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Development and Education

MSMT
MINISTRY OF EDUCATION,
YOUTH AND SPORTS



ATMOSPHERIC CHEMISTRY

Lecture No.: 7

Organisation of study

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e-learning:
<https://e-learning.vscht.cz/course/view.php?id=106>
- Scale of subject: winter semester
14 lectures, 14 weeks, 2 hours/week
- Classification: Exam - written + oral form (depending on result of the test)

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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 obraťte 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

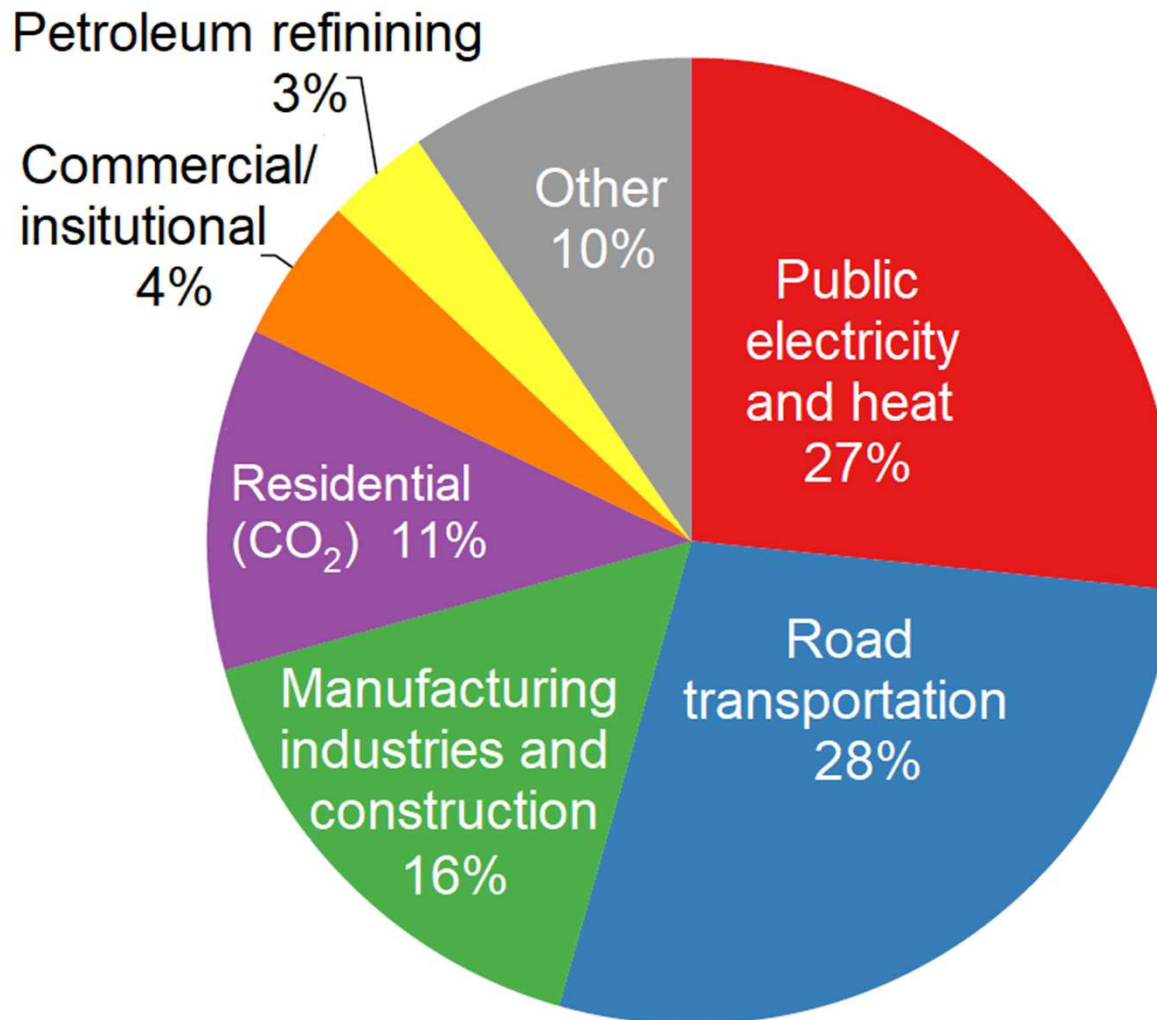
- Power industry as the main source of carbon dioxide emissions
- Relationship between atmospheric concentration of CO₂ and global temperatures – difficulty in their future projections
- Sources of hydrocarbon emissions, particularly methane
- Mechanism of atmospheric decomposition of methane
- Mechanism 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 N₂O

Environmental issues of GHG

- **Sector Energy: Share of largest key source categories in the EU in 2021**

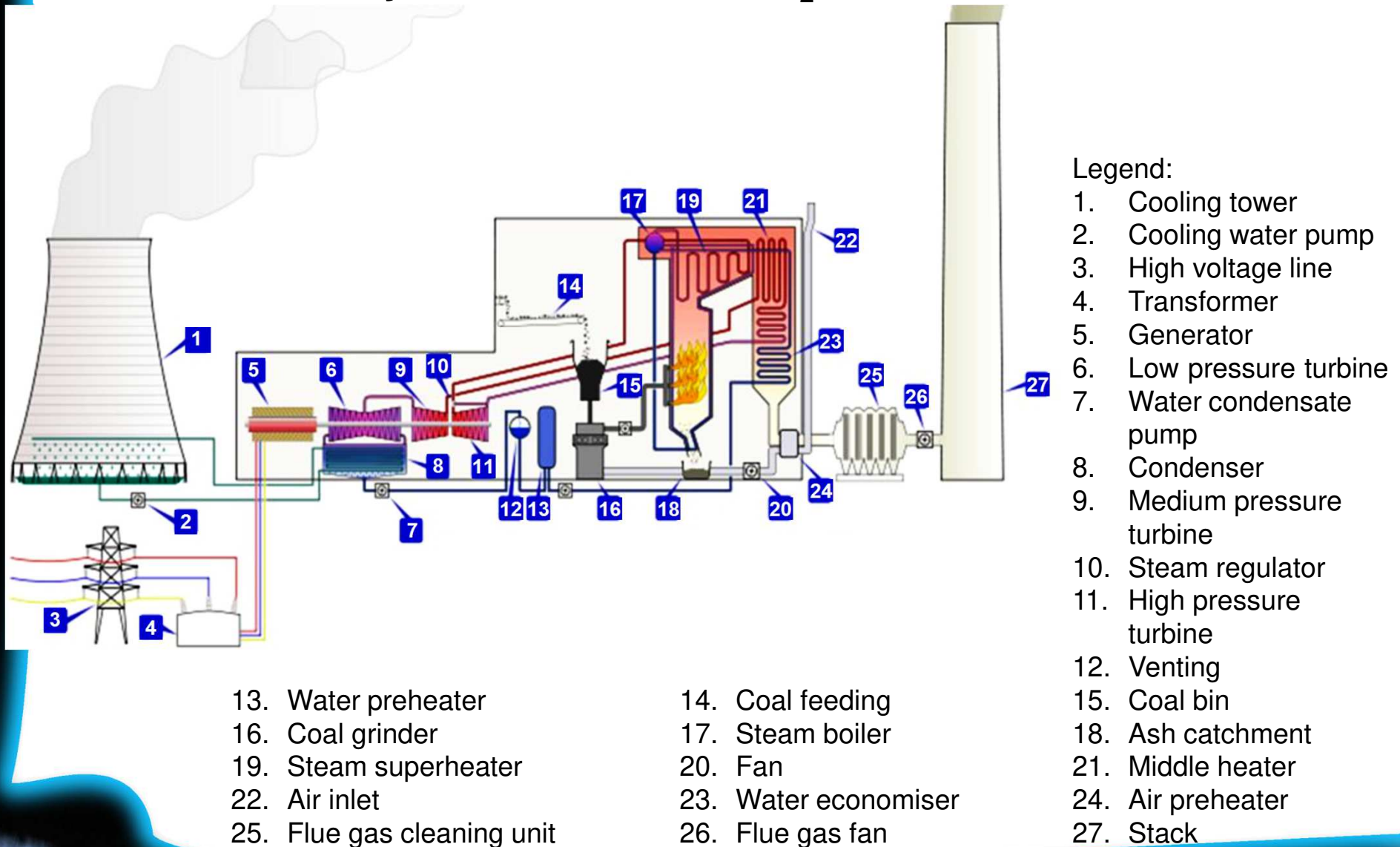


United Nations
Climate Change



Environmental issues of CO₂

- Power industry – main source of CO₂ (Source: <http://slideplayer.cz/slide/3668959/>)



Environmental issues of CO₂

■ Relation between power industry and emissions of CO₂

(Source: Gomes; Carbon Dioxide Capture and Sequestration)

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

Population by 250 %

Energy consumption by 915 %

Content of CO₂ in the air 295 (1900)

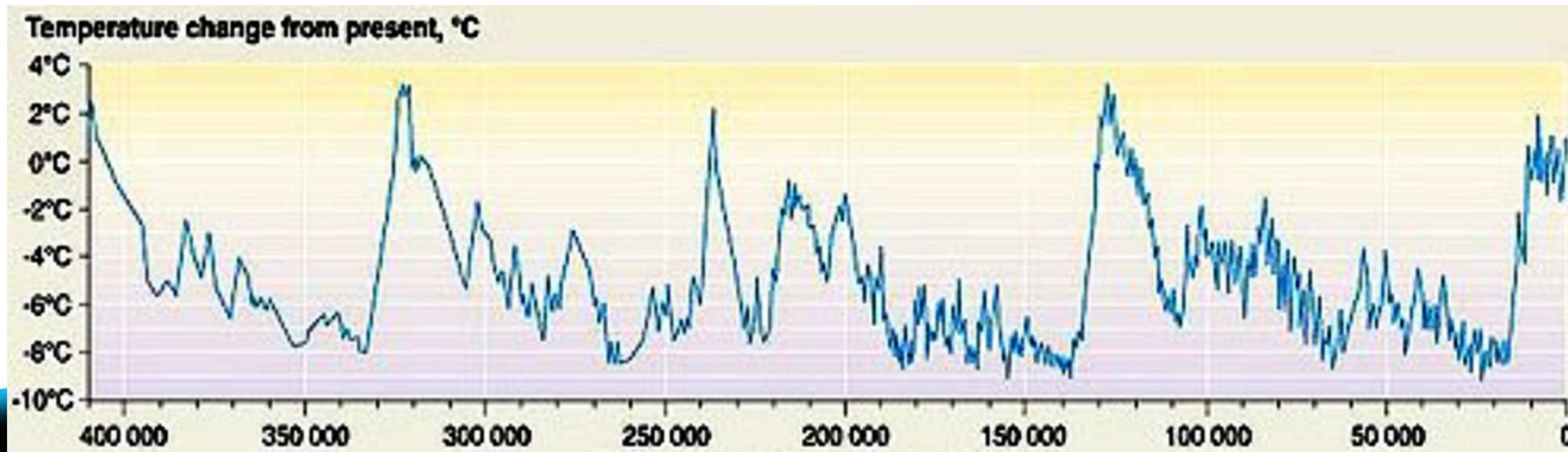
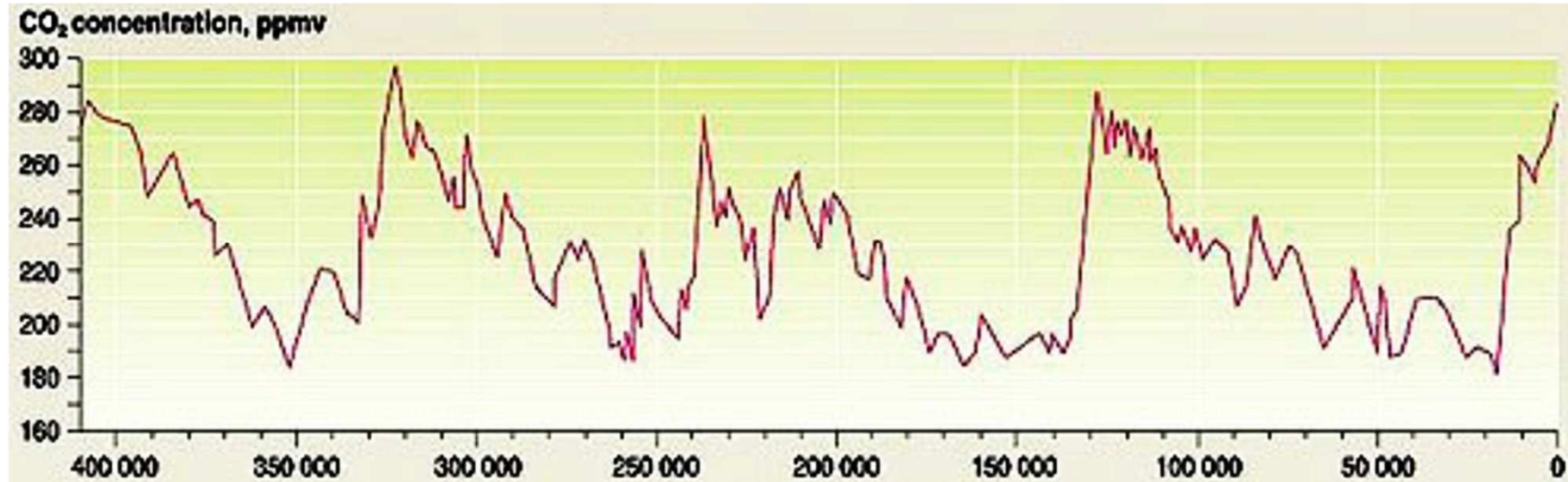
→ 315 (1960)

→ 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 CO₂ (values before 1960 only based on ice core analyses);
- Since 1850, gradual increase of worldwide average temperature with accelerating trend since 1970;
- Causes not proven till present ⇒ disputes still remain;

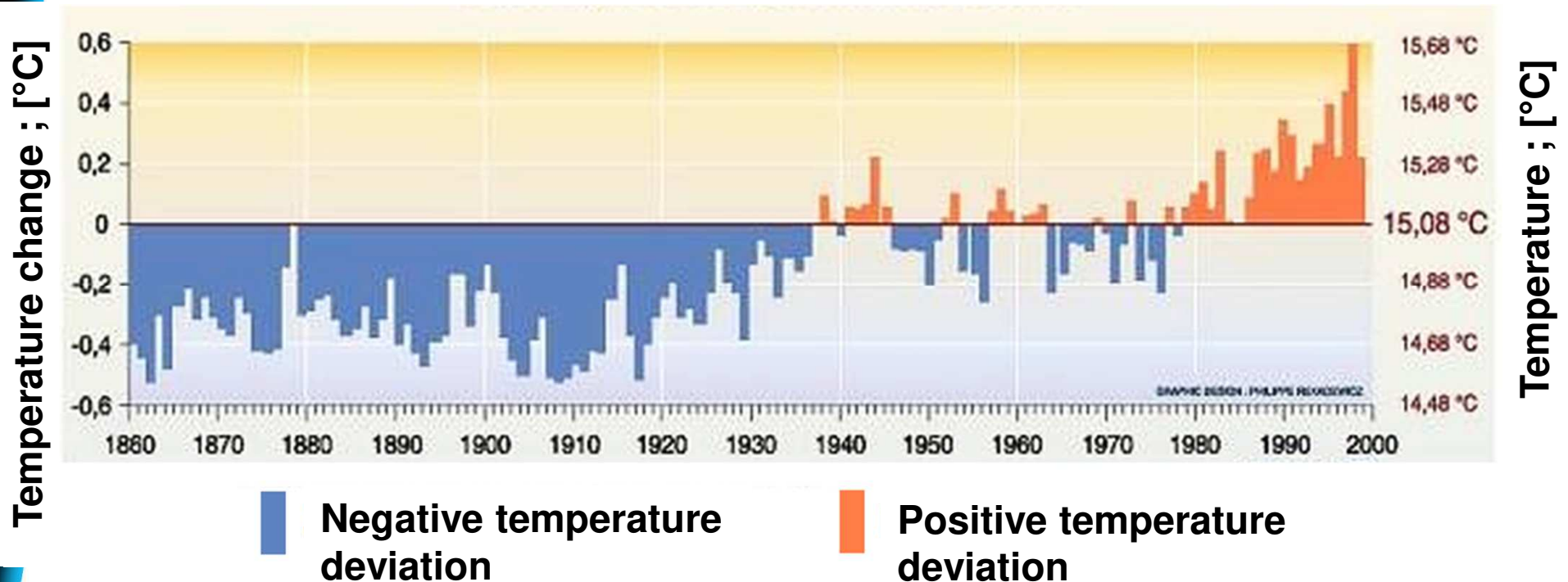
Environmental issues of CO₂

- **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



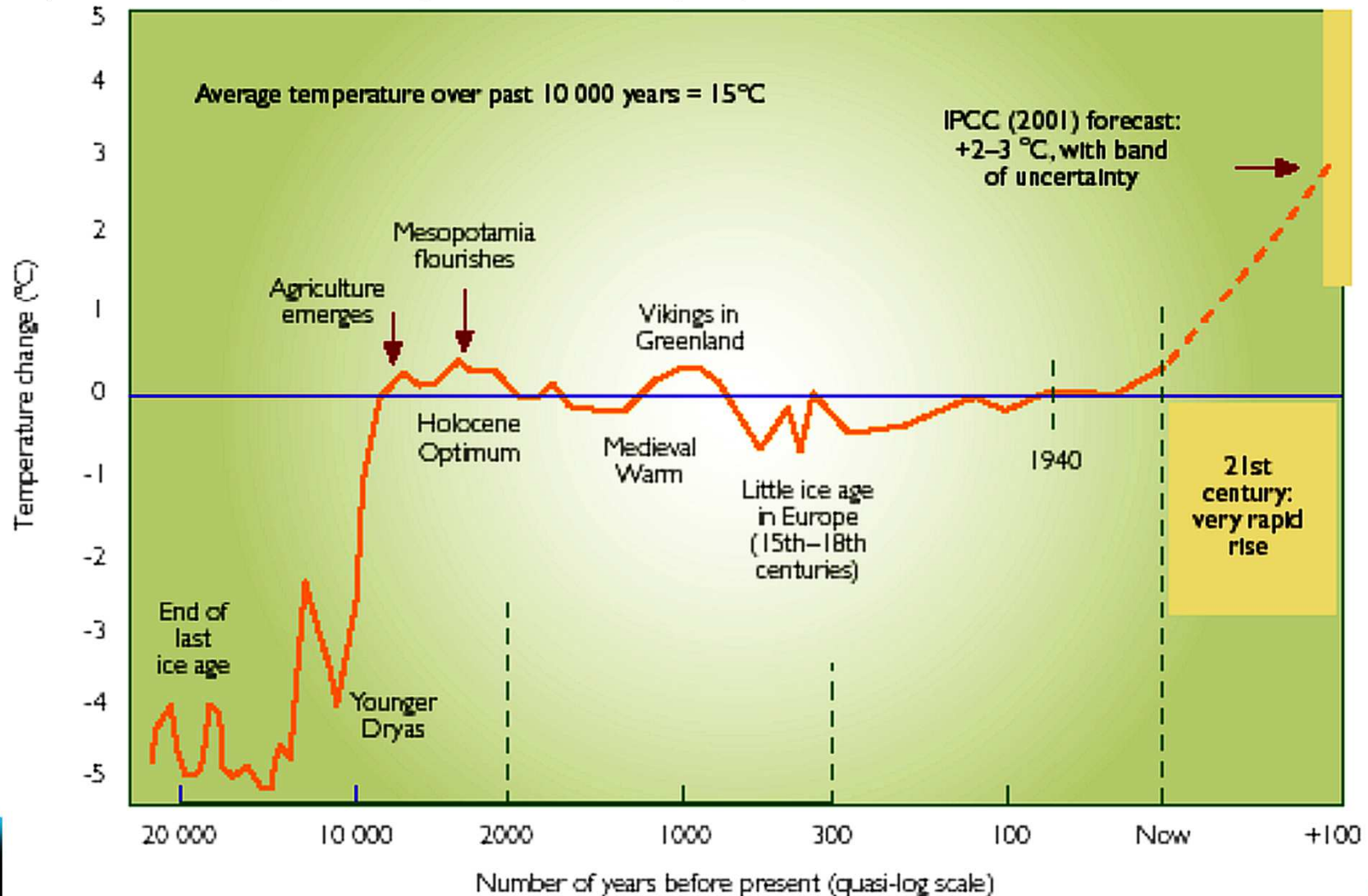
Environmental issues of CO₂

- 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)



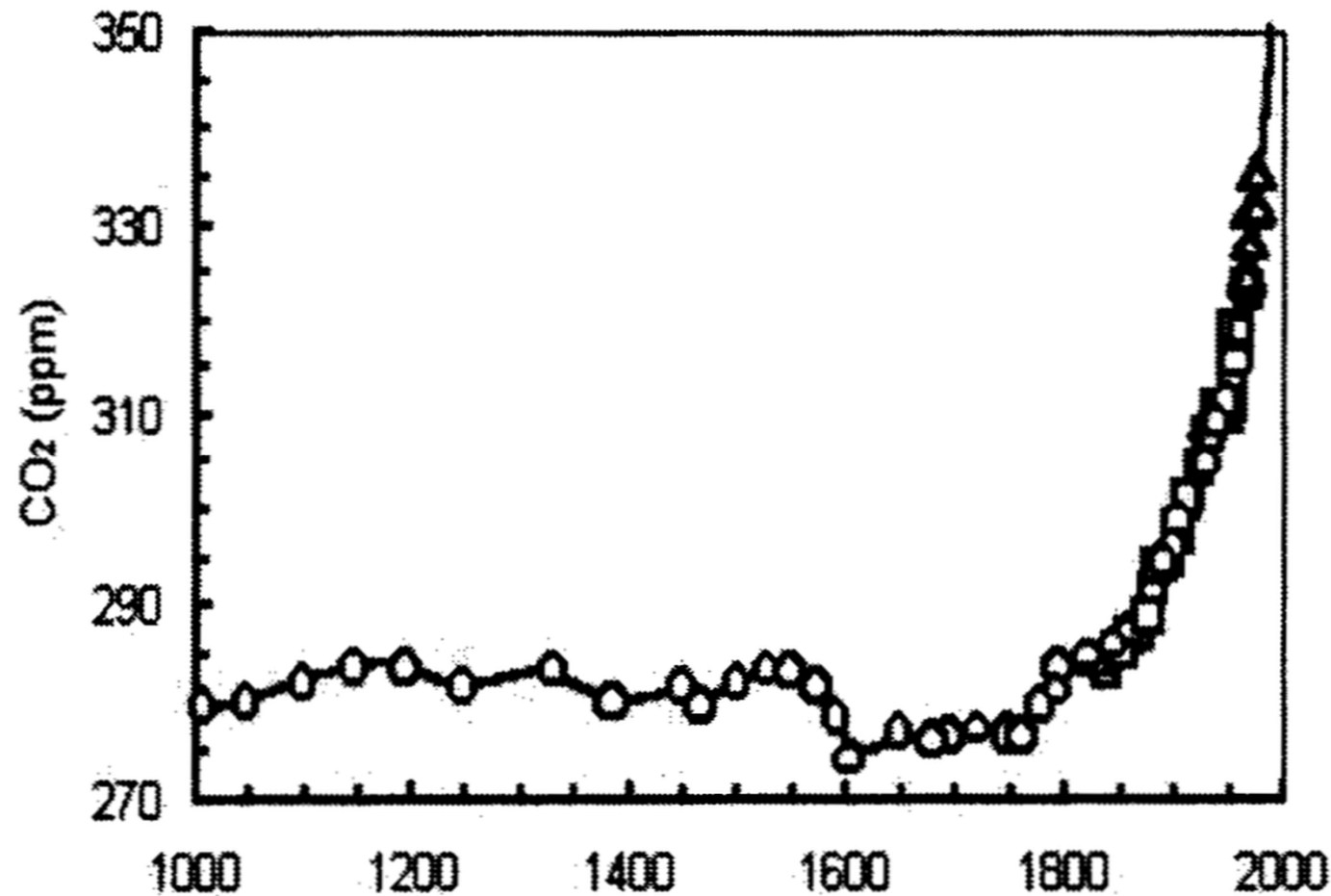
Environmental issues of CO₂

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



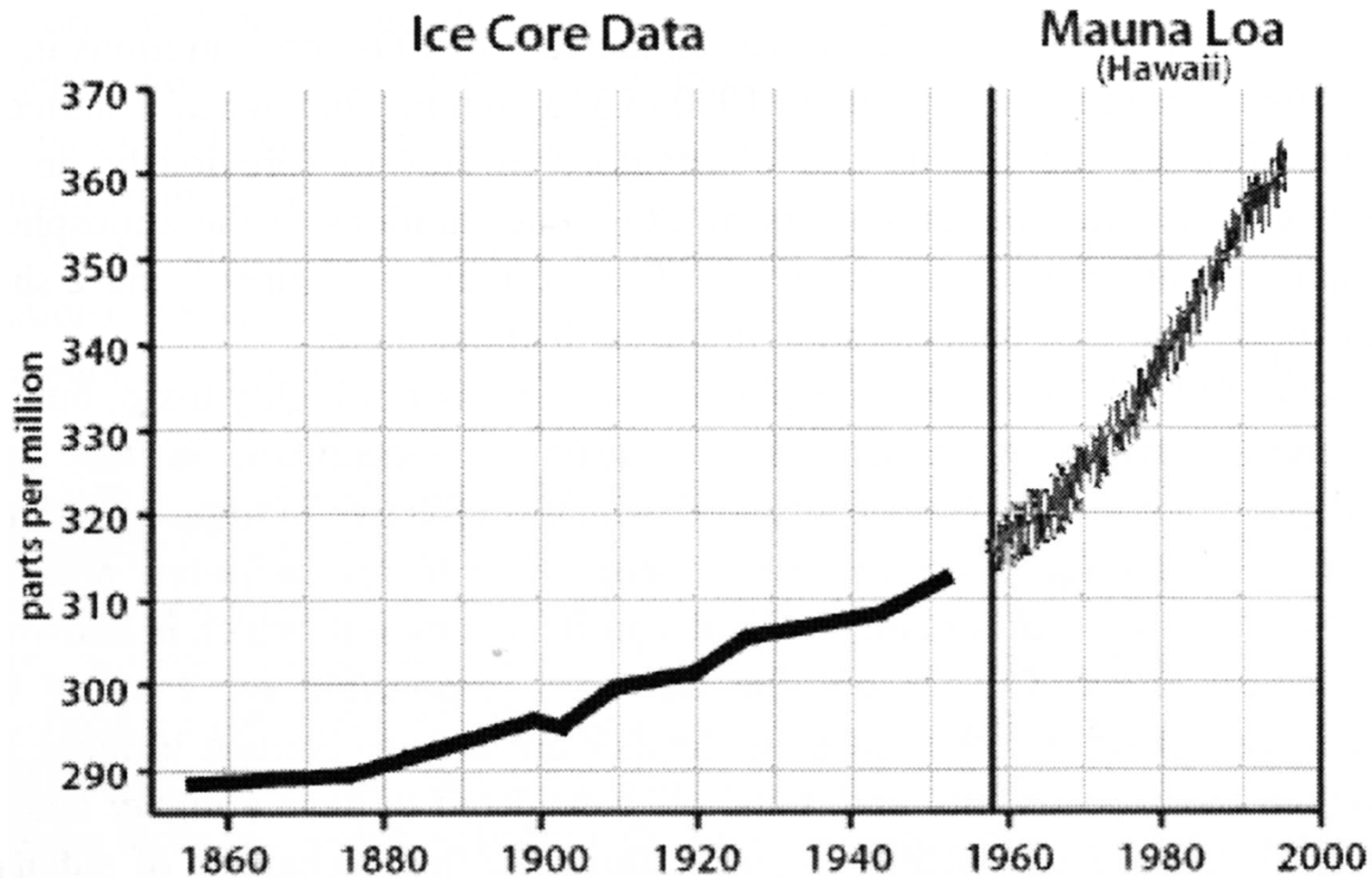
Environmental issues of CO₂

- **Historical variations of CO₂ content in atmosphere** (Source: Gomes; Carbon Dioxide Capture and Sequestration)



Environmental issues of CO₂

- **Historical variations of CO₂ content in atmosphere** (Source: Gomes; Carbon Dioxide Capture and Sequestration)



Environmental issues of CO₂

■ Anthropogenic emissions and retention of CO₂

(Source: Gomes; Carbon Dioxide Capture and Sequestration)

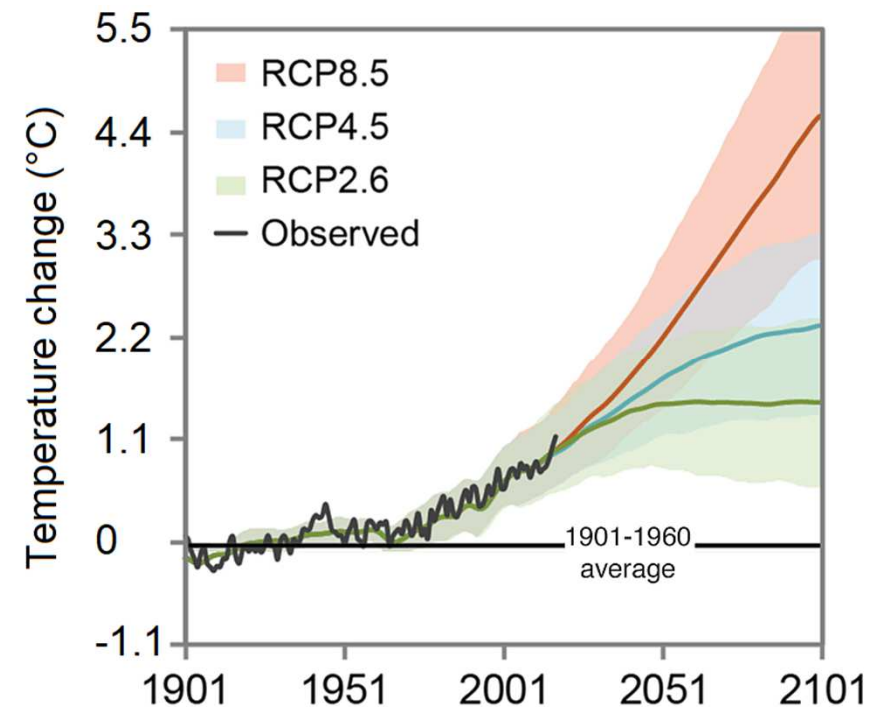
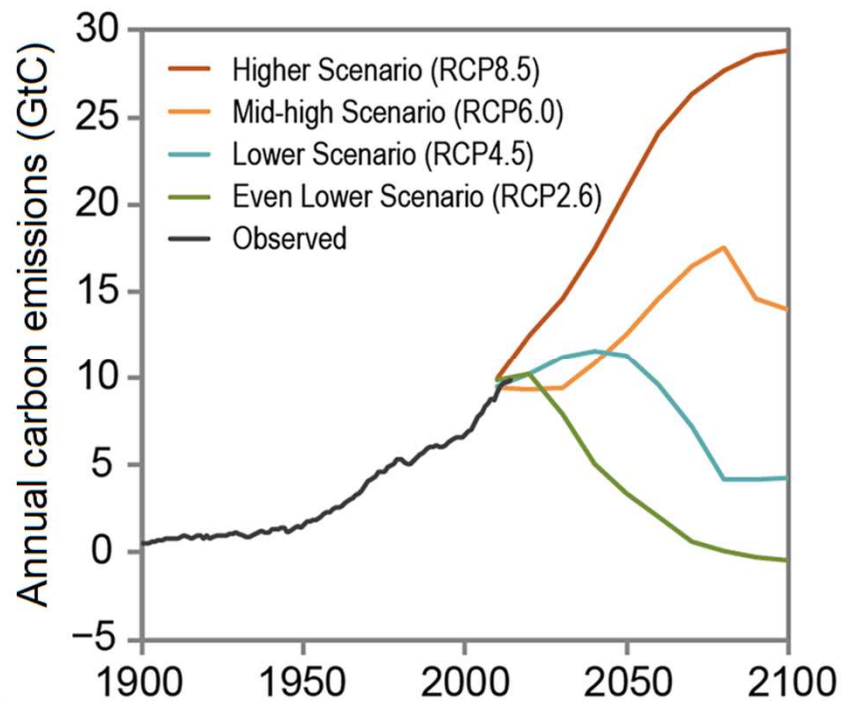
– Climate theory:

- Balance between UV and visible radiation absorbed by the planet and reflection of infrared radiation into space;
- Among all factors, examined in the period of rising temperatures, only atmospheric CO₂ concentration was changing.

- The rise of CO₂ concentration in the atmosphere corresponds to only 55 % of total anthropogenic emissions ⇒ Natural mechanisms are still able to absorb 45 - 50% of the CO₂ produced by human activities.
- Retention capacity of the oceans is about 1.7 Gt (CO₂)/year (in total retained about 38,000 Gt (CO₂));
- Retention capacity of the forests is around 1.4 Gt (CO₂)/year;
- Based on that, scenarios of temp. variations have been prepared.

Global temperature scenarios

- According to authorities (U.S. Global Change Research Program)
- Calculation based on hypothetical pathways of global C emissions
 - called representative concentration pathways (RCP)
 - The dispersion of values in each scenario depends, among other things, on the change in the amount of aerosol in the air.



Environmental issues of CH₄

- Basic characteristic of methane (Source: <http://www.irz.cz/repository/latky/methan.pdf>)
 - Boiling point at normal pressure -161°C;
 - Density under 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 organic compounds, e.g. biogas from moorlands;
 - Product of digestive activity of animals;
 - Share of biological CH₄ emissions in total: 80 %;
 - Ratio between anthropogenic and natural emissions:
 - Anthropogenic: 60 %
 - Natural: 40 % (½ are wetlands)

Environmental issues of CH₄

- 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 CH₄

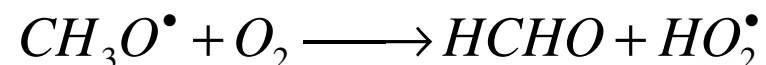
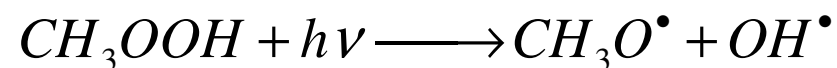
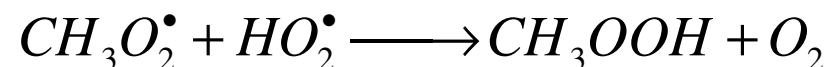
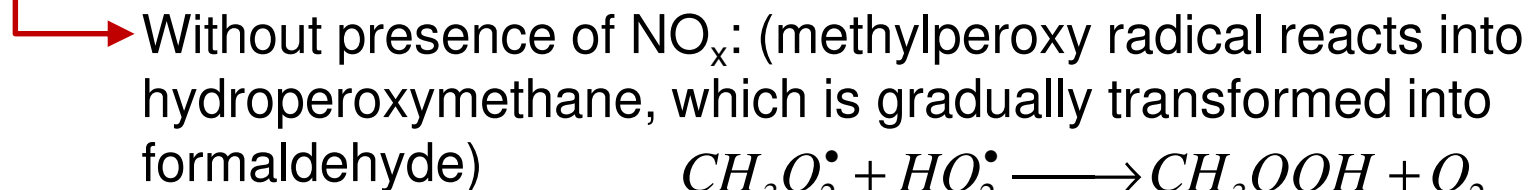
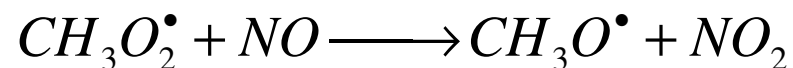
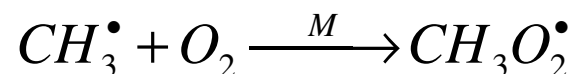
- Anthropogenic sources of methane
(Source: <http://www.irz.cz/repository/latky/methan.pdf>)
- Share of methane from mining and distribution of natural gas:
 - Emissions due to leakage from natural gas processing facilities, transportation and distribution pipelines < 1 % of total anthropogenic emission ⇒ **negligible importance!**



Environmental issues of CH₄

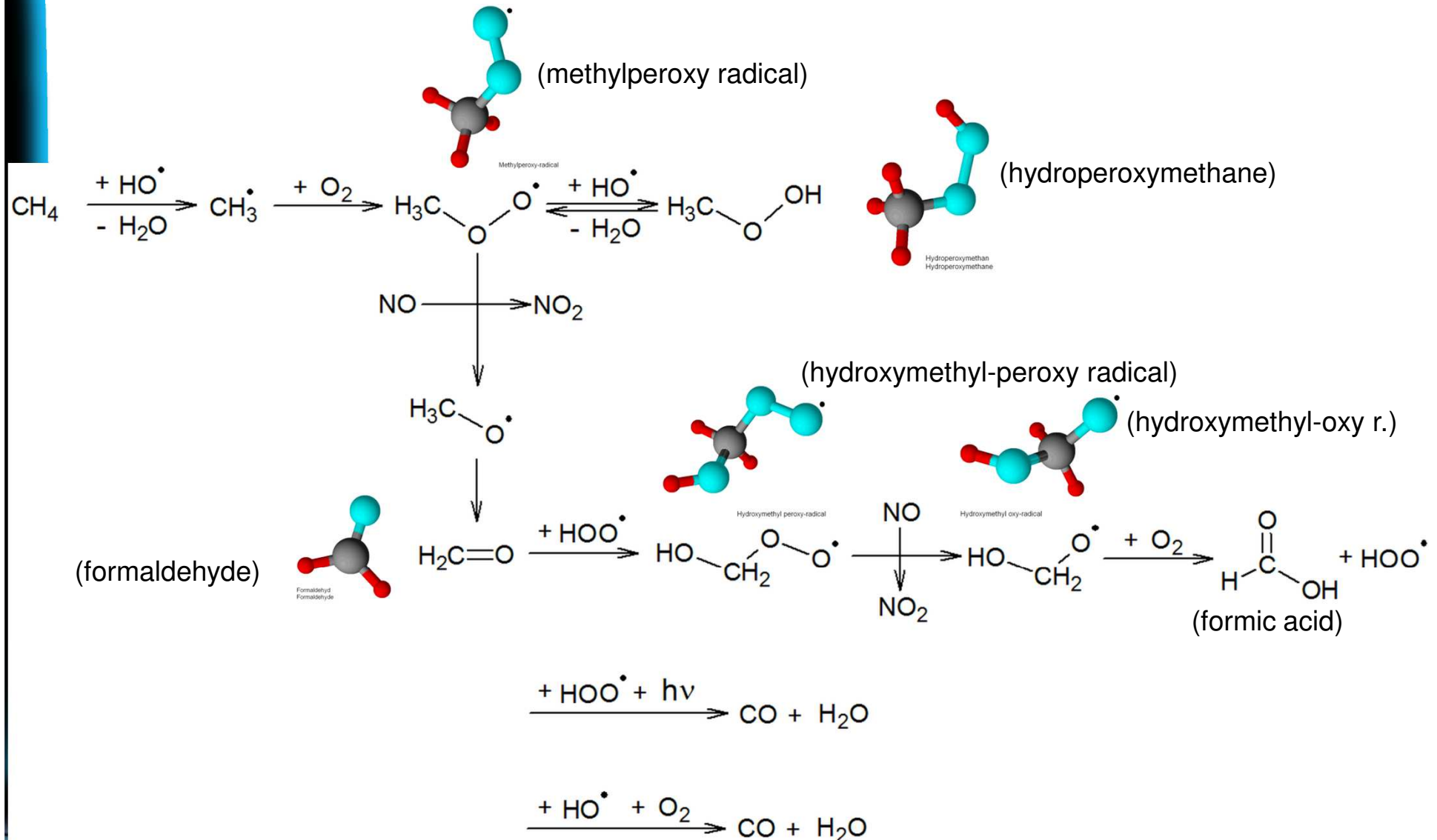
- Lifetime and decay of CH₄ in air (Source: <http://www.irz.cz/repository/latky/methan.pdf>)
 - Lifetime of methane in atmosphere ca. 12 – 17 years;
 - Main mechanism of its decay in **lower troposphere** – **reaction with hydroxyl radical** into CO₂ by means of numerous reactions: (share of this mechanism 91 %)

2 possibilities of the course of initial phase:



Environmental issues of CH₄

- Other transformations of CH₄ (Source: <http://www.irz.cz/repository/latky/methan.pdf>)



Environmental issues of CH₄

- Lifetime and decay of CH₄ in the air (Source: <http://www.irz.cz/repository/latky/methan.pdf>)
 - Reaction with OH• in **stratosphere** plays a minor 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 400,000 years;
 - In 1750 concentration ca. $7 \cdot 10^{-8}$ % vol.;
 - In 1998 $17,45 \cdot 10^{-8}$ % vol.;
 - Between 1999 – 2002, stagnation of the concentration rise at about $17,51 \cdot 10^{-8}$ % vol.
 - After this plateau, the concentration increase started again;

Environmental issues of C_xH_y

- Transformation of higher alkanes
 - Reaction with hydroxyl radical (HO^\bullet) – Fundamental atmospheric oxidation process;
 - The mechanism includes the following steps:
 - Attacking random H in the hydrocarbon chain
 - Oxygen addition onto formed alkyl-radical → creation of alkylperoxyl radical
 - Reaction of alkylperoxyl radical with NO
 - Oxidation of NO → NO_2 and reduction of alkylperoxyl radical into alkyloxy radical
 - or
 - Formation of alkyl nitrate

The ratio of the last two mechanisms grows together with the number of C atoms in the initial hydrocarbon chain in favour of alkyl nitrate.

Environmental issues of C_xH_y

■ Transformation of alkenes

– Due to double bonds, they also react 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 in the hydrocarbon chain (same mechanism as for alkanes):

– Creation of alkyl radical

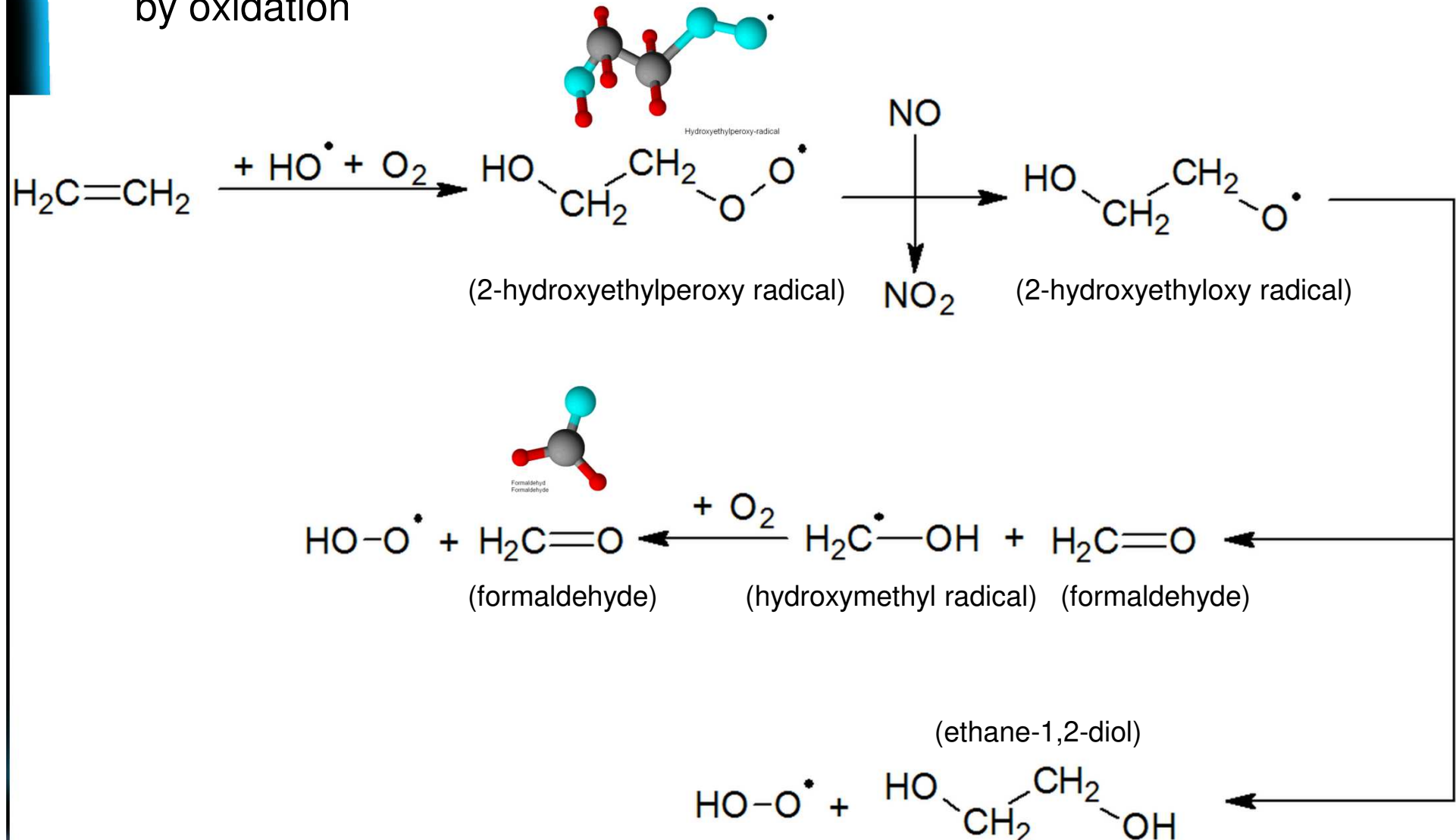
– Addition of oxygen to form alkylperoxyl radical with subsequent reaction with NO:

→ Oxidation of NO \rightarrow NO_2 and reduction of alkylperoxyl radical into alkyloxy radical

→ Or creation of alkyl nitrate

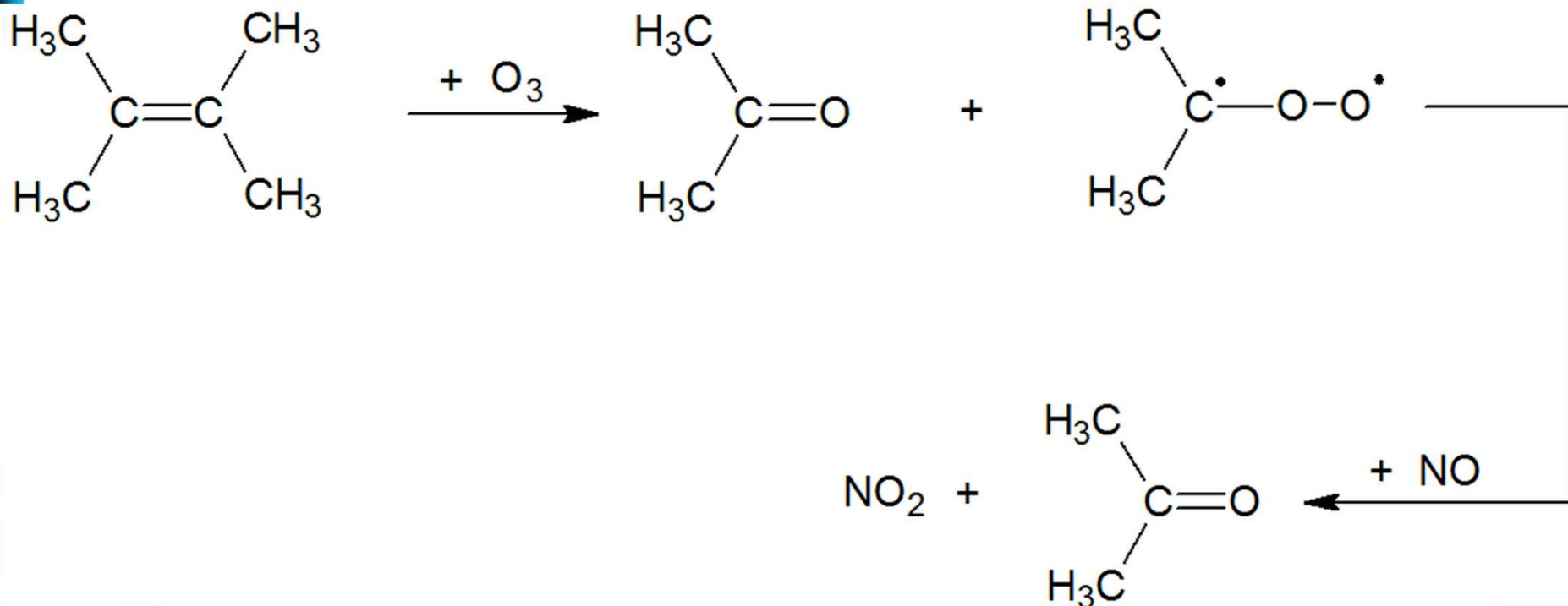
Environmental issues of C_xH_y

- Transformation of alkenes – Addition of HO• onto double bond, followed by oxidation



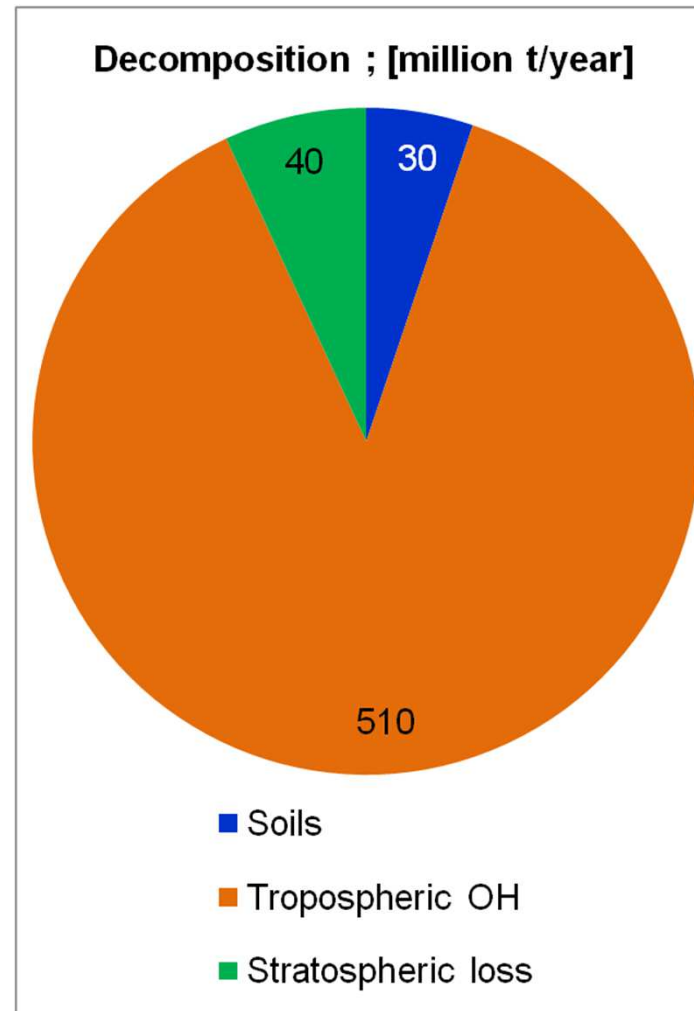
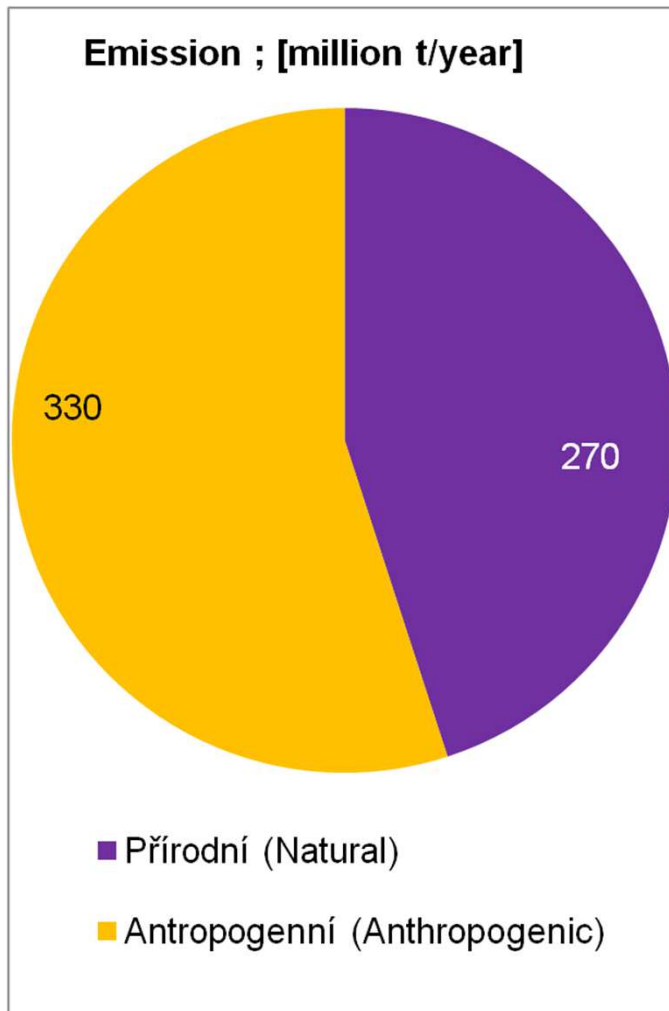
Environmental issues of C_xH_y

- Transformation of alkenes – reaction with $O_3 \rightarrow$ Crieg radicals
 - Crieg alkylperoxyl biradicals – strongly oxidative \Rightarrow 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 CH₄

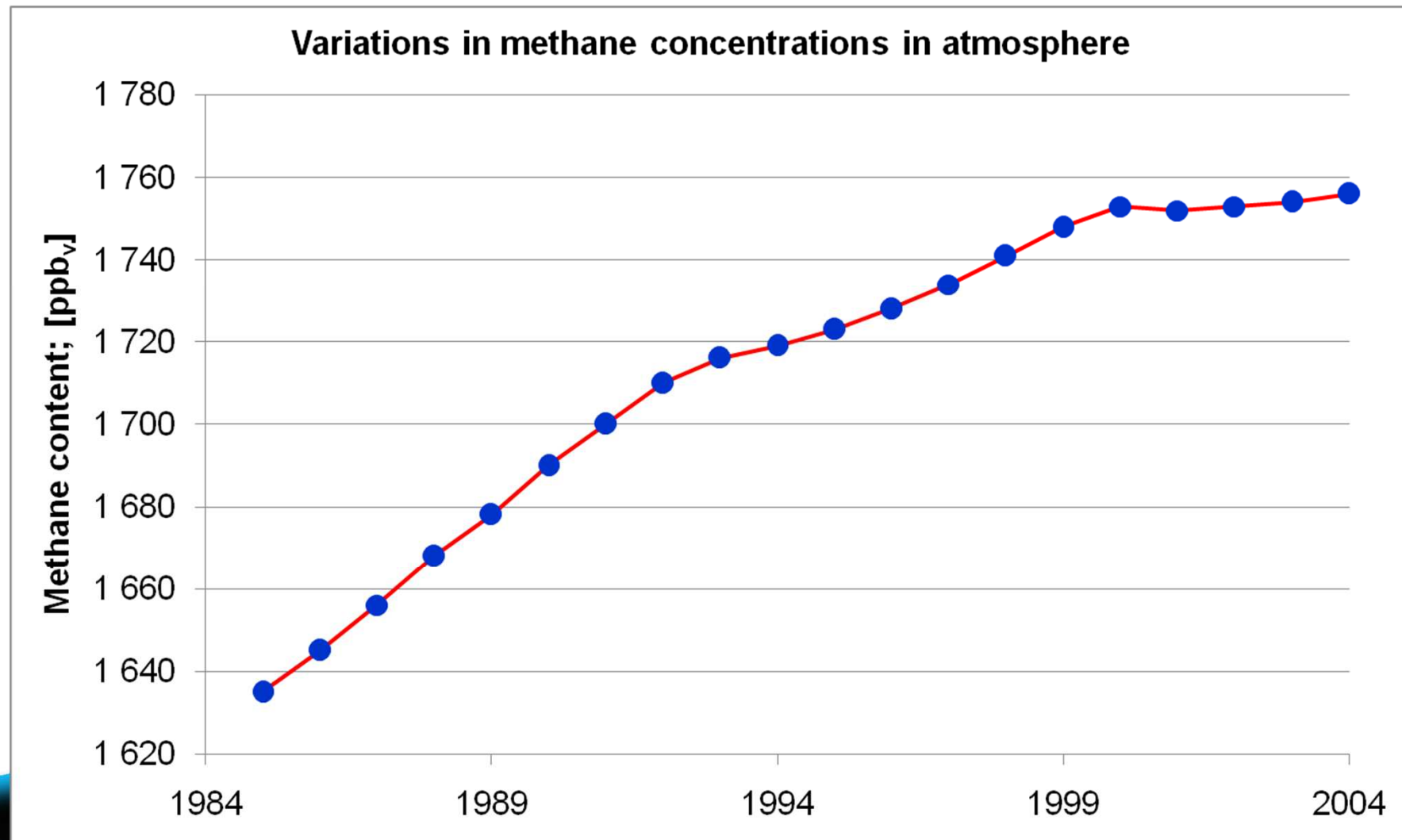
- Ratio between emission and decay of CH₄
(Source: <http://www.irz.cz/repository/latky/methan.pdf>)



Overall misbalance + 20 mil. t/year

Environmental issues of CH₄

- Changes in atmospheric concentration of methane between 1984 - 2004
(Source: <http://www.irz.cz/repository/latky/methan.pdf>)



Environmental issues of N₂O

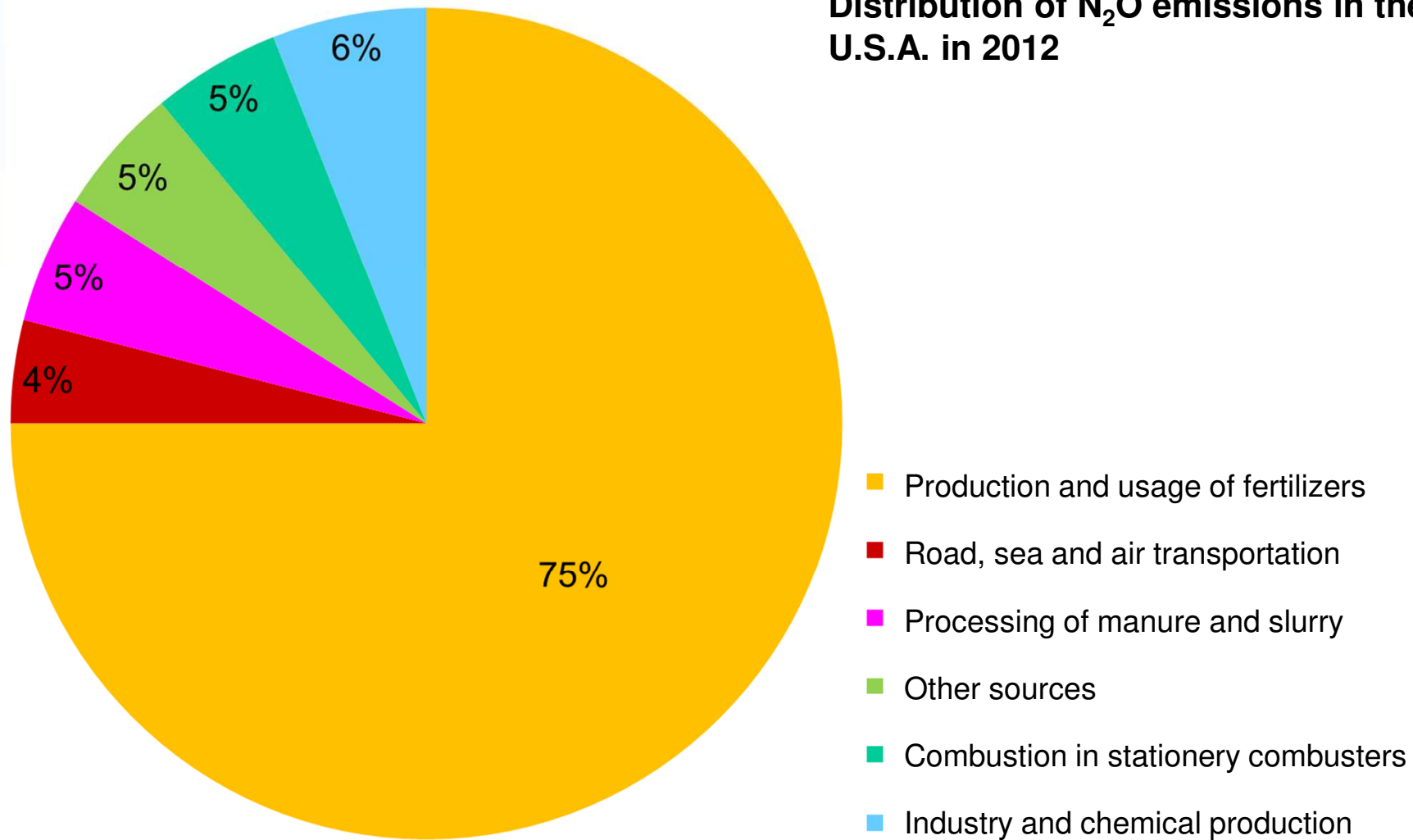
- Nitrous oxide is a member of the group of nitrogen oxides: nitrogen monoxide NO, dioxide NO₂, azoxide N₂O, N₂O₃ and N₂O₅;
- **Formation of N₂O** (Source: IPCC)
 - N₂O is created in the initial phase of combustion at lower temperatures;
 - Content in flue gas is ca. by two orders lower than thermal NO (NO up to 0.3 % vol.; N₂O max. 3·10⁻⁶ % vol.)
In fluidized bed combustors significantly higher N₂O concentrations - max. 2·10⁻⁴ % vol.;
 - It is an important greenhouse gas;
 - Average lifetime in atmosphere is 114 years;
 - GWP of nitrous oxide:
 - according to EEA formerly published GWP(N₂O) = 298
 - according to US EPA 310
 - presently EU ETS in conformity with EPA 310;

Environmental issues of N₂O

- **Formation of N₂O** (Source: EPA)
 - 40 % of N₂O 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: HNO₃ included above among synthetic fertilizers);
 - Natural emissions of N₂O: bacterial decomposition of nitrogen based compounds in soil and oceans;
 - Natural decomposition of released N₂O: metabolised by some species of specialized bacteria, photochemical decomposition under UV radiation.

Environmental issues of N₂O

■ Formation of N₂O (Source: EPA)



Environmental issues of N₂O

- Formation of N₂O beyond combustion processes (Source: W.C.Heraeus, GmbH)
- Production of nitric acid and subsequent products ⇒ the biggest source of nitrous oxide emissions;
- Problematics of HNO₃ production;
 - In the world, there are continuously (not by fits and starts) operated:
 - 600 nitric acid production units
 - Overall N₂O emission estimated at 1.2·10⁶ t/year
 - With GWP 310 times higher than CO₂ ⇒ comparable with operation of 80·10⁶ personal cars!

Environmental issues of N₂O

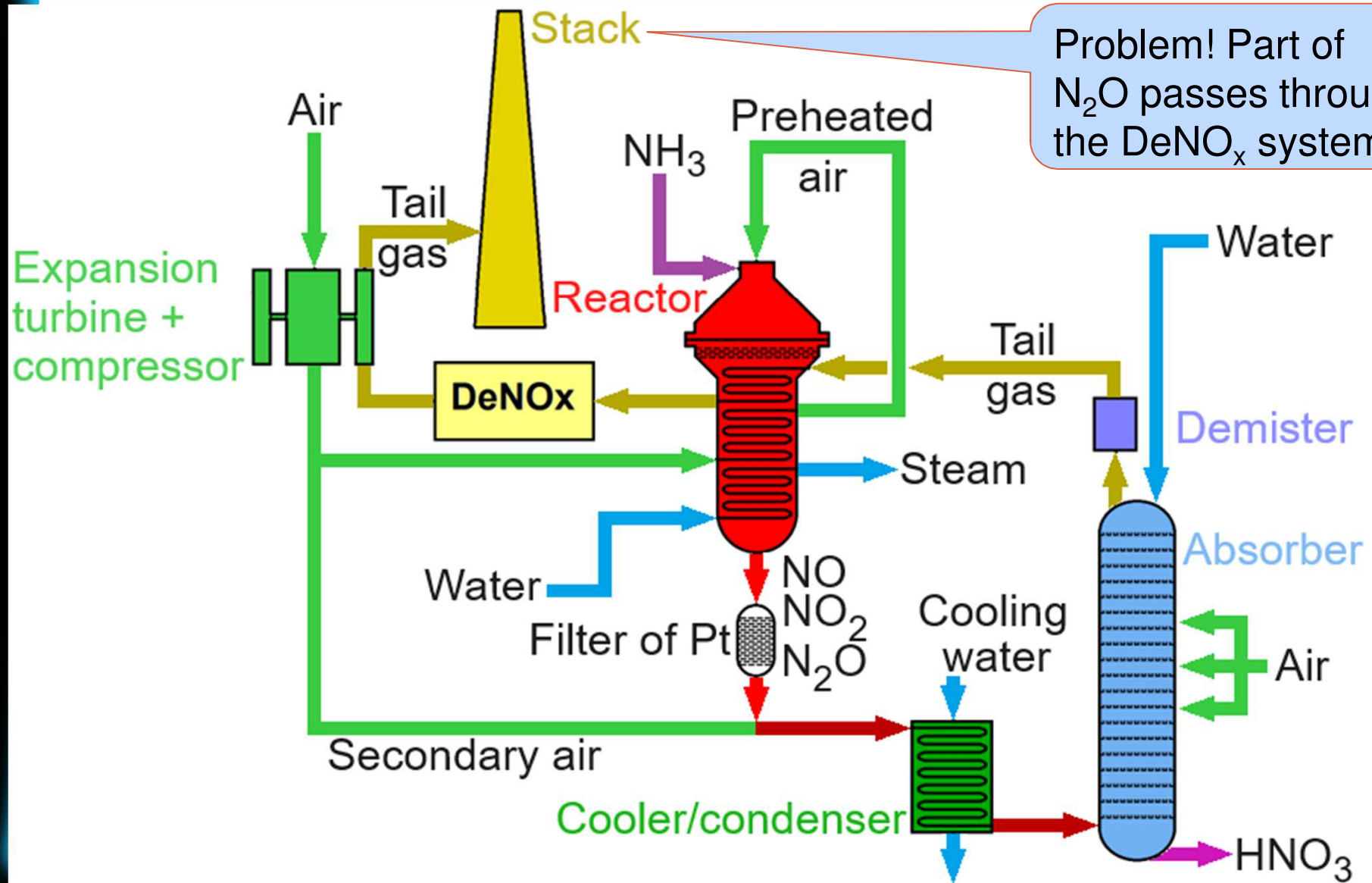
■ Principle of nitric acid manufacture

- Incineration of ammonia-air mixture at higher pressure on Platinum catalyst;
- Released heat is utilised in the production of process steam in boiler;
- Subsequent absorption of NO₂ in demineralised water (counterflow absorber);
- Overpressure released by two ways: older installations have a gas turbine for common incineration with methane, recent installations are equipped with an expansion turbine;
- Possibility of optional installation of 3 levels of catalysts:
 - Primary catalyst – oxidation of NH₃
 - Secondary catalyst – high temperature decomposition of N₂O
 - Tail gas reduction catalyst

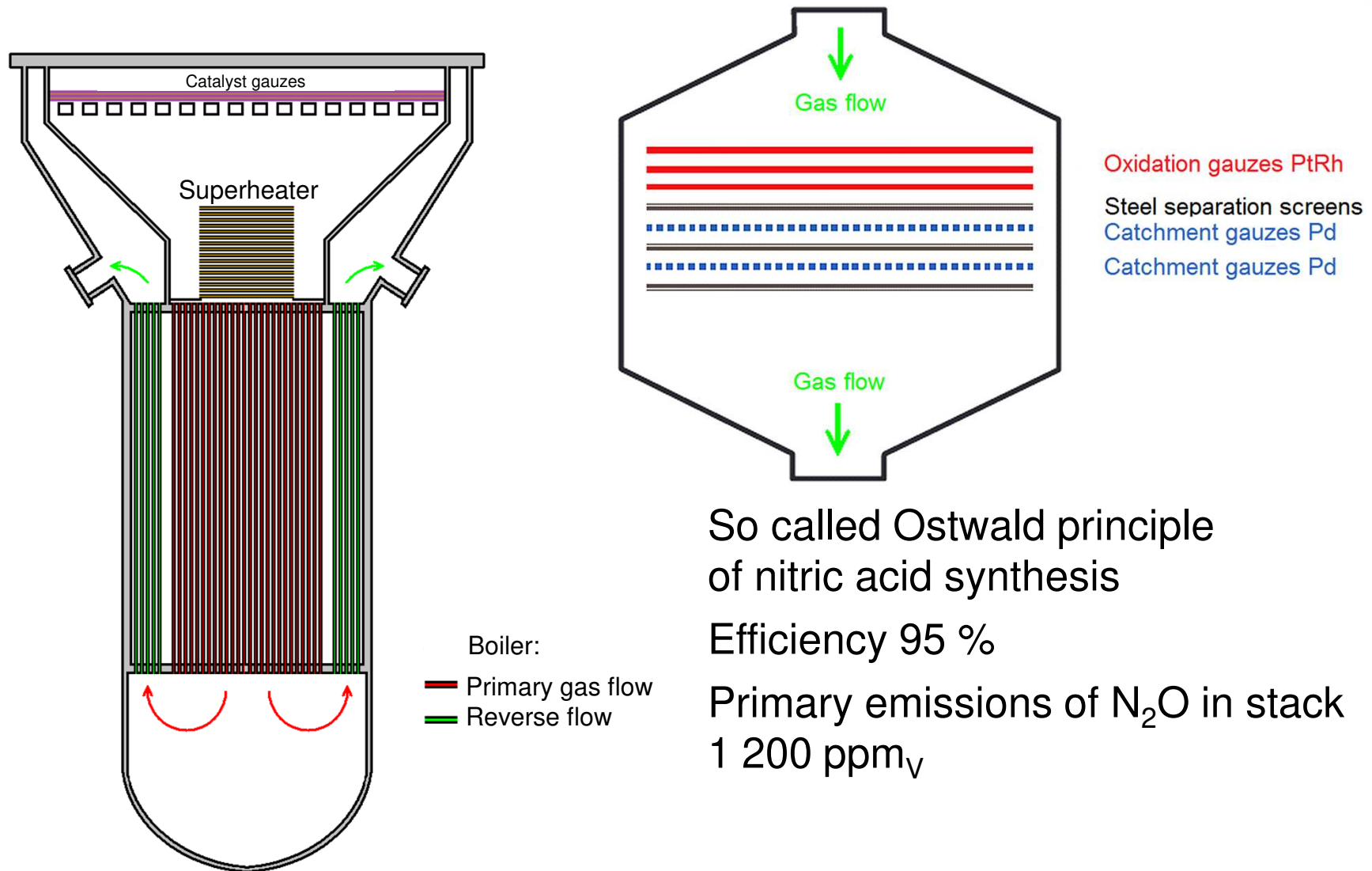
Environmental issues of N₂O

- **Main emission 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 HNO₃ 60 – 68 %;
 - Unit consumption of NH₃ 282 – 284 kg/t_{HNO₃};
 - Unit steam production 600 – 700 kg/t_{HNO₃};
 - Content of NO_x and N₂O in tail gas < 100 ppmv;
 - Conversion efficiency NH₃ to HNO₃ 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 N₂O



Environmental issues of N₂O



— Ammonia combustor (older conception)

So called Ostwald principle of nitric acid synthesis

Efficiency 95 %

Primary emissions of N₂O in stack
1 200 ppm_v

Environmental issues of N₂O

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



Uncovered
upper layer of
catalyst during
maintenance