – because the US refused, it all depended on Russia

    by the year 2004 ratified by 132 parties with the emission share of 61,6 %

    Russia ratified on 2004
  - Became effective: since 2005

International environmental acts

- **Kyoto Protocol**
  - The overall commitment of industrialized countries was following:

    reduction of GHG emissions by 5,2 %
  - Commitment stated for aggregated average emissions of CO_2, CH_4, N_2O, HFCs, PFCs, SF_6

    recalculated to CO_2 using the GWP index

    for N_2O GWP = 310 (i.e. 1 ton N_2O = 310 t CO_2)

    for CH_4 GWP = 21
  - Time frame: reduction commitment over a 5 year period (2008 – 2012)

    reference year for CO_2, CH_4, N_2O 1990

    for HFCs, PFCs, SF_6 optionally 1990

    or 19

International environmental acts

- **Kyoto Protocol**
  - The fulfillment of the commitments is possible directly by reducing the amount of GHG emitted per year;
  - or by 3 additional flexible mechanisms (industrialized countries are entitled to reduce emissions in another country or buy allowances from it)

    1) Emission Trading system (ETS)
    2) Joint Implementation measures (JI);
    3) Clean Development Mechanism (CDM).

International environmental acts

- **Kyoto Protocol**
  - GHG mitigation commitments are not the same for the all signatories:

e.g. Germany, France, Switzerland, Czech Republic etc.

obligation -8 %

USA (theoretically)

obligation -7 %

Canada, Hungary, Japan a Poland

obligation -6 %

Russia, New Zealand and Ukraine

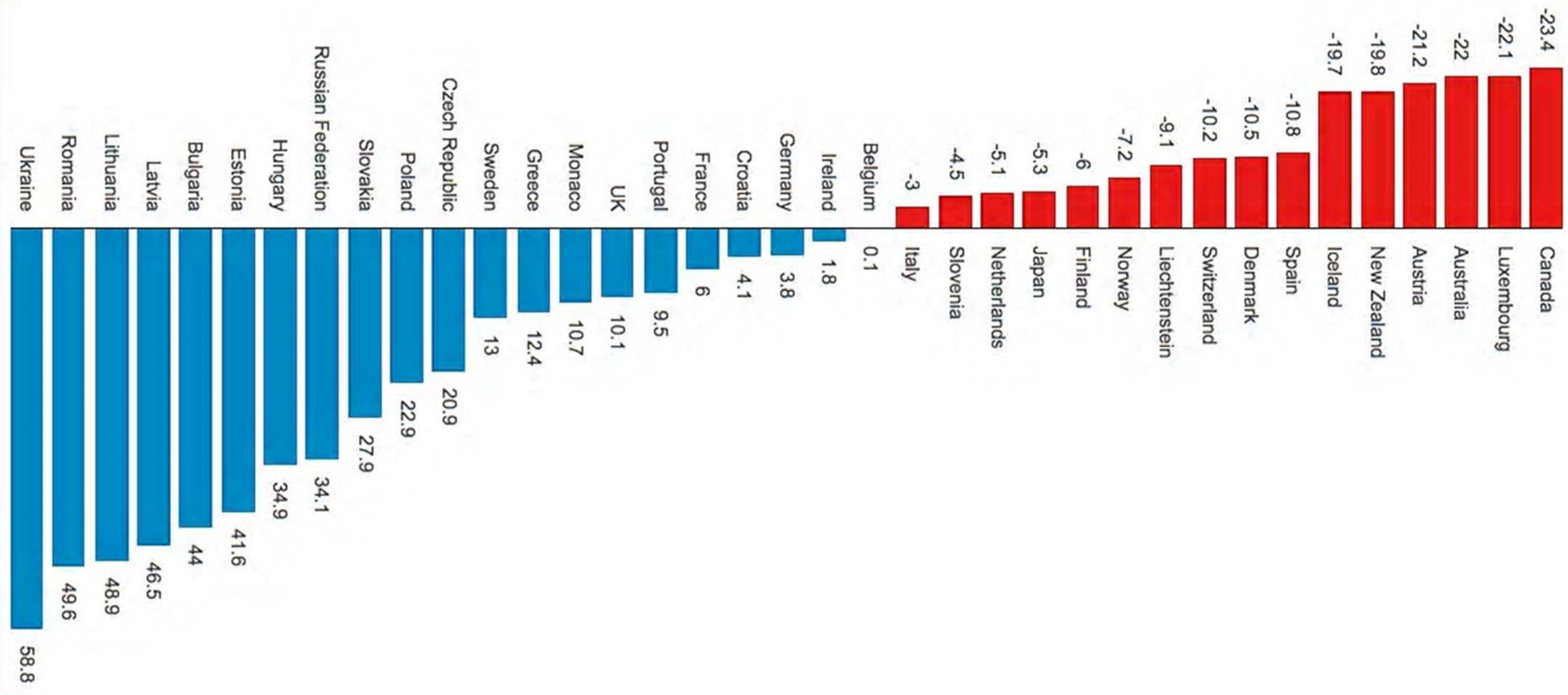
obligation 0 %

Norway obligation + 1 %

Australia (increase allowed) obligation + 8 %

Iceland obligation + 10

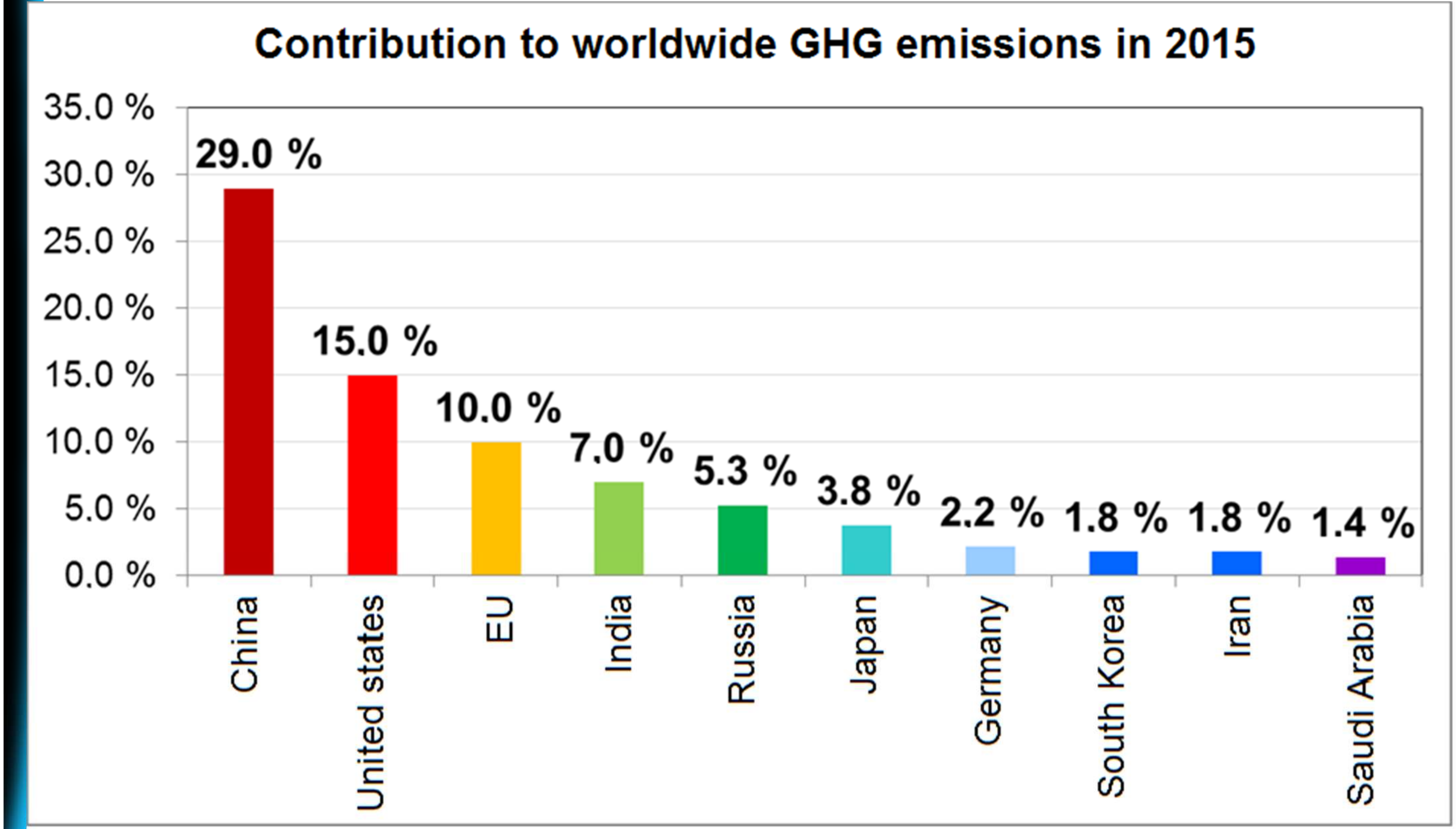
International environmental acts



Kyoto protocol successes (blue) and failures (red) in 2012

(source: https://www.theguardian.com/environment/blog/2012/nov/26/kyoto-protocol-carbon-emissions)

International environmental acts



Overview of the main producers of greenhouse gases

International environmental acts

- **What will continue after Kyoto protocol expiration**
- Before the Paris summit no commonly accepted agreement available.
  - 2012 Qatar conference in Dauhá about prolonging of the Kyoto protocol validity; nev obligations have been adopted (emissions mitigation by 18 % till the year 2020);the obligation was confirmed by the EU + Australia, Belarus, Croatia, Iceland, Kazakhstan, Norway, Switzerland and Ukraine;
  - 2014 Lima at the conference only Lima declaration as the fundament for the next conference in Paris; the EU members agreed on so called “Kyoto protocol II” (mitigation by 30 % till 2020);
  - 2015 Paris COP 21, which means 21st conference of the parties to the UNFCCC; replacement of Kyoto protocol after 2020;

    Agreed by representatives of the 197 pa

International environmental acts

- **Paris conference of parties (COP21)**
  - Stunned by terrorist attacks, accompanied by demonstrations by activists:

International environmental acts

- **Paris agreement as the replacement for Kyoto protocol**
  - Essential condition: ratification by 55 parties, producing at least 55 % of the worldwide GHG emissions;
  - Main target: keeping the increase in global temperature below 2 °C compared to pre-industrial era

    parties will endeavour for keeping the temperature change up to 1,5 °C
  - Secondary target: enhancing adaptability against undesired impacts of climatic changes
  - Implementing articles:

    totally 28

    concluding the fundamental terms, targets and measures together with control mechanisms

International environmental acts

- **Paris agreement as the act replacing the Kyoto protocol**
  - Difference from the Kyoto protocol (KP):

    KP was applied only on developed countries, while Paris agreement imposes obligation to all of the signatory parties to set up their own mitigation commitments.

Commitments of the EU:

to reduce GHG emissions till 2030 by 40 % in comparison with the year 1990.

International environmental acts

- **Paris agreement as the act replacing the Kyoto protocol**
  - Course of ratification (55 parties needed + 55 % of global emissions): after accepting of the document long period of „calm“ breakthrough: 3rd September, 2016 – ratified by the U.S.A. + China

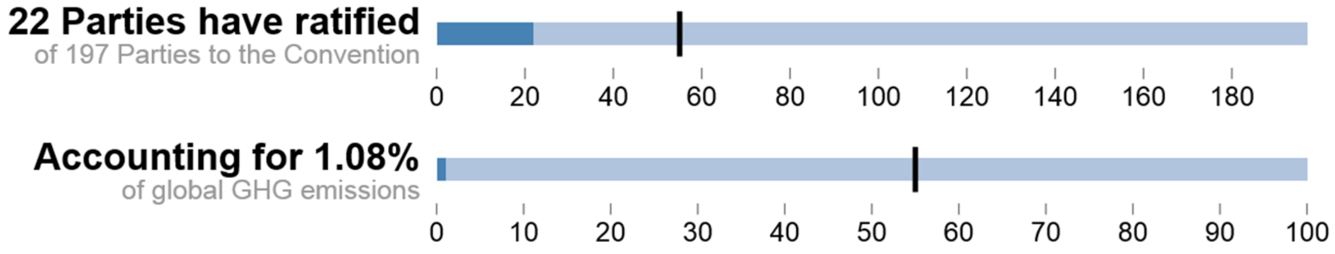
Subsequently India ratified 2nd October, 2016
European union ratified (as one party) on 5th October, when approved by the EP

Both threshold values reached on 2nd October, 2016
agreement entered into force on 4th November (30 days
threshold had been reached)

International environmental acts

- **Succession of the Paris agreement ratification**

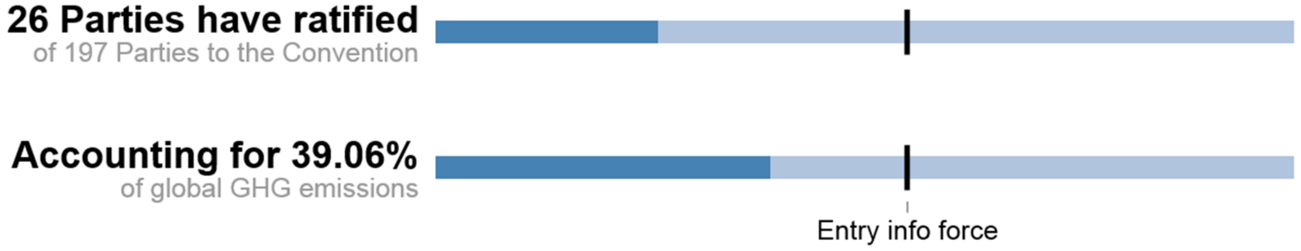
12th August, 2016



22 Parties have ratified
of 197 Parties to the Convention

Accounting for 1.08%
of global GHG emissions

5th September, 2016



26 Parties have ratified
of 197 Parties to the Convention

Accounting for 39.06%
of global GHG emissions

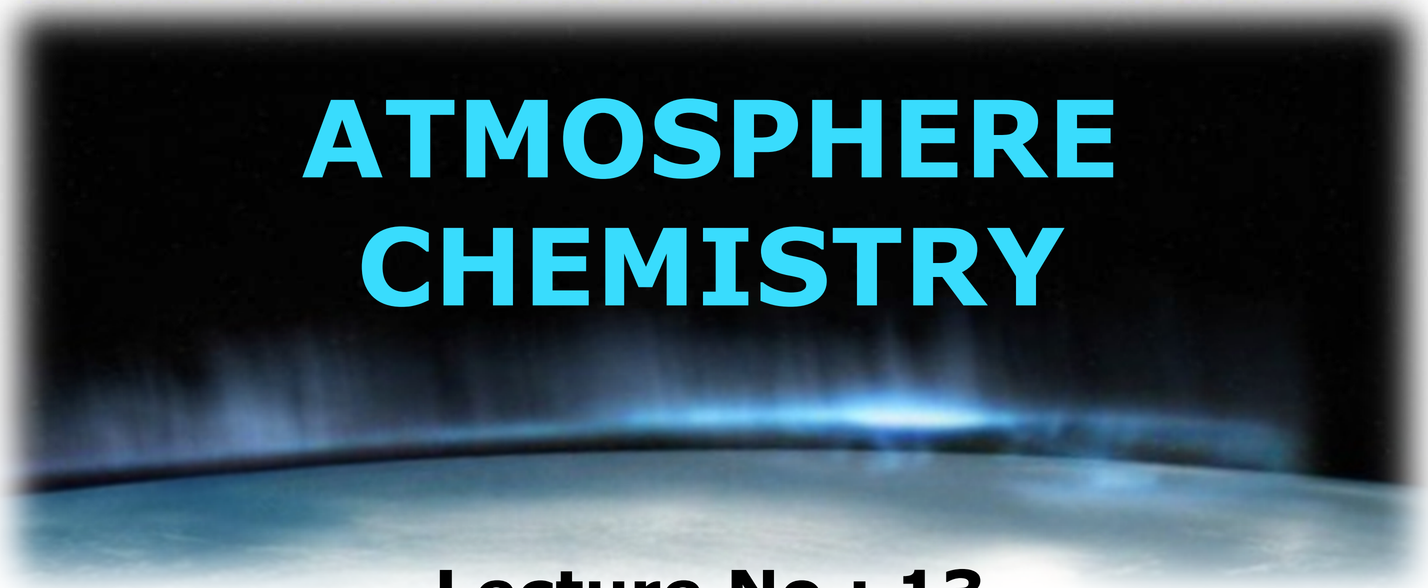
4th October, 2016

63 Parties have ratified
of 197 Parties to the Convention

Accounting for 52.11%
of global GHG emissions

EUROPEAN UNION
European Structural and Investing Funds
Operational Programme Research,
Development and Education

MINISTRY OF EDUCATION,
YOUTH AND SPORTS



ATMOSPHERE CHEMISTRY

Lecture No.: 13

Organisation of study

- Lecturer: Marek Staf, MSc., Ph.D., phone: +420 220 444 458

  e-mail: marek.staf@vscht.cz,

  web: http://web.vscht.cz/~stafm/

  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 - oral form
- Note:

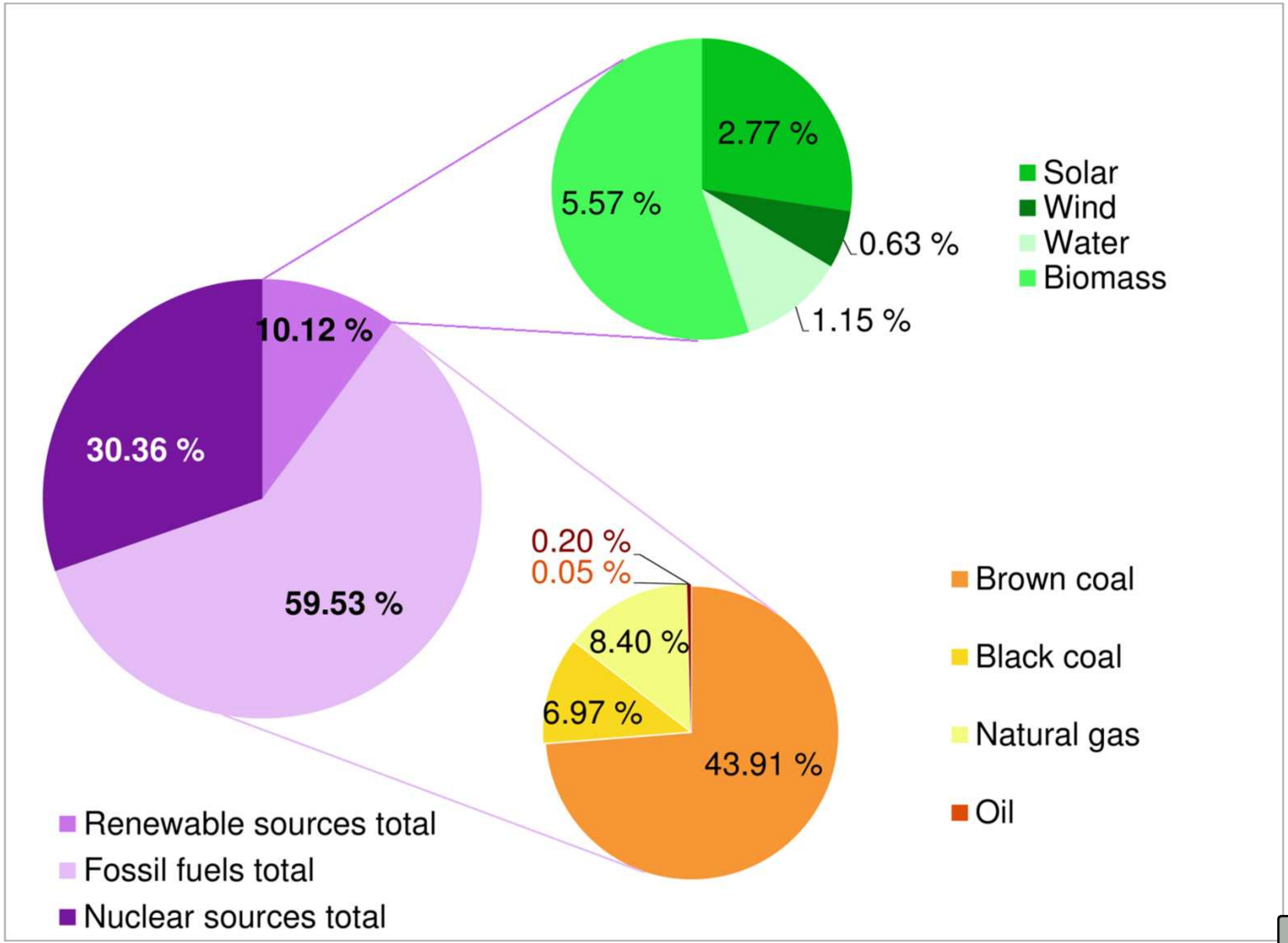
Scope of lecture 13

Power industry as the main contributor to air pollution

- Sources of electricity in the Czech Republic
- Main pollutants released from coal combustion
- Separation of particulate matter (fly ash) from flue gas
- Flue gas desulfurisation
- Flue gas denitrification
- MSW incinerators – actual status and technology in the Czech Republic
- Pyrolysis as alternative to solid wastes combustion
- Application of fly ashes, separated from ESP for CO_2 capture

Energetic mix in the Czech Republic

- In 2016 production of electricity in the Czech Republic was 77.42 tWh and consumption 60.88 tWh



(Sources: http://www.ote-cr.cz/statistika/narodni-energeticky-mix, https://www.eru.cz/documents/10540/462820)

Energetic mix in the Czech Republic

- In 2016 following thermal power plants were operated (without nuclear):

	Owner	No. of facilities	Installed power [MWe]
	Alpiq Generation (CZ) s.r.o	1	472
	ČEZ, a. s.	13	5411
	Elektrárna Dětmarovice, a.s.	1	800
	Elektrárna Počerady, a.s.	1	1000
	Elektrárny Opatovice, a.s.	1	378
	Energotrans a.s.	1	352
	Mondi Štětí, a.s.	1	113
	Plzeňská teplárenská, a.s.	1	149
	Pražská teplárenská a.s.	1	122
	Sev.en EC a.s.	1	820
	Sokolovská uhelná, a. s.	2	590
	TAMEH Czech s.r.o.	1	254
	UNIPETROL RPA, s.r.o.	1	112
	United Energy, a.s.	1	239
	Veolia Energie ČR, a.s.	1	174
Sum:	**15**	**28**	**10986**

Review of main pollutants

- Power industry = the main contributor to emissions of 4 substances;
- Examples of specific national emission limits **(EL)** given for:
  - Dry flue gas at | 273.15 K | 101.325 kPa | $O_{2,\ ref.} = 10\ \%$
  - Nominal heat input > 300 MW (commissioned after Jan. 7, 2014)

- Particulate matter

Fuel:	Solid	Biomass	Liquid	Natural gas
EL [$mg.m^{-3}$]	10	20	10	5

- SO_2

Fuel:	Solid	Biomass	Liquid	Natural gas
EL [$mg.m^{-3}$]	150 200 *	150	150	35

* fluidised bed combustors

- NO_x

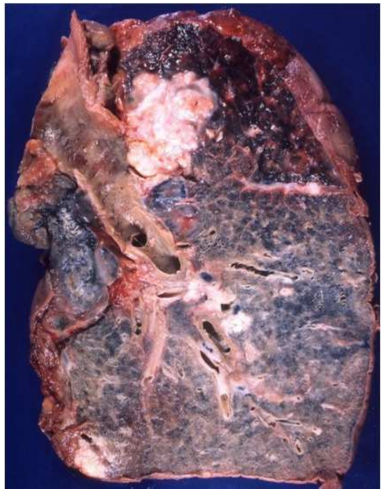
Fuel:	Solid	Biomass	Liquid	Natural gas
EL [$mg.m^{-3}$]	150 200*	150	100 50**	100

* pulverized coal, ** turbines

- CO_2 No specific EL

Particulate matter – health impact

- **PM suspected causing the diseases as follows:** (Source: WHO)
  - Bronchial asthma;
  - Lung tumors;
  - Diseases of the cardiovascular system (myocardial infarction, cerebrovascular accident, embolism);
  - Chronic diseases of the upper and lower respiratory tract (allergic, chronic allergic rhinitis);
  - Premature births, fetal defects, and spontaneous abortions;

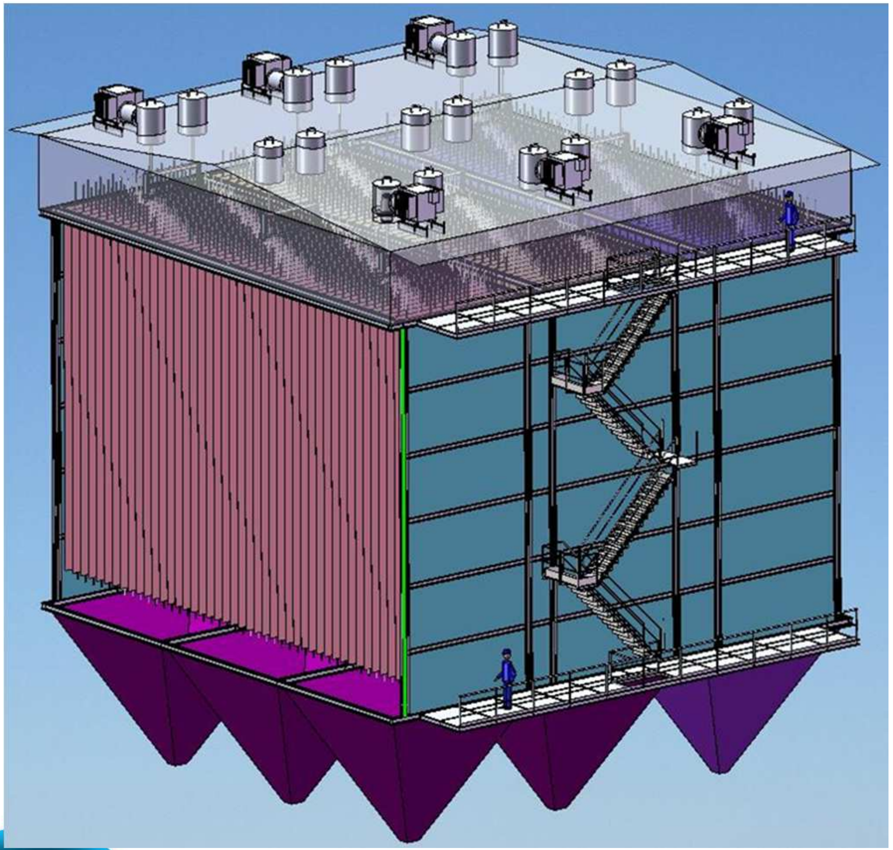


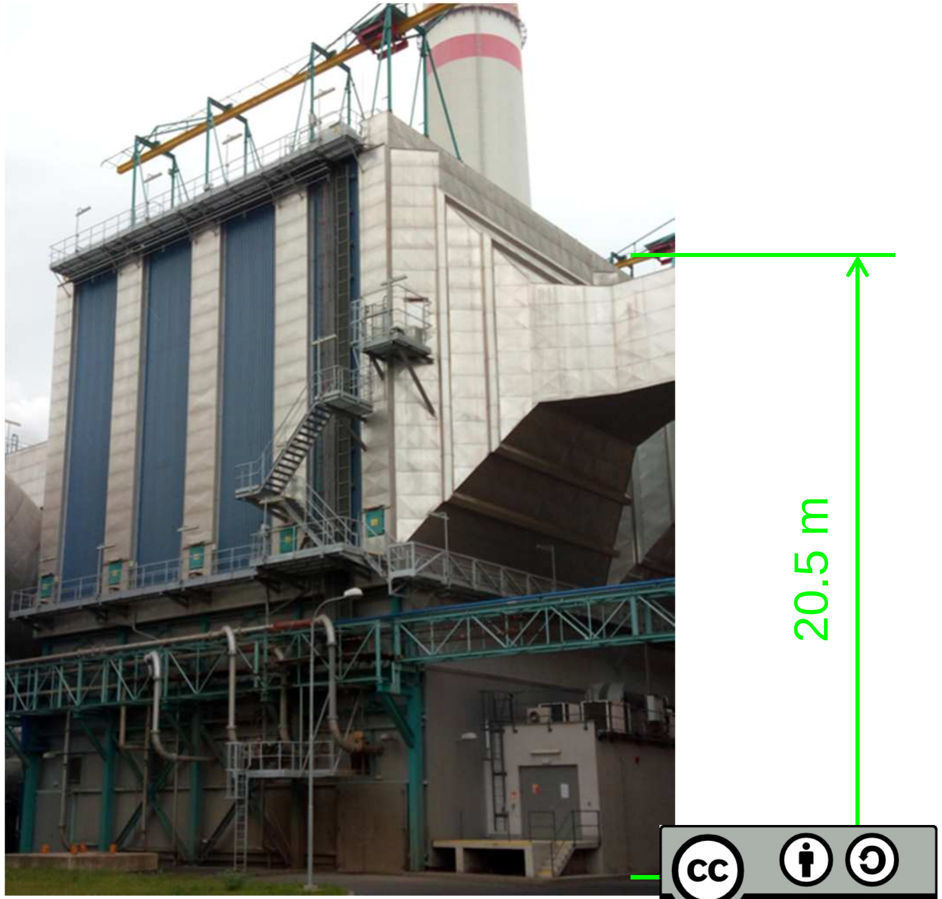
Particulate matter – emission control

- At Czech coal-fired power plants electro static precipitators are predominating (only 1 power plant equipped with bag house filters).
- Typical parameters of ESP for fly ash separation:
  - Voltage between electrodes = 55 – 75 kV,
  - Stable ionization corona discharge between electrodes,
  - Distance between collecting (plate curtains) and discharge electrode (wires) = 15 – 20 cm,
  - Pressure drop = 20 – 50 Pa,
  - Efficiency > 99,9 % for the particle size range 0.01 – 60 µm.
  - Dust removal from collecting electrodes via mechanical vibratory system.

Particulate matter – emission control

- Example of ESP: Power plant Prunéřov II, block 5, nominal power 250 MW_e (actual state after retrofitting in 2016):
- Input fly ash conc. = 30 $g.m^{-3}$, Flue gas flow = 1 300 000 $m^3.h^{-1}$ Separated fly ash quantity = 39 $t.h^{-1}$





Sulfur dioxide – environmental impact

- **Diseases caused by exposition by SO_2** (Source: WHO)
  - Short-term exposure to SO_2 (5 minutes to 24 hours) causes bronchoconstriction and increased frequency of respiratory infections.
  - Effects of chronic and repeated exposure: emphysema (emphysema pulmonum), hematopoietic disorders, heart damage.
- **Environmental alerts – immediate damages of plants + acidification**

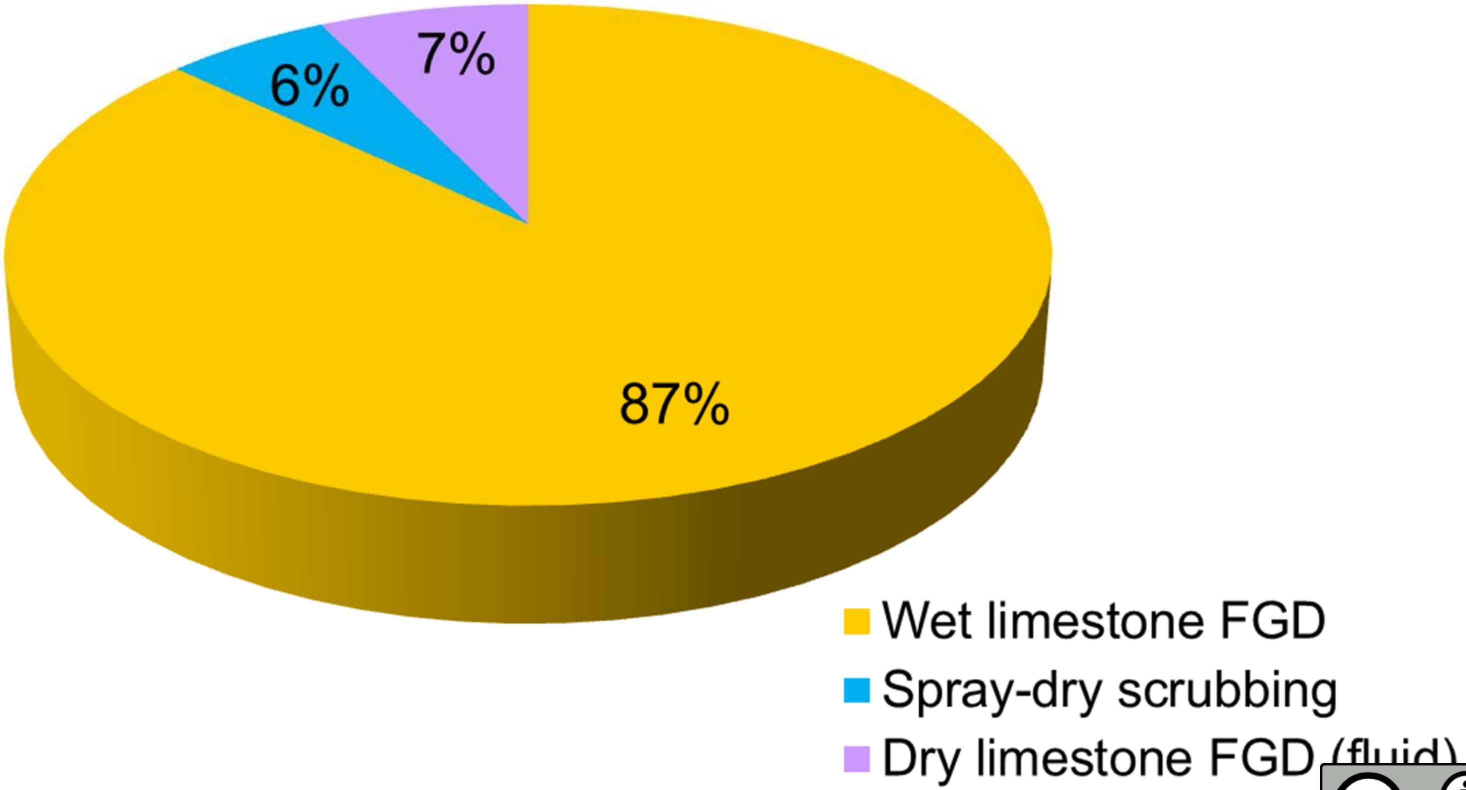
Vegetation type	Critical concentration	Time period
Lichens	10 μg/m^3	Yearly average
Forest ecosystem	20 μg/m^3	Yearly average + Oct. - March
Native vegetation	20 μg/m^3	Yearly average + Oct. - March
Field cultures (crops)	30 μg/m^3	Yearly average + Oct. - March

Sulfur dioxide – environmental impact

- In 1978 Czechoslovakia assessed by the UN as the 3rd most affected country in Europe (1st eastern Germany, 2nd Belgium)
- Installation of FGD started at the beginning of 1990s (finished 1997)
- However! Till present 10.1 of all mountain forests endangered by introskeletal erosion – long term consequence of defoliation in 1970s-1980s

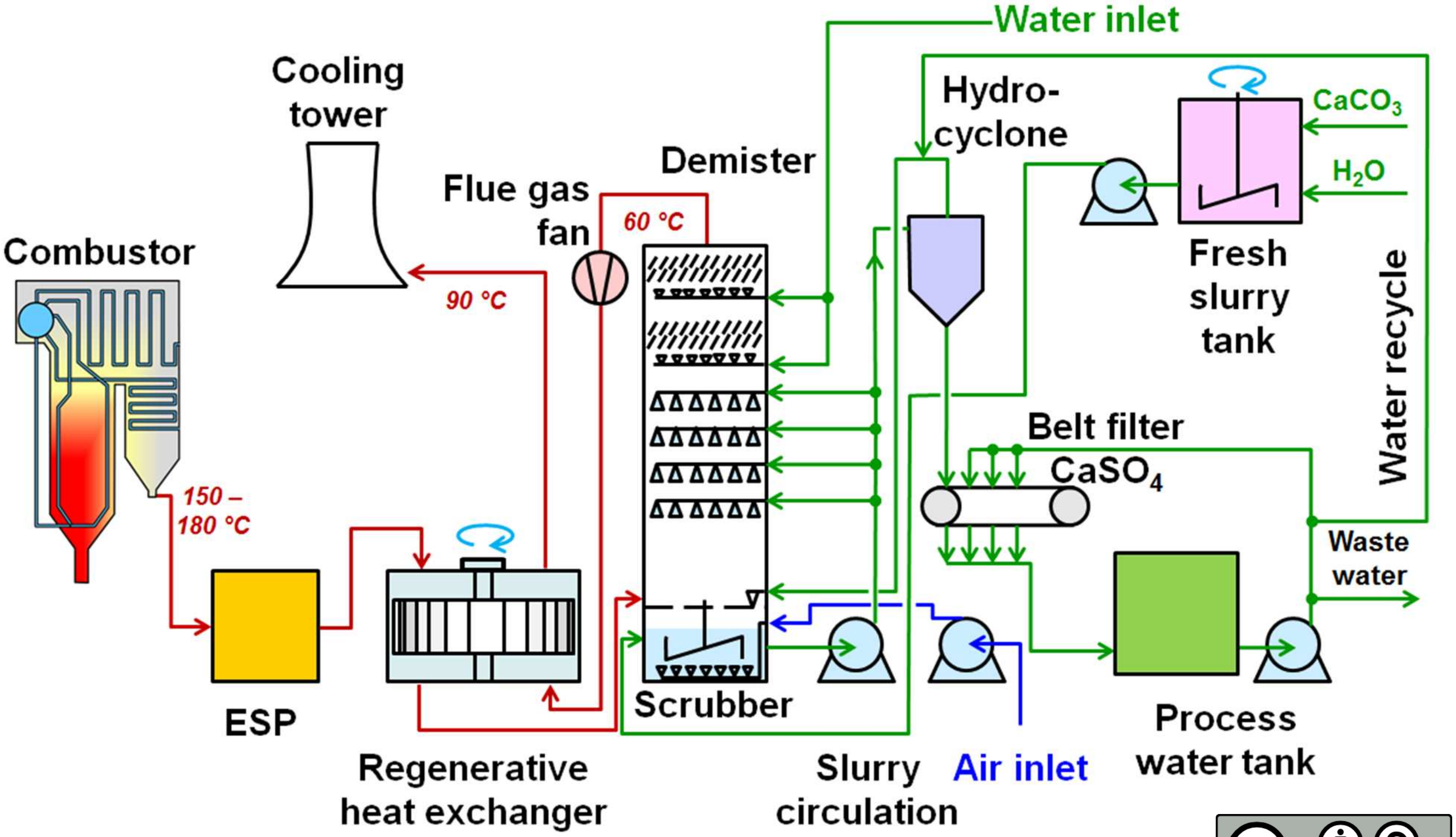
Sulfur dioxide – emission control

- At Czech coal-fired power plants wet scrubbing using a slurry of natural limestone is predominating FGD method:



Sulfur dioxide – emission control

- The most used wet limestone FGD has the scrubber installed after the ESP in order to produce pure gypsum for civil engineering:



Nitrogen oxides – emission control

- **In fact two way lead to NO_x abatement in combustion technology**
  - Primary measures – optimizing combustor and process;
  - Secondary measures – NOx reduction within a separate reaction;
- **Primary measures**
  - Decrease of air preheating;
  - Installation of low-NO_x burners;
  - Optimization of combustion regime (air distribution)
  - Flue gas recirculation.
- **Secondary measures**
  - Selective non-catalytic reduction (urea injection);

Used at Czech power plants

  - Selective catalytic reduction (on V_2O_5 WO_3); → Used at MSW incinerators
  - Special combined deNO_x + FGD → Not used

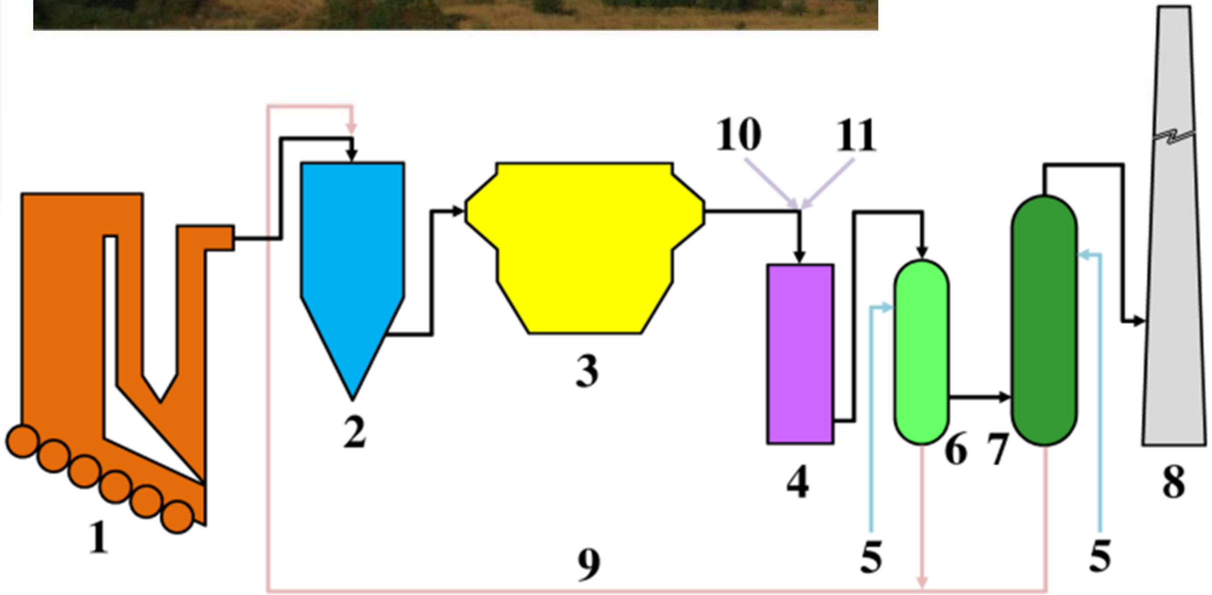
MSW incinerators – emission control

- Total annual production of wastes (not only MSW) > 34×10^6 t
  (Source: https://www.czso.cz/csu/czso/produkce-vyuziti-a-odstraneni-odpadu-2015)
- Production of energy = 3.1 %, recycling = 25 %, landfilling = 10.3%
- In the Czech Republic only 4 MSW energy recovery facilities:
  - **Prague**
    → capacity 4 × 15 $t_{MSW}.h^{-1}$ = 60 $t_{MSW}.h^{-1}$
  - **Liberec**
    → capacity 1 × 12 $t_{MSW}.h^{-1}$ = 12 $t_{MSW}.h^{-1}$
  - **Brno**
    → capacity 2 × 16 $t_{MSW}.h^{-1}$ = 32 $t_{MSW}.h^{-1}$
  - **Pilsen - Chotíkov**
    → capacity 1 × 12 $t_{MSW}.h^{-1}$ = 12 $t_{MSW}.h^{-1}$

Total capacity = 116 $t_{MSW}.h^{-1}$

MSW incinerators – emission control

- Unlike power plants all the MSW energy recovery facilities have a SCR + DeDiox systems



1 – combustor + boiler
2 – spray-dryscrubber,
3 – ESP,
4 – SCR + DeDiox
5 – fresh suspension inlet $Ca(OH)_2$ + activated carbon
6 – quench + scrubber
7 – scrubber
8 – stack
9 – used slurry recycle
10 – natural gas inlet + air
11 – NH_4OH inlet

e.g. Prague: electricity 45 000 MWh/year + heat 0.85×10^6

Emission control – actual research

- Following slides presents two examples of actually running research:
  - **Conversion of waste biomass via pyrolysis**

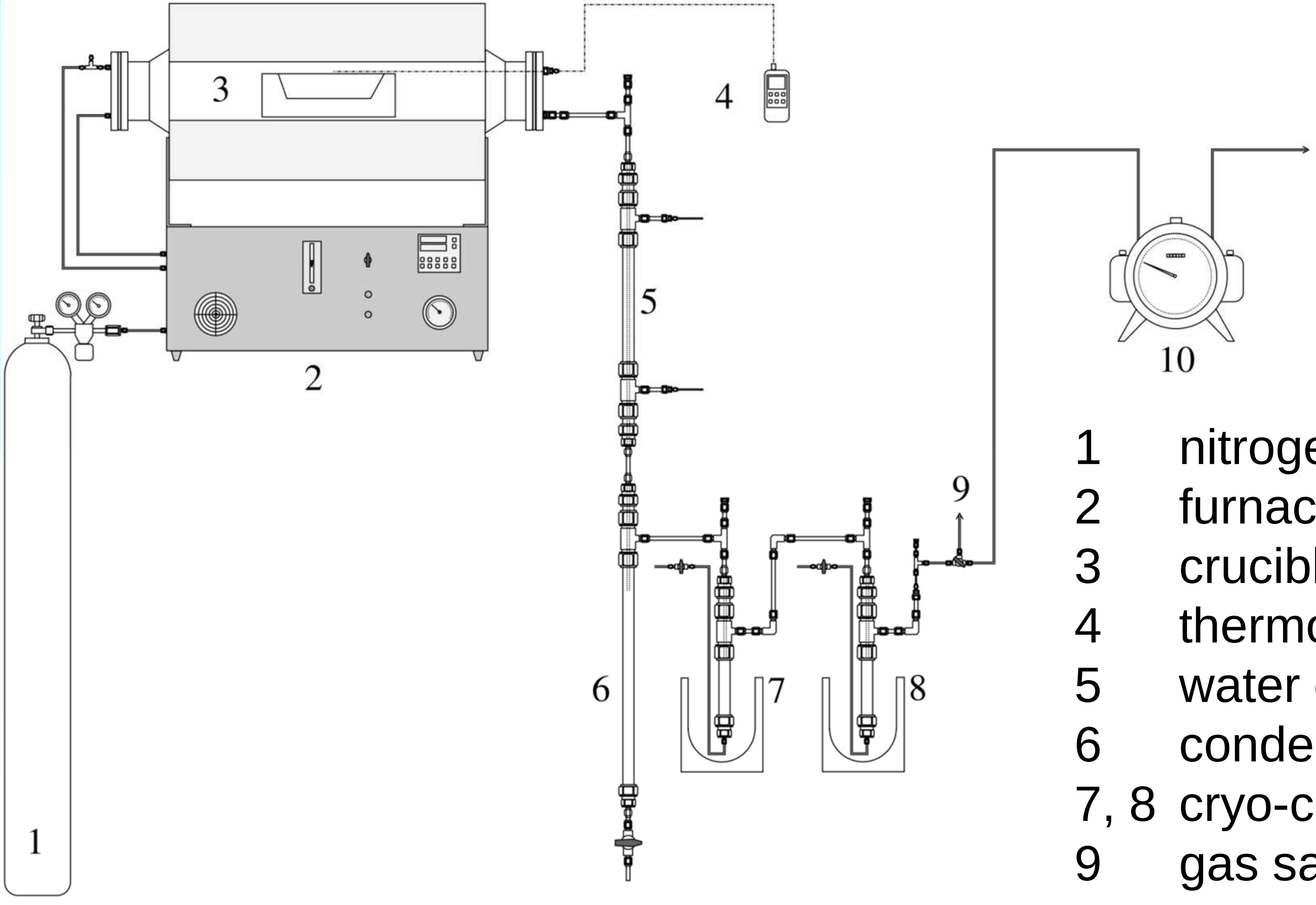
    Preperation of activated carbon base adsorbents
  - **Application of fly ashes from ESP fo CO_2 capture**

    Usage of ashes in carbonate looping process

    Conversion of ashes into synthetic zeolites

Pyrolysis as alternative to incineration

- Research of waste biomass pyrolysis at Department of solid and gaseous fuels and air protection;



1	nitrogen inlet
2	furnace + vacuum pump
3	crucible with sample
4	thermometer
5	water cooler
6	condensate collector
7, 8	cryo-collectors
9	gas sampling
10	gas meter

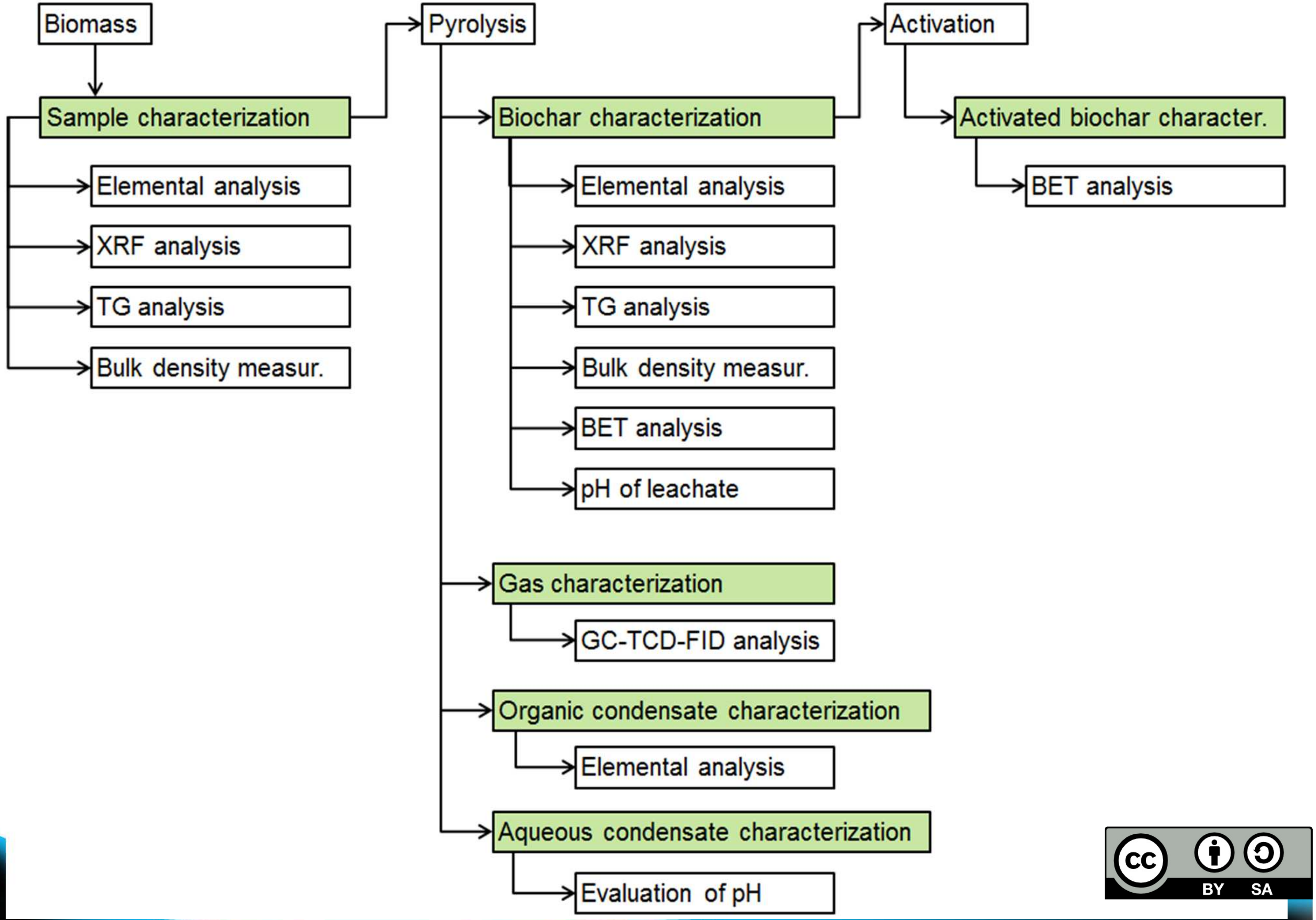
Pyrolysis as alternative to incineration

- The aim of the research = obtaining combustible gas + oil + production of biochar;
- Biochar externally activated by steam under various atmospheres;
- System flexible for operative balancing of the pyrolysis products;
- Example of three waste biomass materials:

	Product amount related to the sample weight [wt. %]		
Product	Spruce	Coffee	Hardwood
Biochar	21,2 %	22,09 %	20,96 %
Humidity	7,3 %	6,84 %	10,82 %
Pyrolytic water	13,6 %	14,45 %	22,98 %
Organic condensate	2,8 %	6,36 %	2,09 %
Low boiling	1,9 %	0,54 %	0,53 %
Gas	51,0 %	46,85 %	40,03 %
Loses	2,2 %	2,87 %	2,59 %

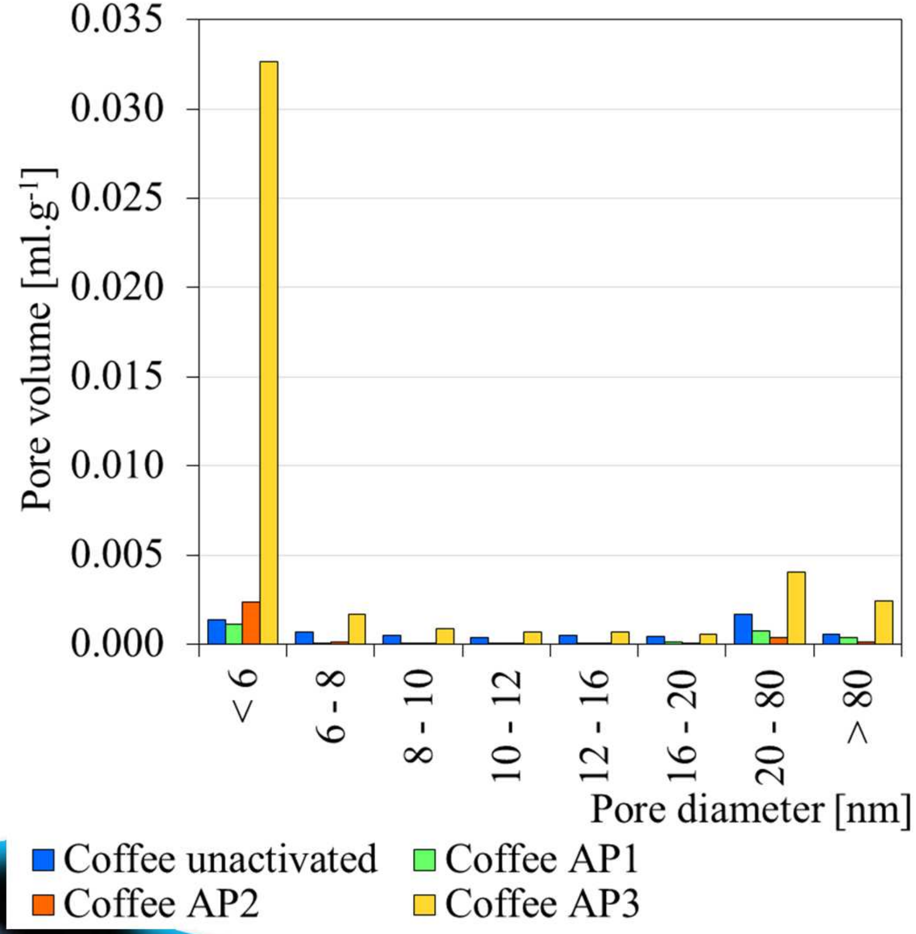
Pyrolysis as alternative to incineration

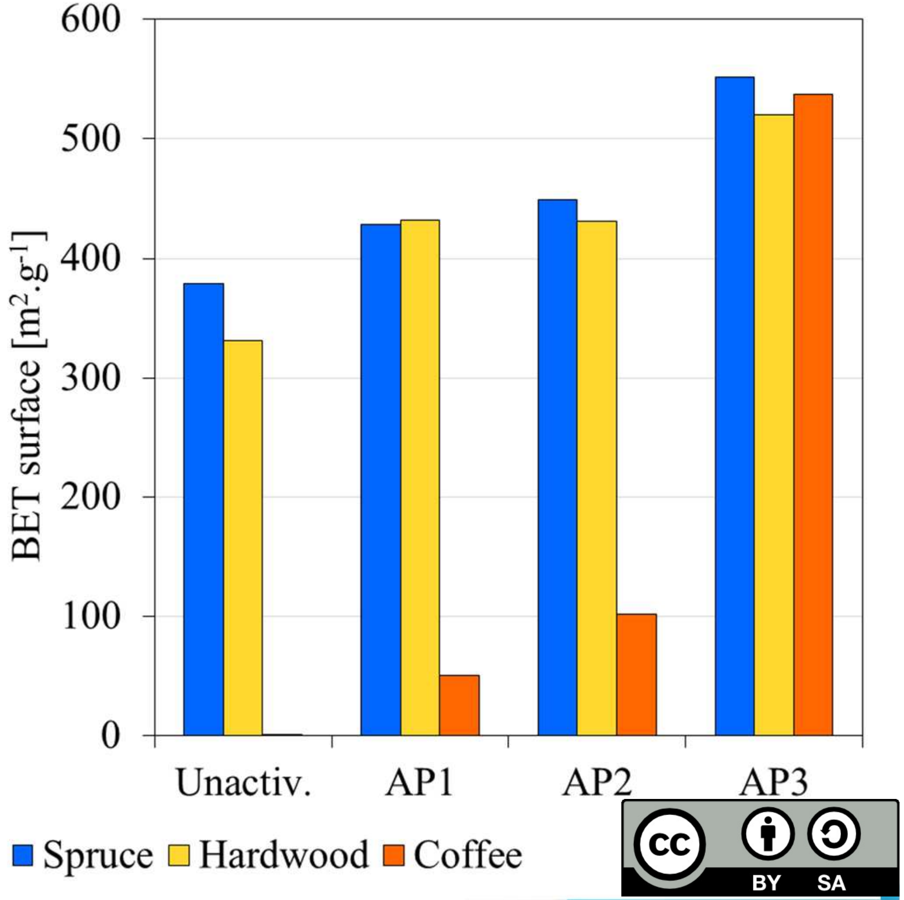
- Basic workflow



Pyrolysis as alternative to incineration

- Example of activation results, received at three different conditions
  - AP1: atmosphere CO_2, steam 250 °C, sample t = 700 °C
  - AP2: atmosphere CO_2, steam 250 °C, sample t = 800 °C
  - AP3: atmosphere N_2, steam 250 °C, sample t = 800 °C

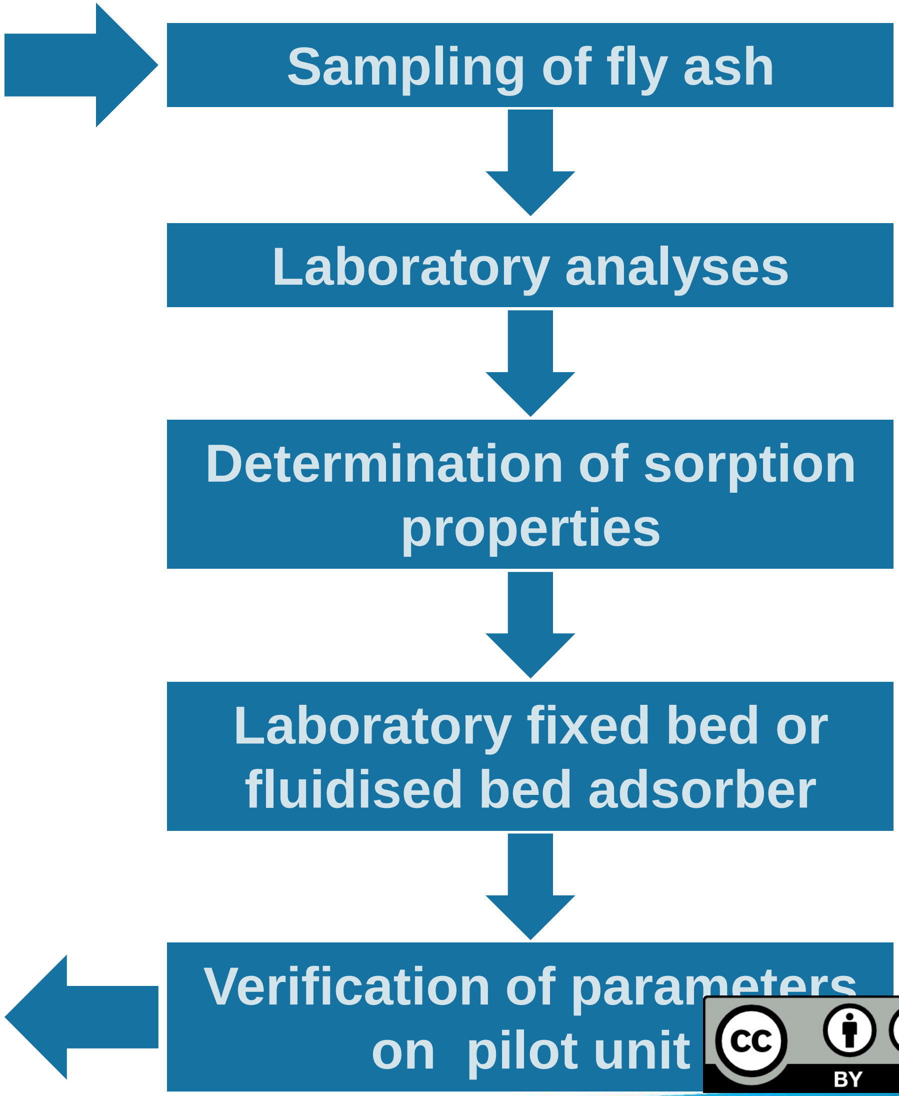




Fly ash – potential sorbent for CO_2

- Fly ash is considered promising as an adsorbent able to capture CO_2 from flue gas.

ESP



Sampling of fly ash

Laboratory analyses

Determination of sorption properties

Laboratory fixed bed or fluidised bed adsorber

Verification of parameters on pilot unit

Data set for industrial applications

Particulate matter – emission control

- In 2017 institutions UCT, CERTH, TU-BAF, GIG, VUHU and UJV launched the project:
  „Innovative management of COAL BY-PROducts leading also to CO_2 emissions reduction“

COALBYPRO

- Supported by European Commission (project no. 754060)

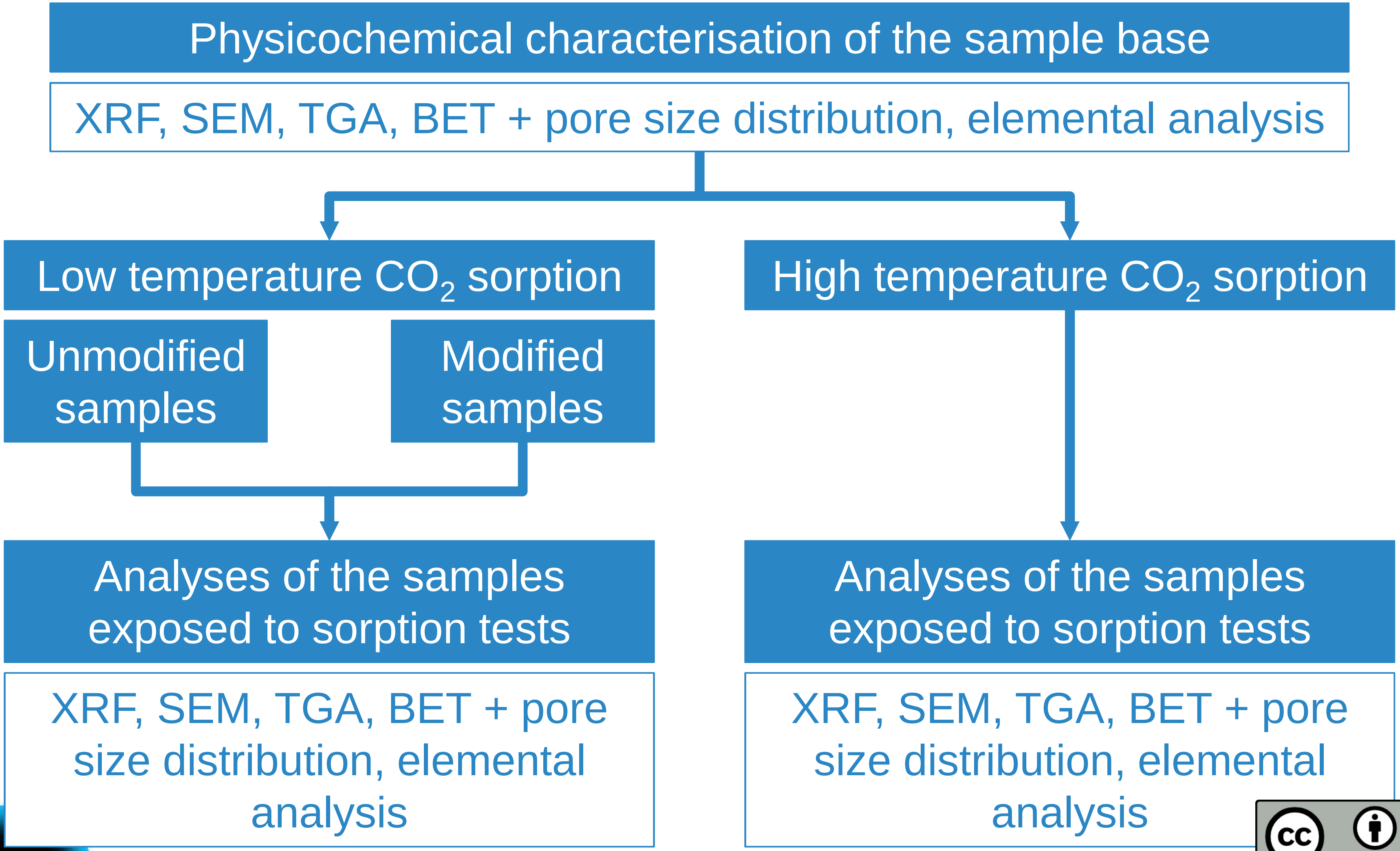
Research Fund for Coal & Steel

- Until present following samples have been collected and processed:

Czech Republic	21 ashes
Greece	10 ashes
Poland	4 ashes

Laboratory research workflow

- The research activities were divided into two separate groups of activities:



Physicochemical characterisation of the sample base

XRF, SEM, TGA, BET + pore size distribution, elemental analysis

Low temperature CO_2 sorption

Unmodified samples

Modified samples

Analyses of the samples exposed to sorption tests

XRF, SEM, TGA, BET + pore size distribution, elemental analysis

High temperature CO_2 sorption

Analyses of the samples exposed to sorption tests

XRF, SEM, TGA, BET + pore size distribution, elemental analysis

Fly ashes characterisation (for CO_2)

- **Samples characterized using following instrumental methods:**
  - Quantitative elemental analysis (C, H, N, S, O)
  - Semi quantitative XRF analysis
  - Thermogravimetry
  - Evaluation of BET surface area and pore size distribution
  - Comparative evaluation of sorption capacities (Autosorb-iQ, DVS Advantage)
  - SEM, XRD, physical parameters…

Decision if the ash is more suitable for high temperature sorption or it should be converted to synthetic zeolite.

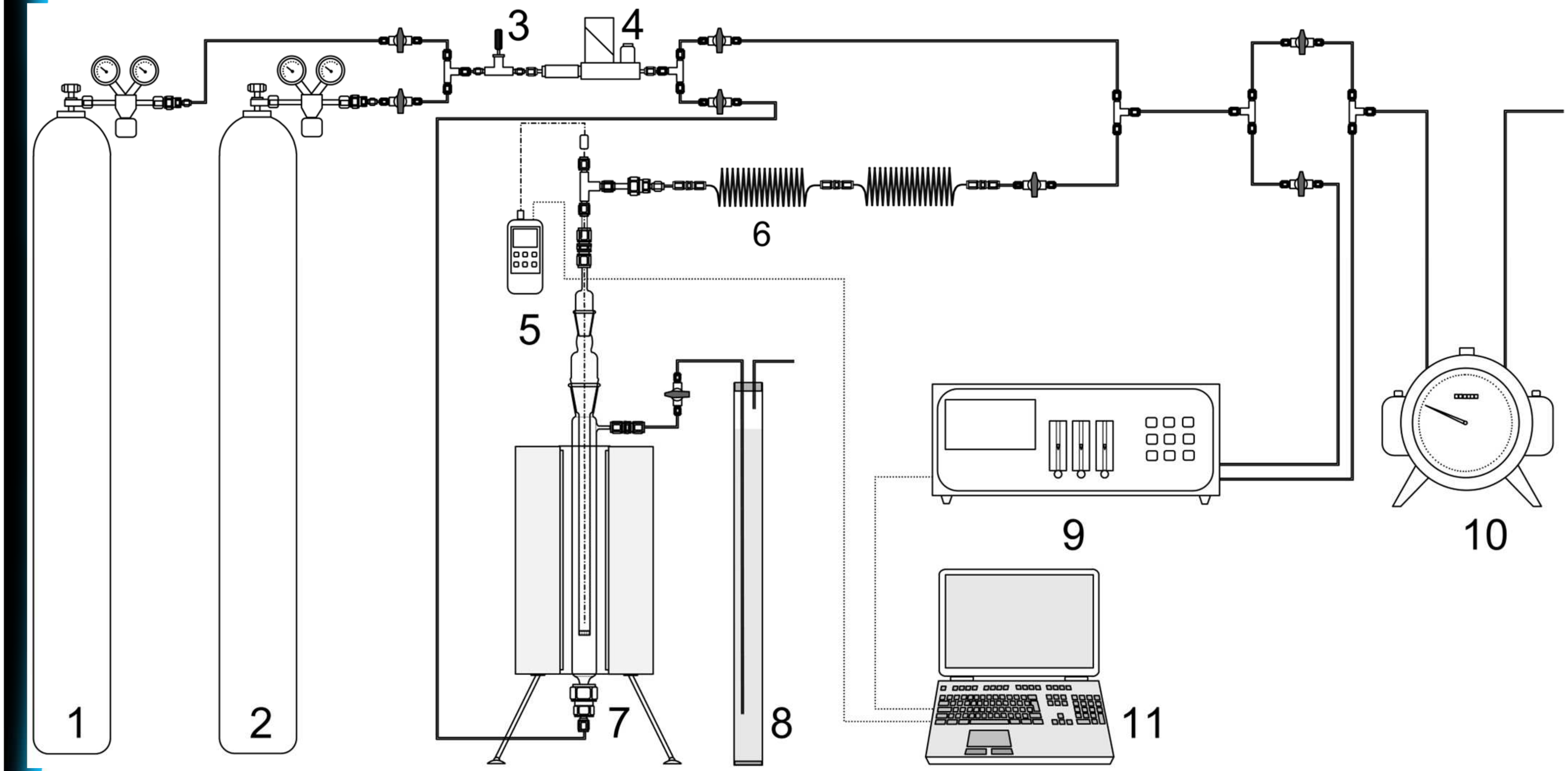
High temperature apparatuses

- Only samples with high $CaO/CaCO_3$ content subjected to High temperature chemisorption tests.
- Series of cyclical sorption/desorption tests in laboratory conditions and subsequent evaluation of sorption capacities for CO_2
- Two laboratory apparatuses are used: Fixed bed apparatus (A)
  Fluidized bed apparatus (B)


(A)


(B)

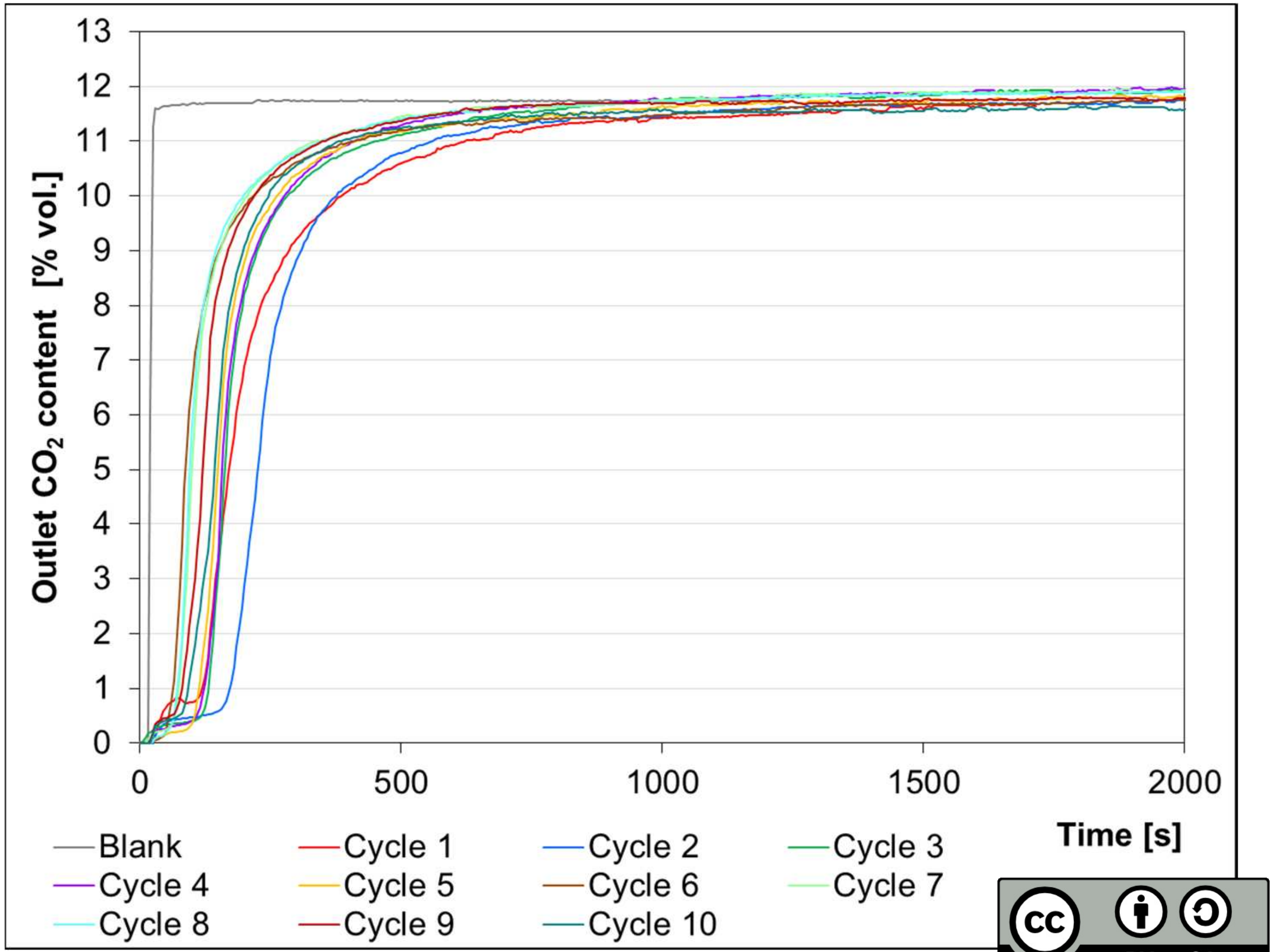
Fluidised bed apparatus



- Legend: 1, 2 – pressure cylinders, 3 – needle valve, 4 – mass flow meter/controller, 5 – thermometer, 6 – air cooler, 7 – oven with quartz adsorber, 8 – manostat, 9 – IR spectrometer, 10 – gas met

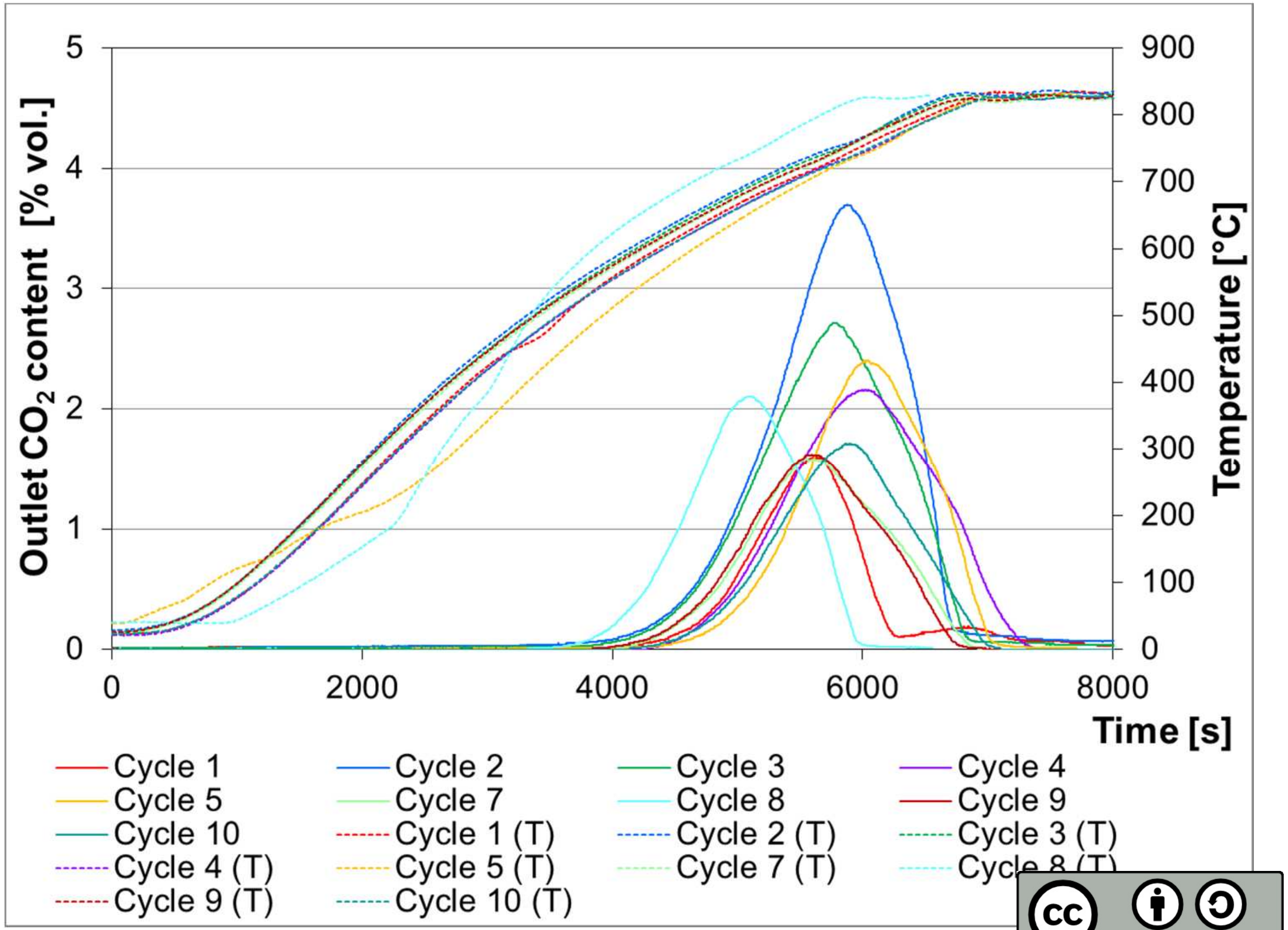
High temperature capacities for CO_2

- Sorption capacities calculated from breakthrough curves
- Example: Fixed bed apparatus, gas mixture flows through calcined sample at 650°C.
- Sample ID:
  Z 30/18 Ledvice
- Gas mixture:
  CO_2 = 11.96 %
  O_2 = 11.94 %
  N_2 = balance
- Gas flow:
  1.2 $dm^3.min^{-1}$
- Sample intake:
  50 g



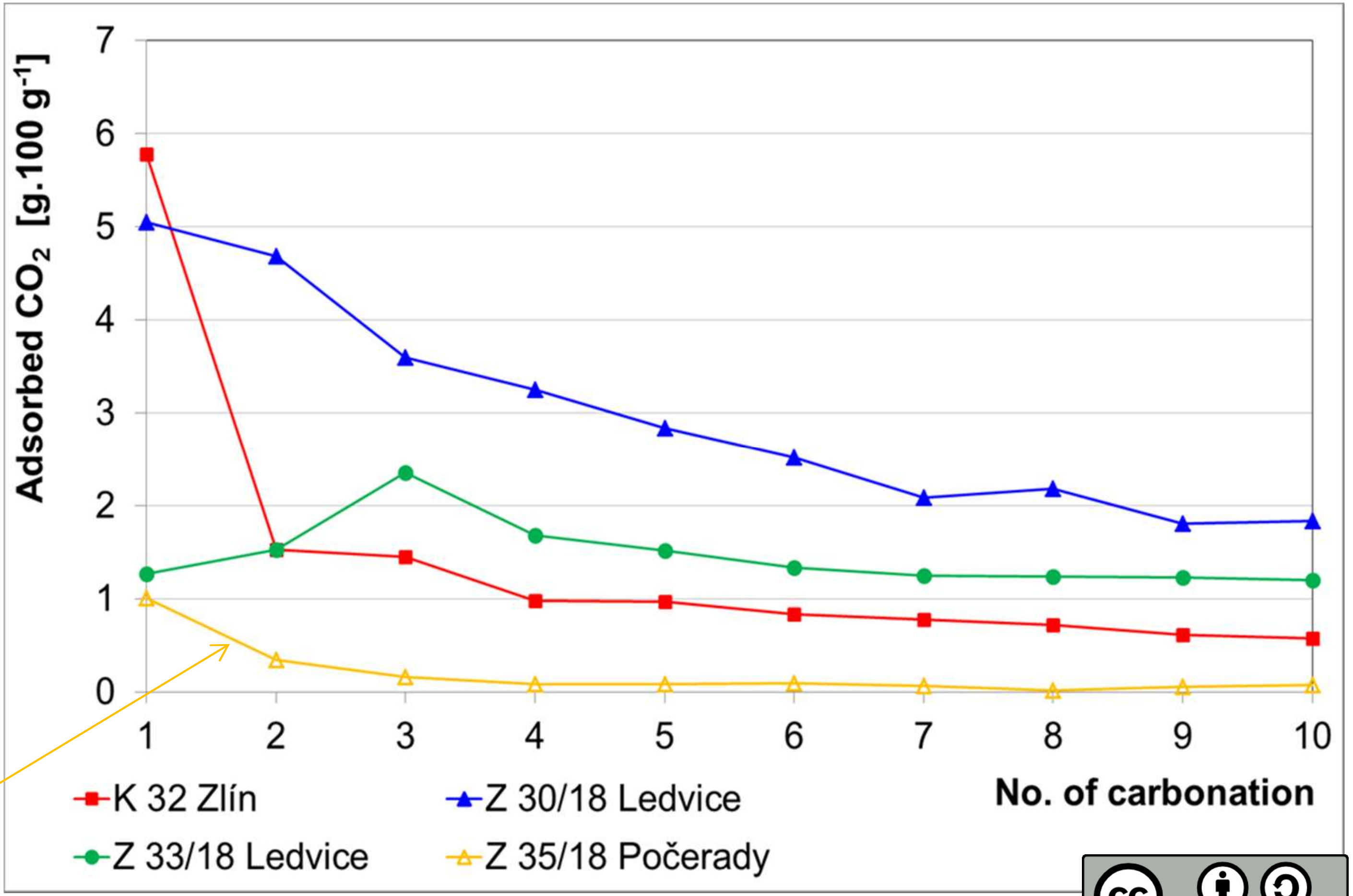
High temperature capacities for CO_2

- Desorbed CO_2 calculated from the curves recorded during calcination.
- Example: Fixed bed apparatus, gas mixture flows through slowly heated up to at 850°C.
- Sample ID:
  Z 30/18 Ledvice
- Heating rate:
  10 $°C.min^{-1}$
- Desorption gas:
  N_2 = 100 %
- Gas flow:
  1.2 $dm^3.min^{-1}$
- Sample intake:
  50 g



High temperature capacities for CO_2

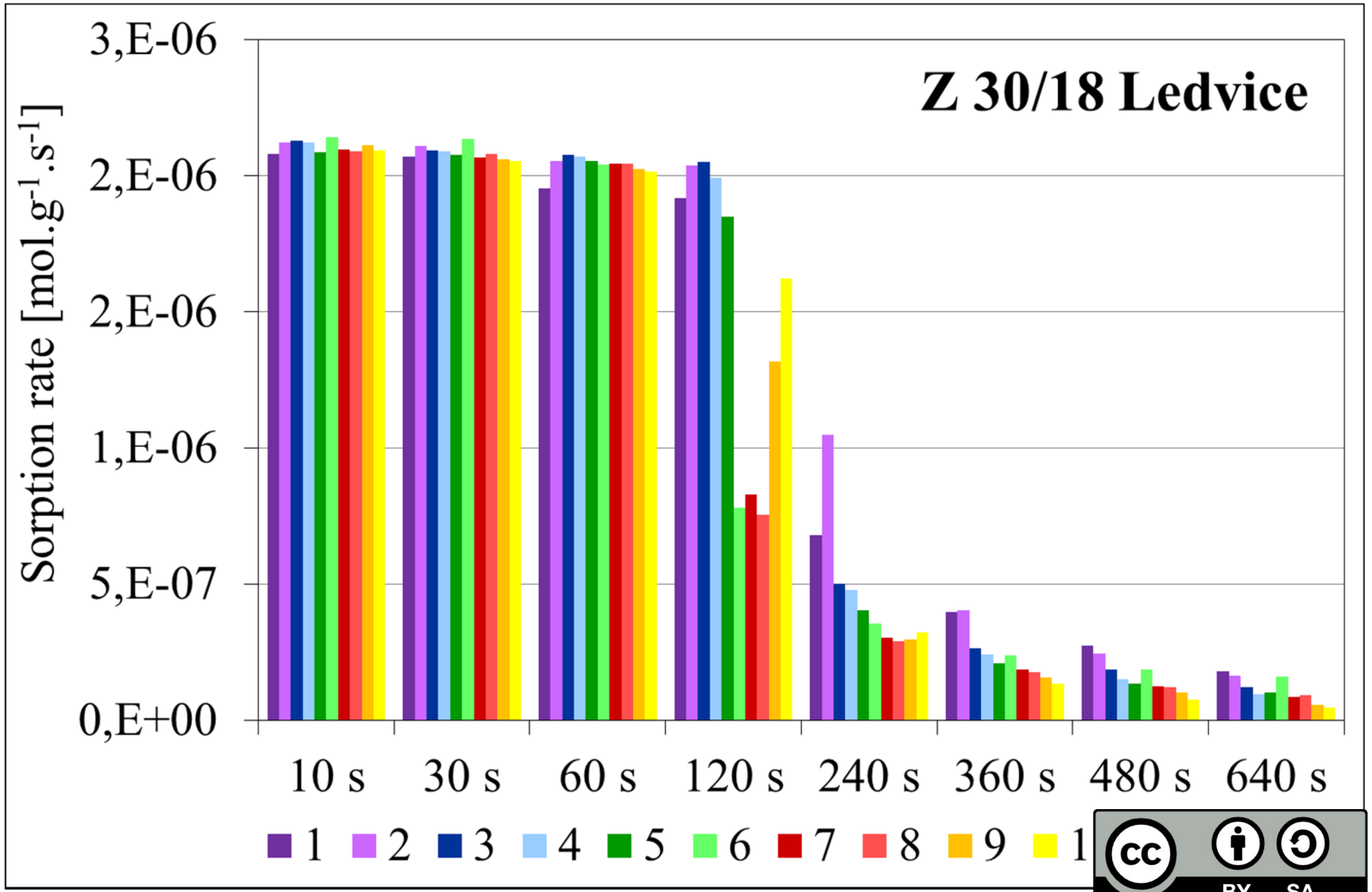
- Example of changes in capacities during 10 cycles of repeated calcinations and carbonations in fluidised bed apparatus.
- Isotherm
  650 °C
- Gas mixture
  CO_2 = 11.96 %
  O_2 = 11.94 %
  N_2 = balance
- Gas flow:
  1.0 $dm^3.min^{-1}$
- Sample intake:
  20 g



High Na_2O + MgO = sintering !

High temperature capacities for CO_2

- Sorption rate can be also calculated from breakthrough curves
- Example of changes in kinetic during 10 cycles measured in fluidised bed apparatus.
- Isotherm
  650 °C
- Gas mixture
  CO_2 = 11.96 %
  O_2 = 11.94 %
  N_2 = balance
- Gas flow:
  1.0 $dm^3.min^{-1}$
- Sample intake:
  20 g



Low temperature capacities for CO_2

- Results of static adsorption method using pure CO_2 introduced into the sample from the Tedlar sampling bag are as follows.
- The raw samples offer negligible capacity at 30 °C
- Treating with boiling 40% NaOH solution with subsequent thorough washing with H_2O increases the BET surface as well as the adsorption capacity.

Sample	BET surface [$m^2.g^{-1}$]		Capacity of treated sample [$g.100g^{-1}$]
	Before treatment	NaOH treated	
Z 1999/17	8.4	28.0	0.8
Z 2052/17	1.9	21.1	0.6
Z 31/18.	2.0	31.1	0.7
Z 261/18	2.9	34.8	0.6
Z 35/18	1.7	23.3	3.7

Research on CO_2 sorption on ashes

- Fundamental question: Can be fly ash used for CO_2 capture?
- Answer:
  - Yes, it could be cheap alternative to limestones, hydrotalcite-like compounds and similar high temperature sorbents.
  - Fly ashes with sufficient content of CaO or $CaCO_3$, rare capable to capture CO_2 up to ca. 5 g.100 g^{-1} once, and repeatedly up to 1.8 g.100 g^{-1}.
  - Low temperature tests applied on the samples treated with 40% NaOH solution demonstrated good ability of the ashes to be converted into more efficient adsorbents.
  - Potential chemical conversion of fly ashes into zeolites with higher sorption capacity is actually a subject for intensive research

EUROPEAN UNION
European Structural and Investing Funds
Operational Programme Research,
Development and Education

MINISTRY OF EDUCATION,
YOUTH AND SPORTS

ATMOSPHERE CHEMISTRY

Lecture No.: 14

Organisation of study

- Lecturer: Marek Staf, MSc., Ph.D., phone: +420 220 444 458
  e-mail: marek.staf@vscht.cz,
  web: http://web.vscht.cz/~stafm/
  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 - oral form
- Note:

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Scope of lecture 14

Road transport as a contributor to air pollution

- The most important reactants and products, forming photochemical smog
- Evolution of automotive industry and its impact on air quality
- Technical improvements leading to emissions reduction from spark ignition and compression ignition engines
- Replacement of fossil fuels (oil) by bofuels
- Potential of hybrids, plug-in hybrids and fully electrical vehicles

Photochemical smog

- Cars = main source sou reactants for so called photochemical smog;
- Photochemical smog = products of UV radiation promoted reactions of the following substances:
  - NO_x
  - VOCs
- highly negative health impact have following substances belonging to the photochemical smog mixture:
  - Suspended particulate matter;
  - Ground-level ozone.
- Within the compounds forming photochemical smog, following substances predominates:
  - Aldehydes and other VOCs,
  - $NO + NO_2$,
  - Peroxyacyl nitrates,
  - Tropospheric ozone.

Photochemical smog

- Classification of pollutants involved within the photochemical smog:
  - Primary pollutants,
  - Secondary pollutants.
- Primary pollutant = unchanged compound directly from a source;
- Secondary pollutant = substance generated by atmospheric reactions of the primary pollutants (precursors);
- Typical examples of secondary pollutants:
  - Ozone – generated by recombination of hydrocarbons and NO$_x$, in the presence of UV radiation
  - NO2 – as a product of several reactions, such as:

$$HOO^{\bullet} + NO \longrightarrow NO_2 + OH^{\bullet}$$

or

$$O_3 + NO \longrightarrow NO_2 + O_2$$

Photochemical smog

- Mechanism of photochemical reactions and basic photochemical reactants were described in 1950s.
- The first method for collecting reactants from the polluted air proposed in 1948 by Arie Haagen-Smit;
- A., H., Smit discovered following:
  - successfully identified O_3 as a component of Los Angeles smog,
  - NO_x (from cars + C_xH_y from refineries) exposed to sunlight, are key reactants for tropospheric O_3 formation,
  - In cooperation with Arnold Beckman constructed first applicable systems for detecting compounds involved within smog.

Photochemical smog

- The sequence of the main reactions producing substances of the Los Angeles type of smog is as follows:

$$NO_2 \xrightarrow{UV} NO + O$$

$$O + O_2 \longrightarrow O_3$$

$$NO + O_3 \longrightarrow NO_2 + O_2$$

$$O + C_xH_y \longrightarrow RCO^{\bullet} \xrightarrow{O_2} RCO_3^{\bullet}$$

$$RCO_3^{\bullet} + C_xH_y \longrightarrow CH_2{=}O \text{ … ketones etc.}$$

$$RCO_3^{\bullet} + O_2 \longrightarrow RCO_2 + O_2$$

$$RCO_3^{\bullet} + NO \longrightarrow RCO_2 + NO_2$$

$$RCO_3^{\bullet} + NO_2 \longrightarrow RCO_3NO_2 \text{ i.e. peroxyacetyl nitrate}$$

History of road transport vehicles

- Nicolas Joseph Cugnot: fardier à vapeur (1770)
  - Weight 2,5 t, effective load 4 t, max. speed 9 km.h^{-1}
  - Driving with saturated steam → the boiler not equipped with a superheater
  - The three-wheels version evaluated as unstable by the french army

History of road transport vehicles

- Karl Benz: gasoline tricycle, German patent no. 37435a (1886)
  - The engine = modified four-stroke Otto's engine (patent from 1877), performance 0,66 kW at 400 rpm, cylinder volume 954 cm^3, real speed 11 km.h^{-1}, max. 16 km.h^{-1}


Nicolaus Otto

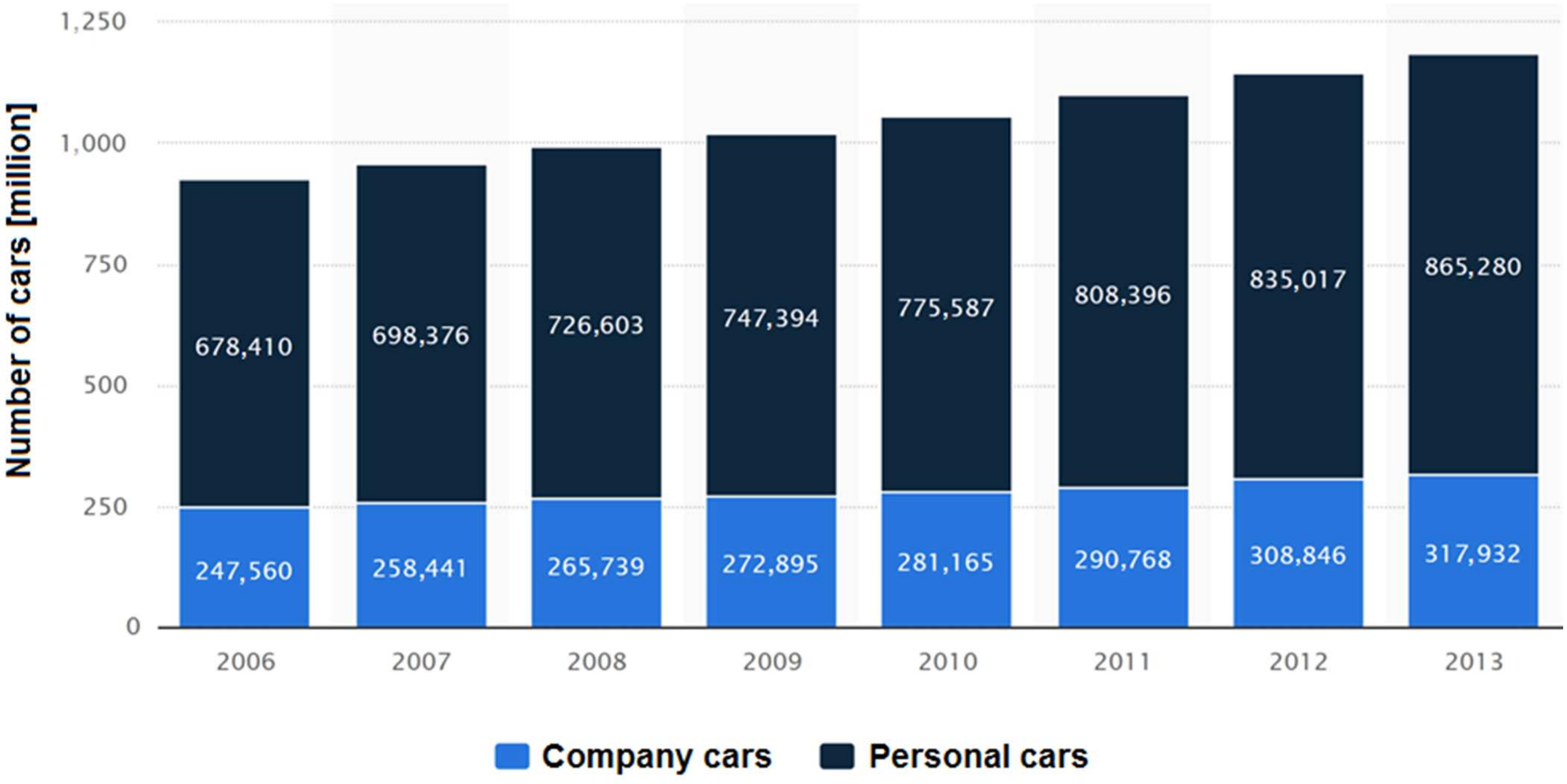

Karl Benz

History of road transport vehicles

- Pioneer of world motorization – Henry Ford
  - The first T model car was built on September 27, 1908 at the Piquette Plant in Detroit – commencement of mass production of vehicles

Development of road transport

- Number of registered motor vehicles in the world



Source: www.statista.com

Actually used power sources

- Combustion engines
  - Spark-ignition engines
    - Gasoline 95, 98 or 100 octanes containing up to 5 % of ethanol (within annual count min. 4.1 %)
    - Ethanol E85 with concentration 70 – 85 % according to season
    - Compressed Natural Gas (CNG)
    - Liquefied Petroleum Gas (LPG) in winter 40 % of butane, in summer 60 % of butane
  - Compression-ignition engines
    - Diesel oil containing rapeseed methyl ester or other fatty acids methyl ester up to 7 %
    - Mixed diesel oil containing 31 % FAME
- Hybrid propulsion (classic hybrid cars and plug-in hybrids)
- Electric propulsion
  - Accumulators Li-ion, or Li-pol respectively

Engines with internal combustion

- Differences between spark-ignition engines (SI engines) and compression-ignition engines (CI engines) are in the way of igniting the air-fuel mixture.
- Spark-ignition engines

Efficiency $\eta_{\text{Otto cycle}} = 25 – 38\ \%$

  - In the first stage, a mixture of air fuel is drawn into the cylinder, compressed by a piston and subsequently ignited by an electric spark;
  - Older engines use the carburettor system (the mixture is ready before filling the cylinder);
  - Newer engines use the injection system (fuel injected into the cylinder at the beginning of compression);
  - Excess air coefficient (in relation to stoichiometry) λ = ca. 1 ± 0.1;
  - In most cases, Otto's four-stroke cycle is used;
  - However, there is also a two-cycle cycle, Miller's or Atkinson cycle.

Engines with internal combustion

- Compression-ignition engines

Efficiency η_{Diesel} = 30 – 42 %

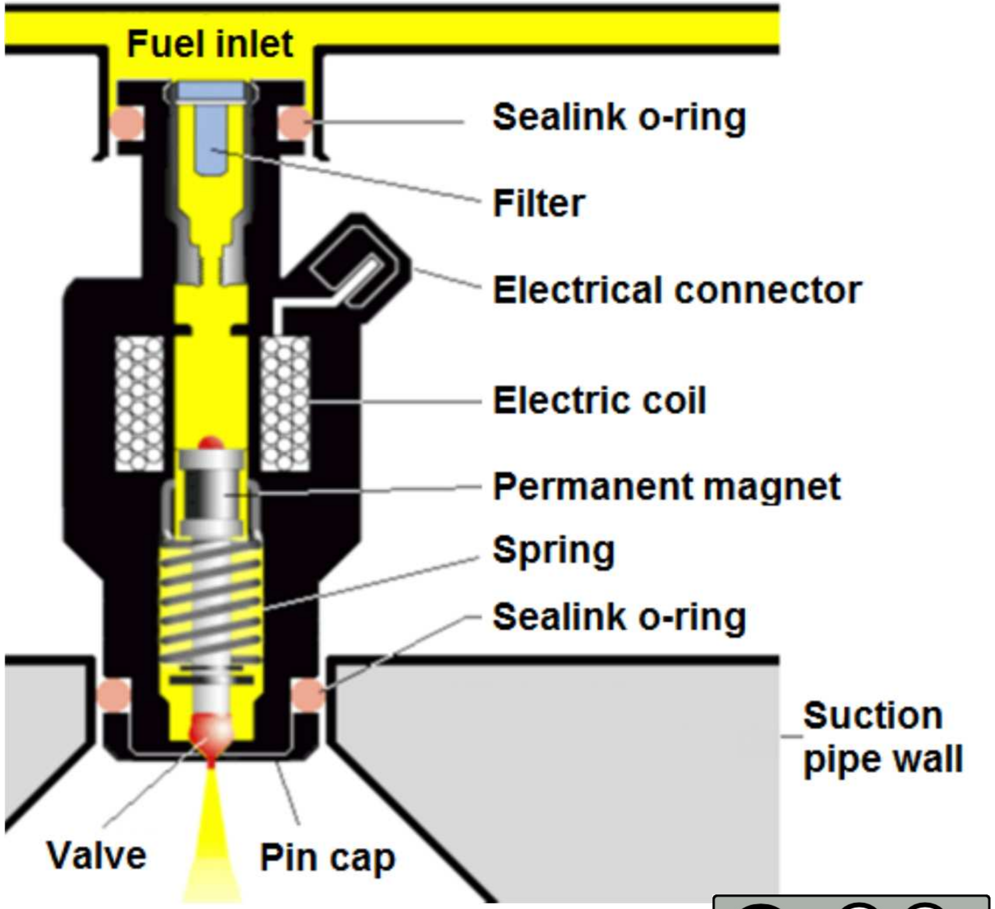
  - In the first phase only the air is fed to the cylinder and after its adiabatic compression to a temperature of 700-900 °C, which is above the flammability limit of the fuel (320-380 °C), the fuel is injected into the cylinder by a high-pressure pump and nozzle.
  - Excess air coefficient (in relation to stoichiometry) λ = ca. 1.3 – 1.4;
  - Excess air coefficient at full load of the turbocharger λ =1.6 – 1.8 and in some cases up to 2.0;
  - Atmospheric engines have low power, turbocharger is the most prevalent:

Measures leading to lower emissions

- Improvements of the engine construction
  - improved preparation of the fuel mixture,
  - improved ignition (longer electrode distance ⇒ longer spark time),
  - exhaust gas recirculation,
  - reduction of tolerances in combustion parts of the engine,
  - introducing the SI engines working with $\lambda > 1 \Rightarrow$ lower C_xH_y and CO,
  - lambda regulation of combustion process (continuous control of fuel / air ratio),
  - control of the mixture motion inside the cylinder,
  - switching off some cylinders,
  - variable valves timing ….. and so on.
- Reducing exhaust emissions already produced
  - Application of catalysts ⇒ destruction of NO_x, CO, C_xH_y
  - Application of filters ⇒ capturing particulate matter

Four stroke SI engines

- System for direct fuel injection
  - Unlike the older carburettor system allows λ-regulation
  - λ-regulation = precise control of the fuel/air ratio
  - λ-regulation is essential condition for function of the three-way catalysts for exhaust gas cleaning



Four stroke SI engines

- The probe detects O_2 in the exhaust gas, the ECU then controls the fuel / air ratio
  - Voltage between the electrodes represents signal from the most common probe type.
  - The signal varies sharply:

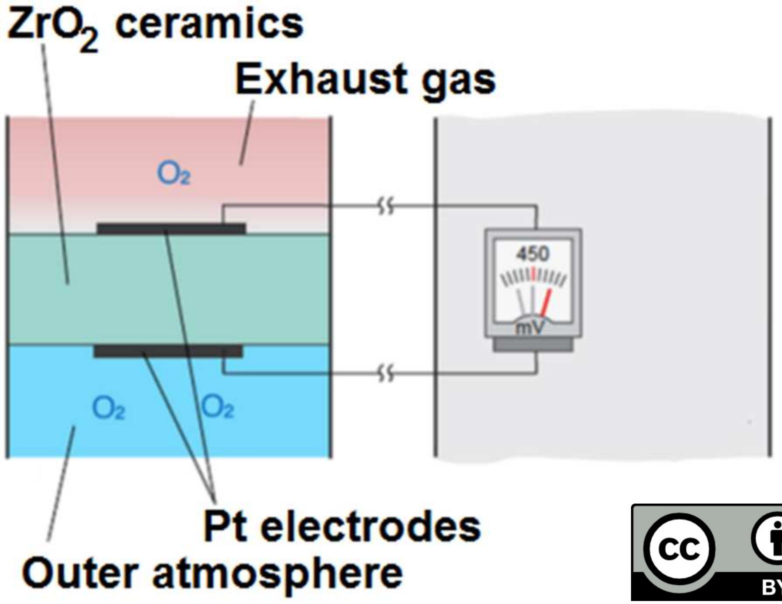
$\lambda > 1$ induces 0,1 - 0,2 V ⇒ prolong injection time

$\lambda = 1$ induces 0,45 V (stoichiometric combustion) ⇒ time okay

$\lambda < 1$ induces 0,7 – 1,0 V ⇒ shorten injection time

Connector incl. internal heating at 350 °C

Source of photo: *http://www.fae.es*



Four stroke SI engines

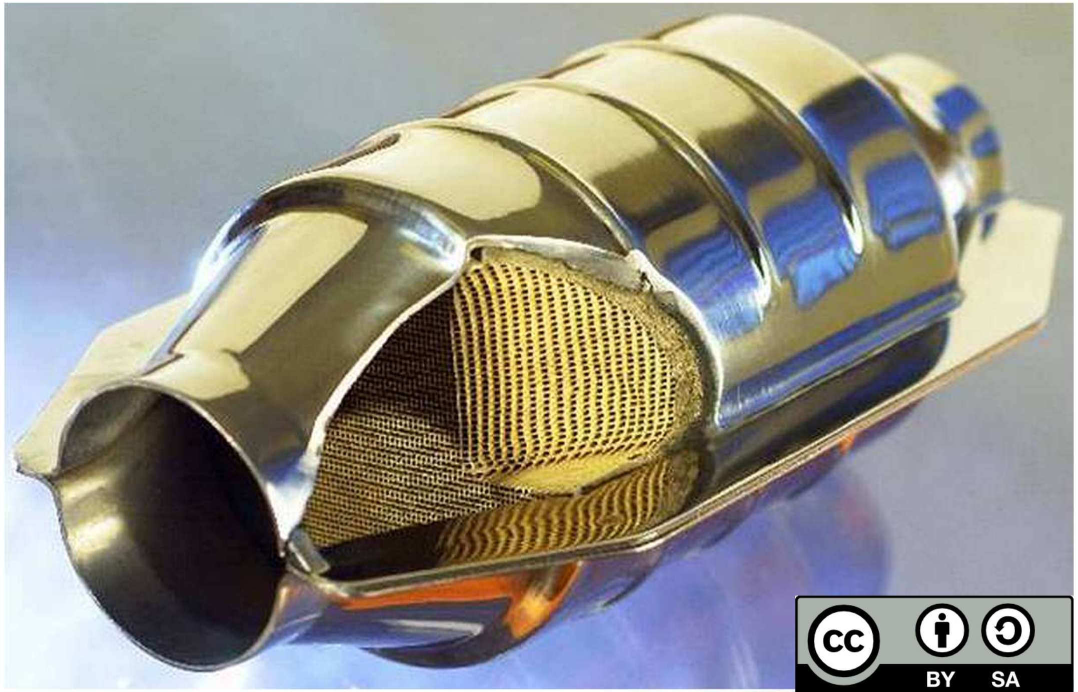
- Three-way catalyst: complete decomposition of C_xH_y, CO and NO_x
  - Usually ceramic carrier with an active ingredient (Pt + Pd + Rh) on the surface
  - Everything mounted inside metal, internally sprung container;
  - Support = ceramic block made of magnesium-aluminium-silicate with a surface layered by Al_2O_3
  - Operational temperatures

    min. 300 °C

    optimum 400 – 800 °C

    risk T < 1 000 °C

    desctruction T > 1 000 °C



Source of photo: *Johnson Matthey*

Four stroke SI engines

- Three-way catalysts
  - Reaction principle:
  - Carbon monoxide and hydrocarbons are oxidized, while nitrogen oxides are reduced.
  - Oxygen for oxidation is taken from nitrogen oxides and not from air (because $\lambda = 1 \pm 0.02$)

$$2CO + O_2 \rightarrow 2CO_2$$

$$C_xH_y + \left(x + \frac{y}{4}\right)O_2 \rightarrow xCO_2 + \frac{y}{2}H_2O$$

$$2NO + 2CO \rightarrow N_2 + 2CO_2$$

$$2NO_2 + 2CO \rightarrow N_2 + 2CO_2 + O_2$$

$$2H_2 + O_2 \rightarrow 2H_2O$$

$$2NO + 2H_2 \rightarrow N_2 + 2H_2O$$

Source: Johnson Matthey

CI diesel engines

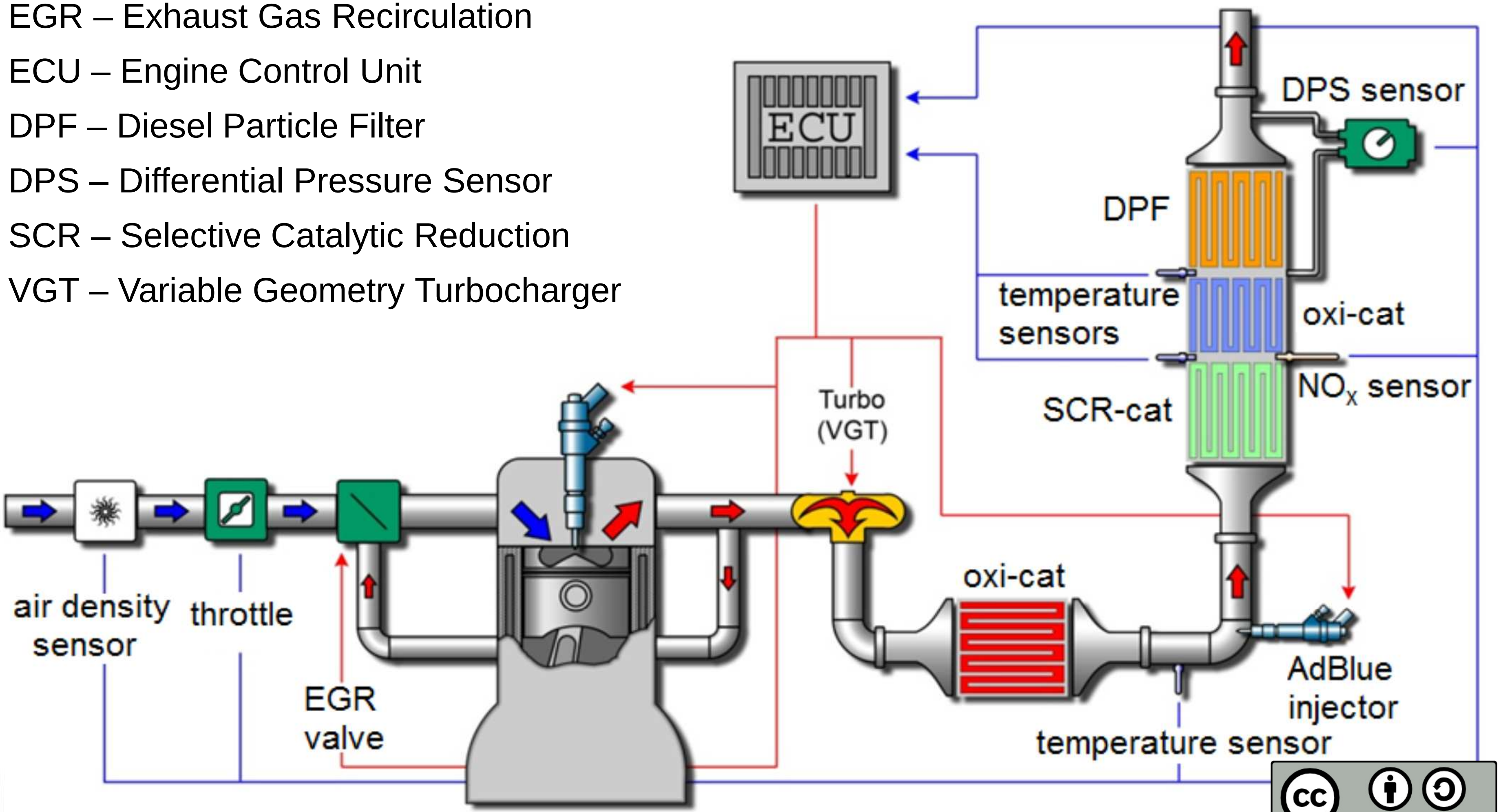
- More complicated system of emission control – due to $\lambda > 1$;
- Instead of a spark ignition engines, NO_x must be reduced by SCR and the solid particles separated by filtration in the DPF filter;
- Principle of SCR (for emission limits Euro IV and higher): reduction via urea injection (so called AUS 32 = 32.5% urea + 67.5% water) with the crystallisation point -11 ℃;
- The urea solution is supplied under the trade name AdBlue.
- For low temperature operation an AdBlue tank with electric heating is needed or solution flow through the engine coolant.
- At the US markets there is compatible solution available with the trade name DEF(Diesel Exhaust Fluid);
- AdBlue is injected before the exhaust gas catalyst (combustion with flue gas followed by decomposition to $NH_3 + CO_2$).

Source: Johnson Matthey

CI diesel engines

- Selective catalytic reduction
  - Current state of diesel engines = nearly mobile chemical factory!

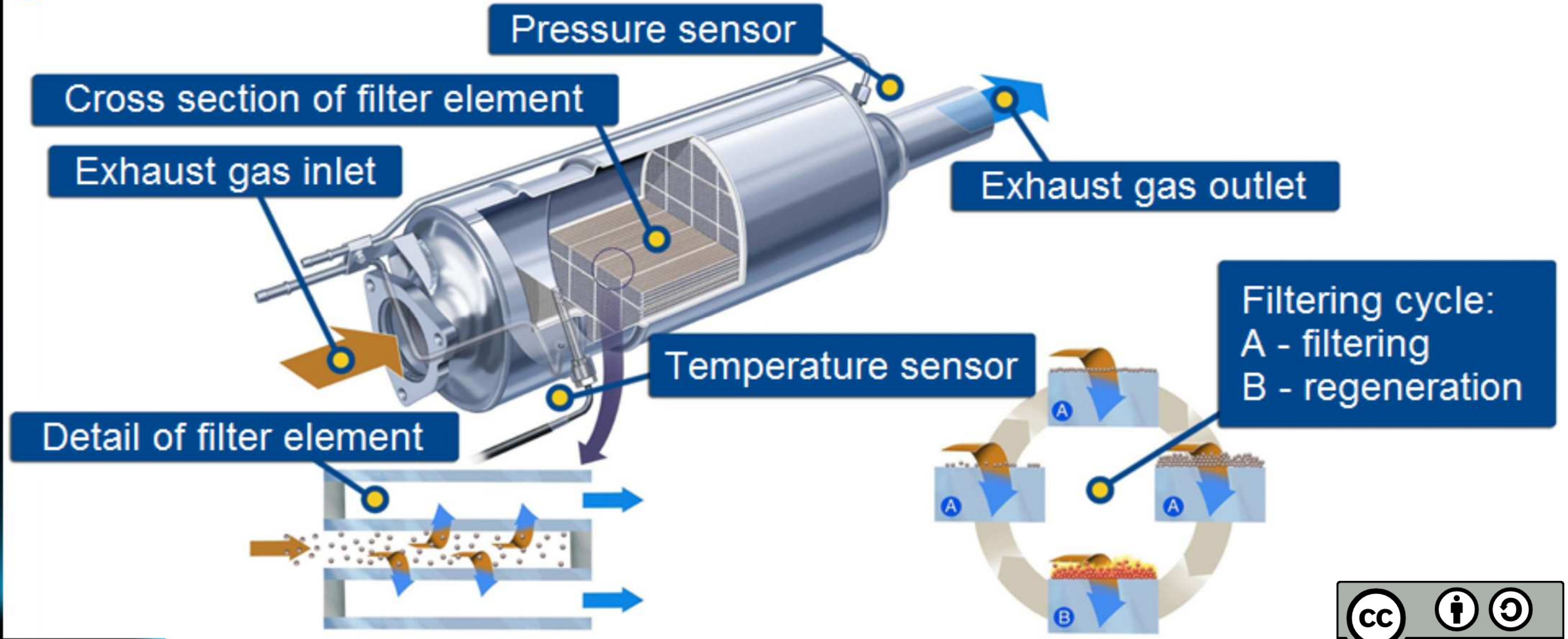
EGR – Exhaust Gas Recirculation
ECU – Engine Control Unit
DPF – Diesel Particle Filter
DPS – Differential Pressure Sensor
SCR – Selective Catalytic Reduction
VGT – Variable Geometry Turbocharger



Source: Motor expert s r.o.

CI diesel engines

- Installation of DPF in new cars mandatory since Euro 5 norm (September 2009)
  - capture carbon black with automatic regeneration each 300-500 km;
  - regeneration by heating to ca. 600 °C with subsequent soot burnout;
  - heating by fuel injection into cylinders with opened exhaust valves;



Source: www.motoringassist.com

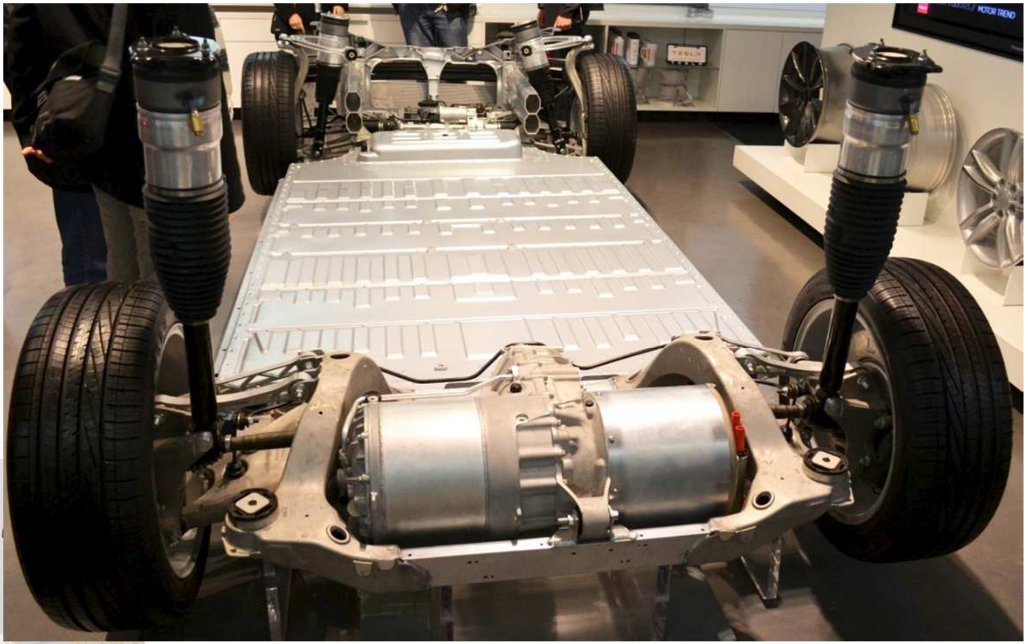
Biofuel or food production?

- Biofuel production (FAME by transesterification or ethanol by fermentation and subsequent distillation): 82.3 million tons of oil equivalent per year
  - Ethanol production: corn, grain, potatoes, sugar cane and sugar beet;
  - Production of FAME: soybean oil, palm oil, sunflower oil or rape seed oil.
- Food production:
  - world population 7.58 billion
  - ca. 815 mil. people suffering with leak of food (UN, 2016)

Source: eurostat

Electric cars – promising way?

- At present – two possible solutions
  - Direct drive system (without gearbox)
Frequently the chassis on the frame



  - Similar to classic car
Self-supporting body
Engine with gearbox (automatic)

Sources: http://d2ojs0xoob7fg0.cloudfront.net/evtv-word-press/wp-content/uploads/2014/07/Tesla_Motors_Model_S_base.jpg, https://auto.idnes.cz/foto.aspx?r=auto_testy&c=A130506_143517_auto_testy_fdv&foto=FDV4b12ef__DLS8134.jpg

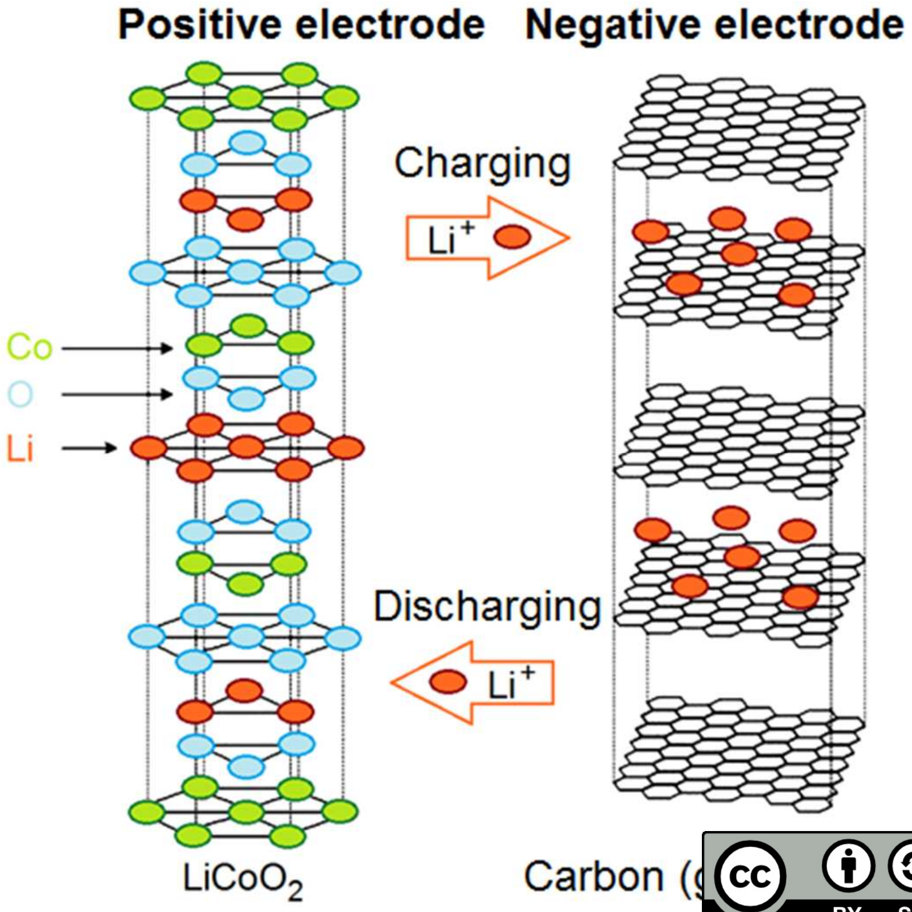
Lithium-ion accumulators

- Principle of their function
  - Transport of Li ions
  - Cathode on the basis of oxides:

$LiCoO_2$, $Li_xMn_2O_4$, $LiNiO_2$, LiV_2O_5 etc.

  - Graphite anode
  - Electrolyte liquid, gel or polymer
  - The most widespread liquid electrolyte: lithium-hexafluorophosphate in solvents ethylen carbonate

+ dimethyl carbonate and so on



Sources: http://oze.tzb-info.cz/akumulace-elektriny/13612-lithiove-akumulatory