EUROPEAN UNION
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Development and Education

MINISTRY OF EDUCATION,
YOUTH AND SPORTS

ATMOSPHERIC CHEMISTRY

Lecture No.: 7

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

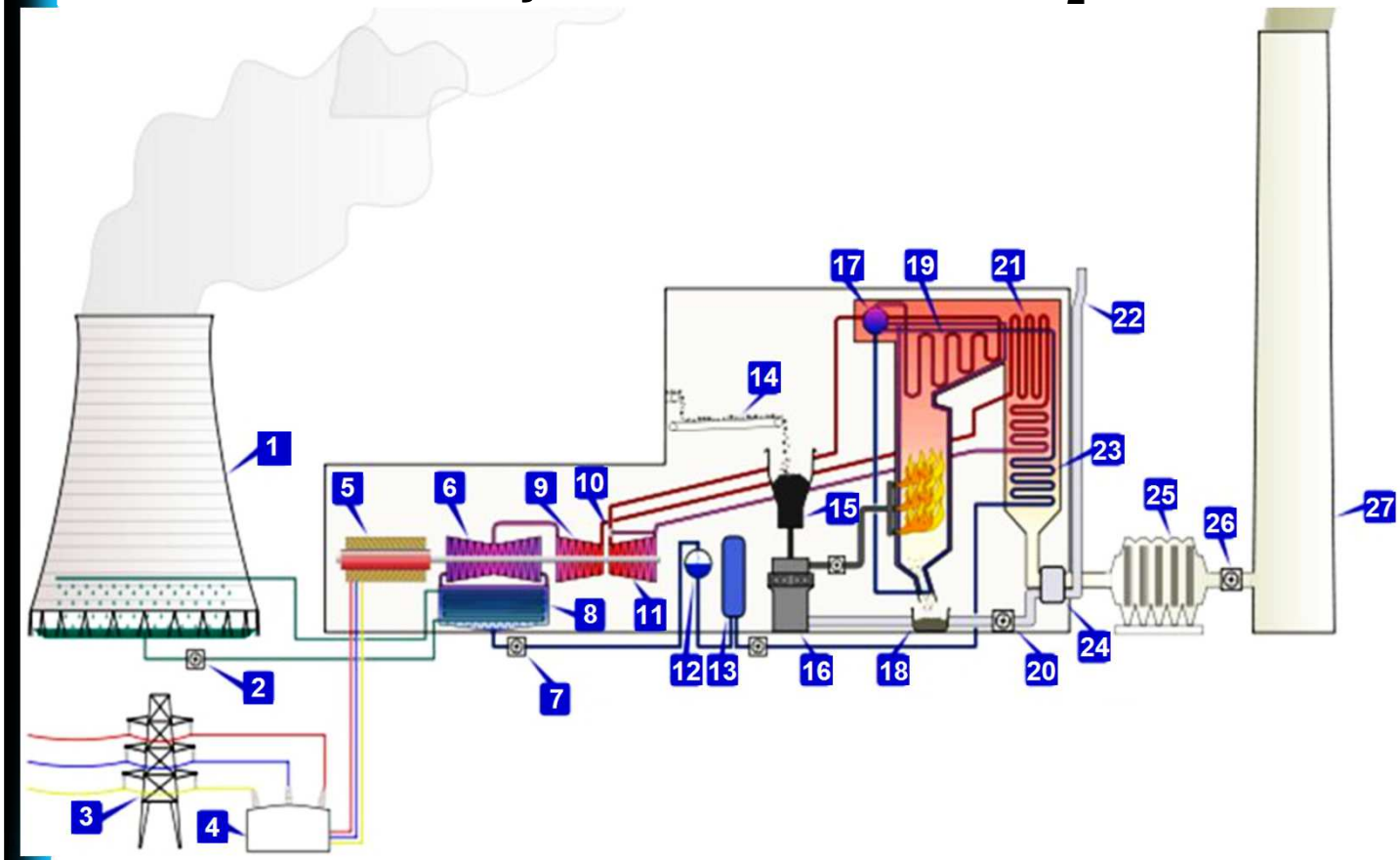
Scope of lecture 7

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 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 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 preheater
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)

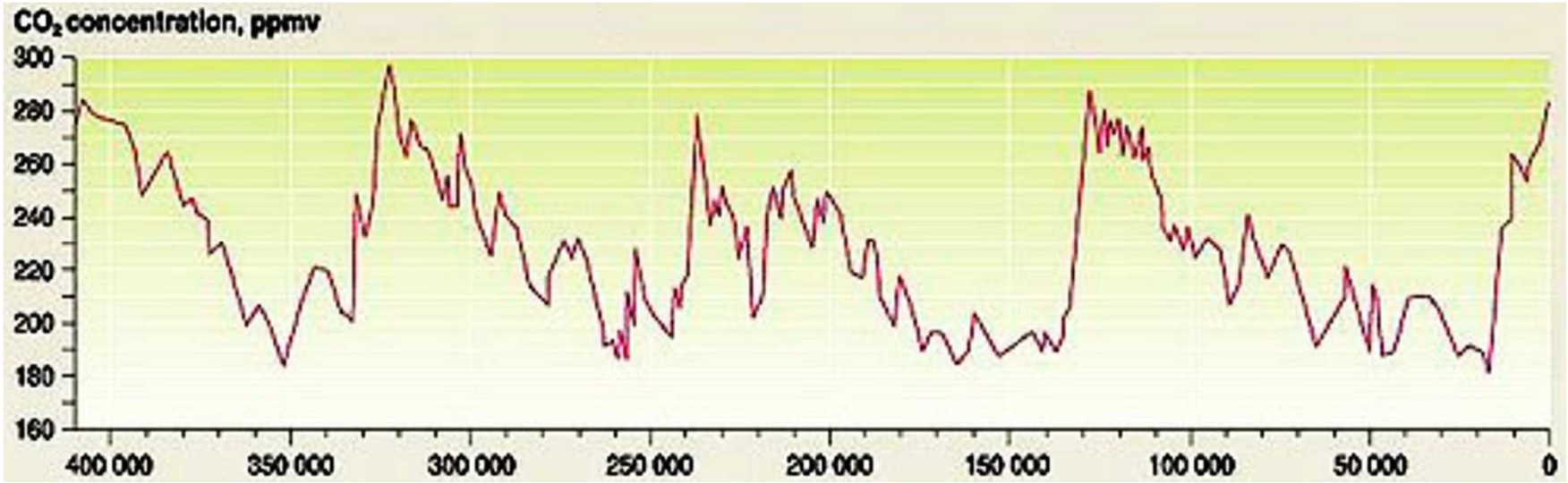
  - During 100 years (1900 – 2001) increase of:

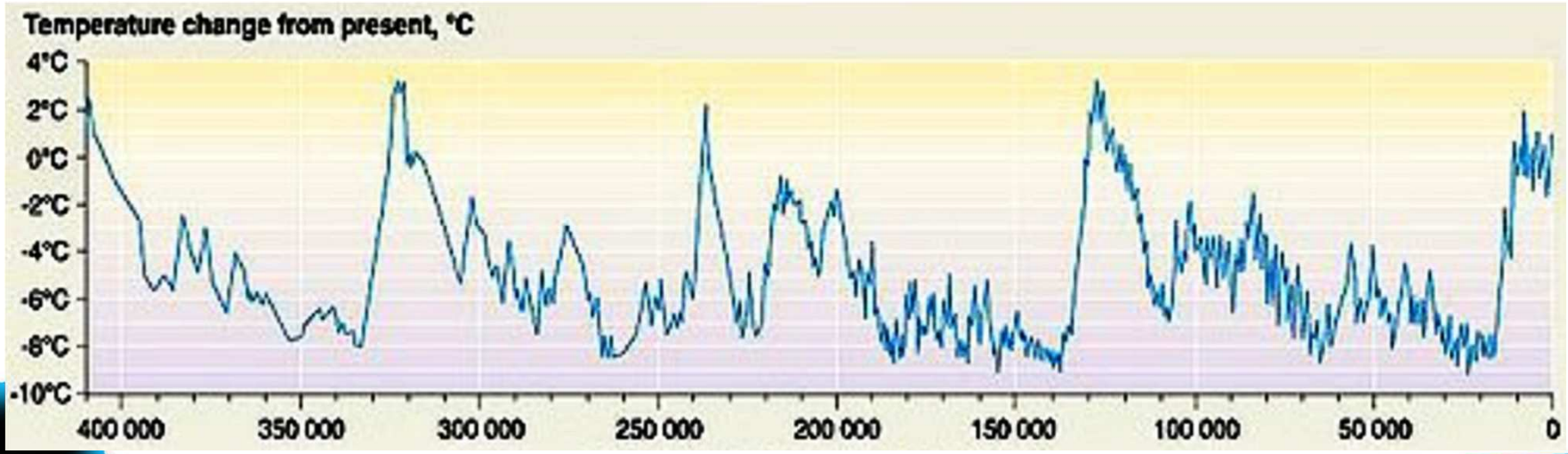
Population	by 250 %
Energy consumption	by 915 %
Content of CO_2 in the air	295 (1900)
	$\rightarrow$ 315 (1960)
	$\rightarrow$ 371 $ppm_{vol.}$(2001)

  - 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 1960 only based on ice core analyses);
  - Since 1850, gradual increase of worldwide average temperature with accelerating trend since1970;
  - Causes not proven till present $\Rightarrow$ disputes still remain;

Environmental issues of CO_2

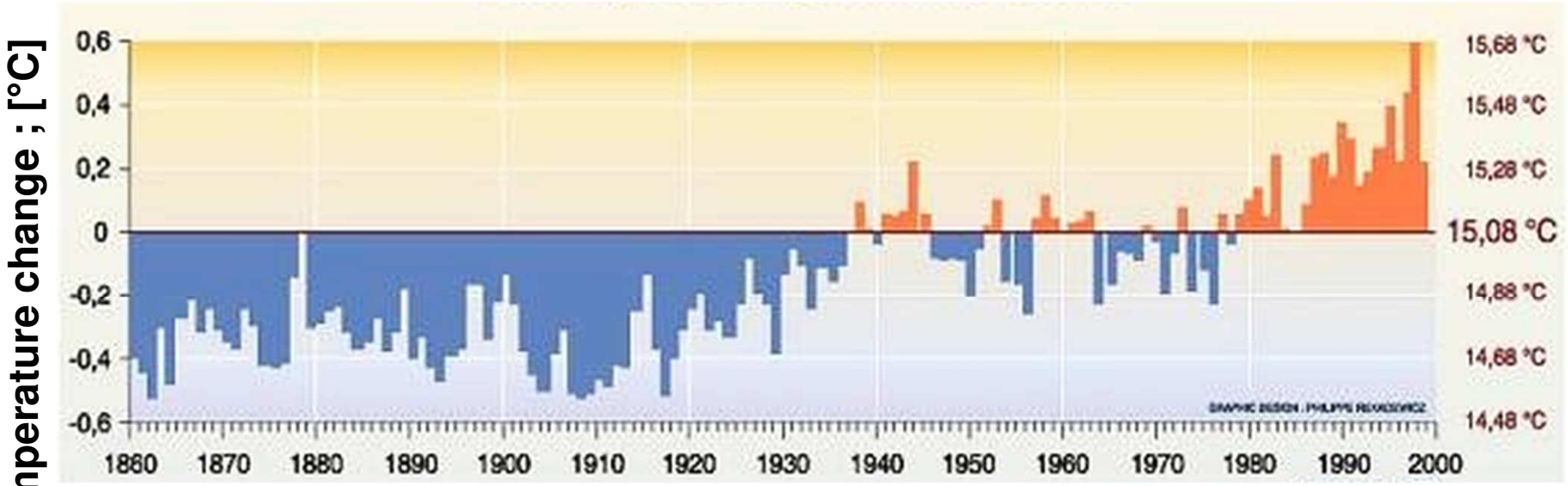
- **Variations in global temperatures over last 400,000 years** (Source: http://www.global-greenhouse-warming.com/ice-ages-and-sea-levels.html) – **Vostok ice core**





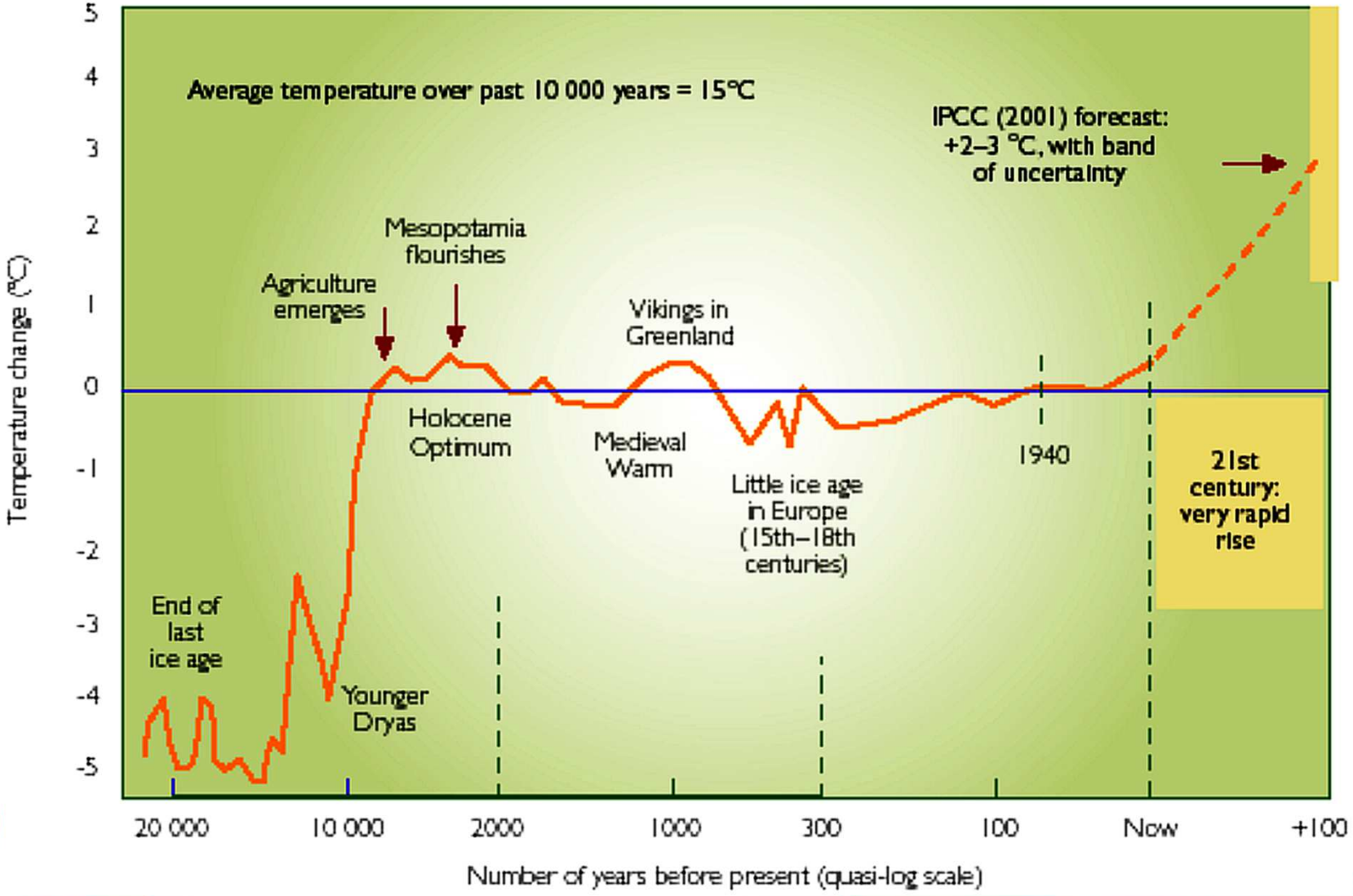
Environmental issues of CO_2

- 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)



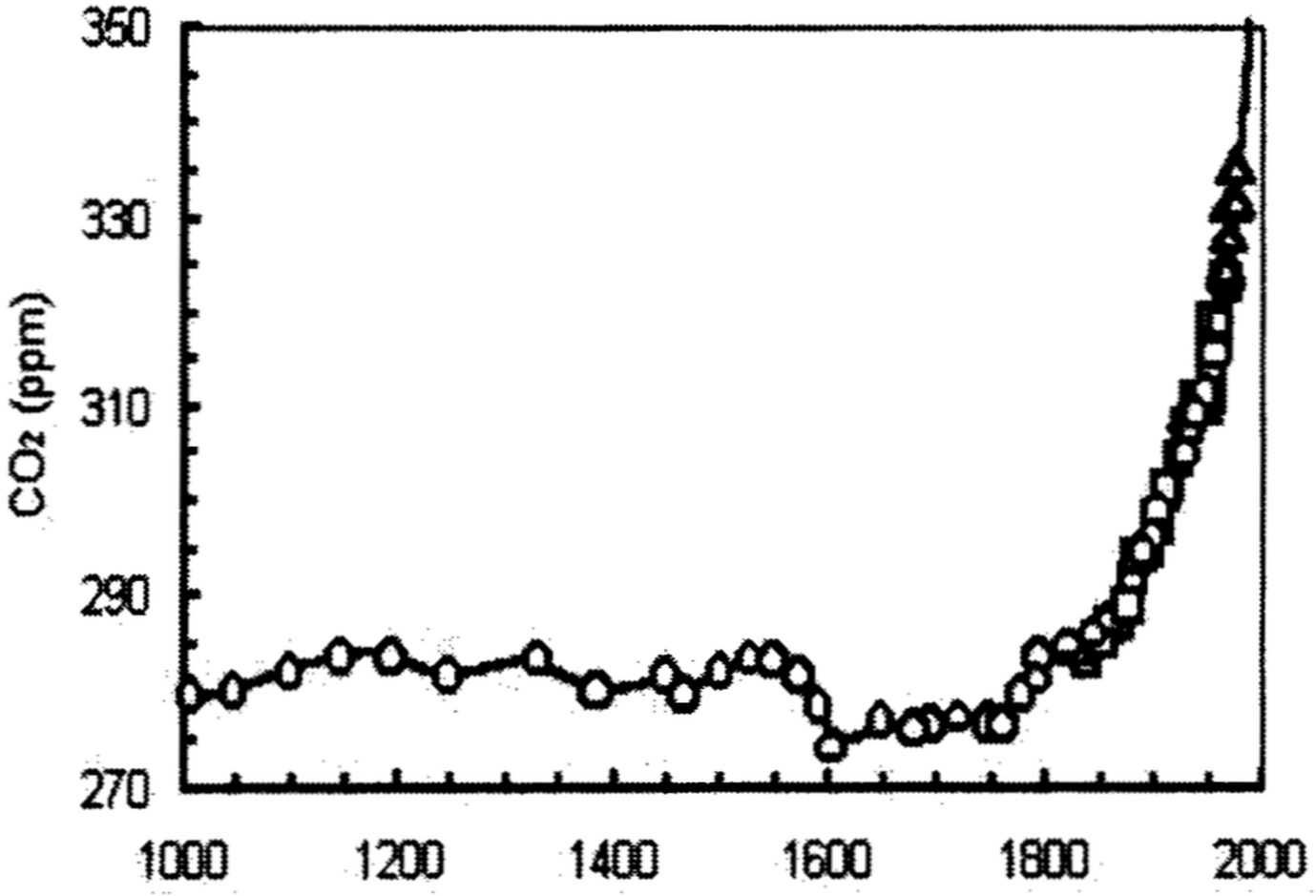
Environmental issues of CO_2

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



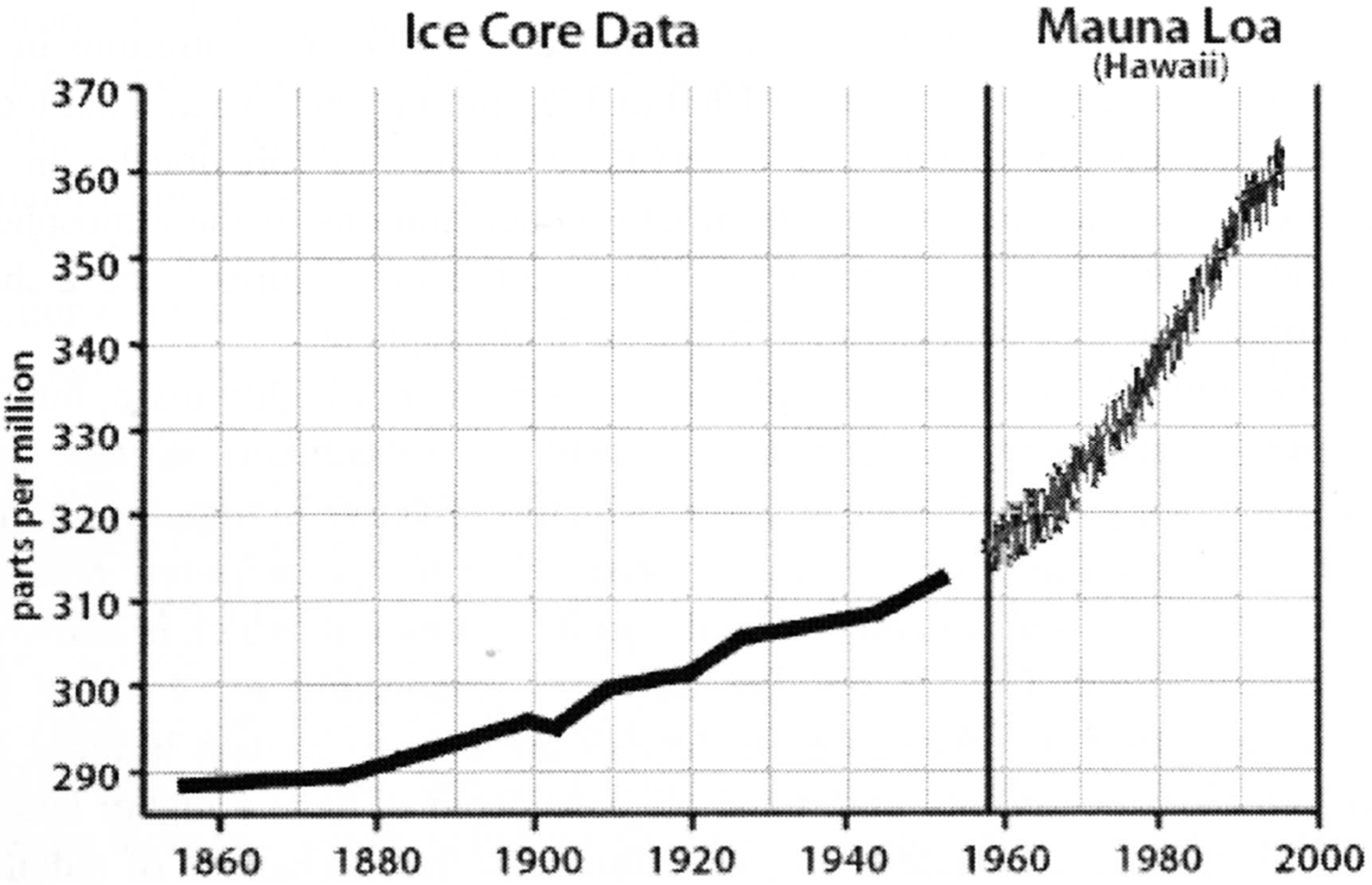
Environmental issues of CO_2

- **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 and retention of CO_2**

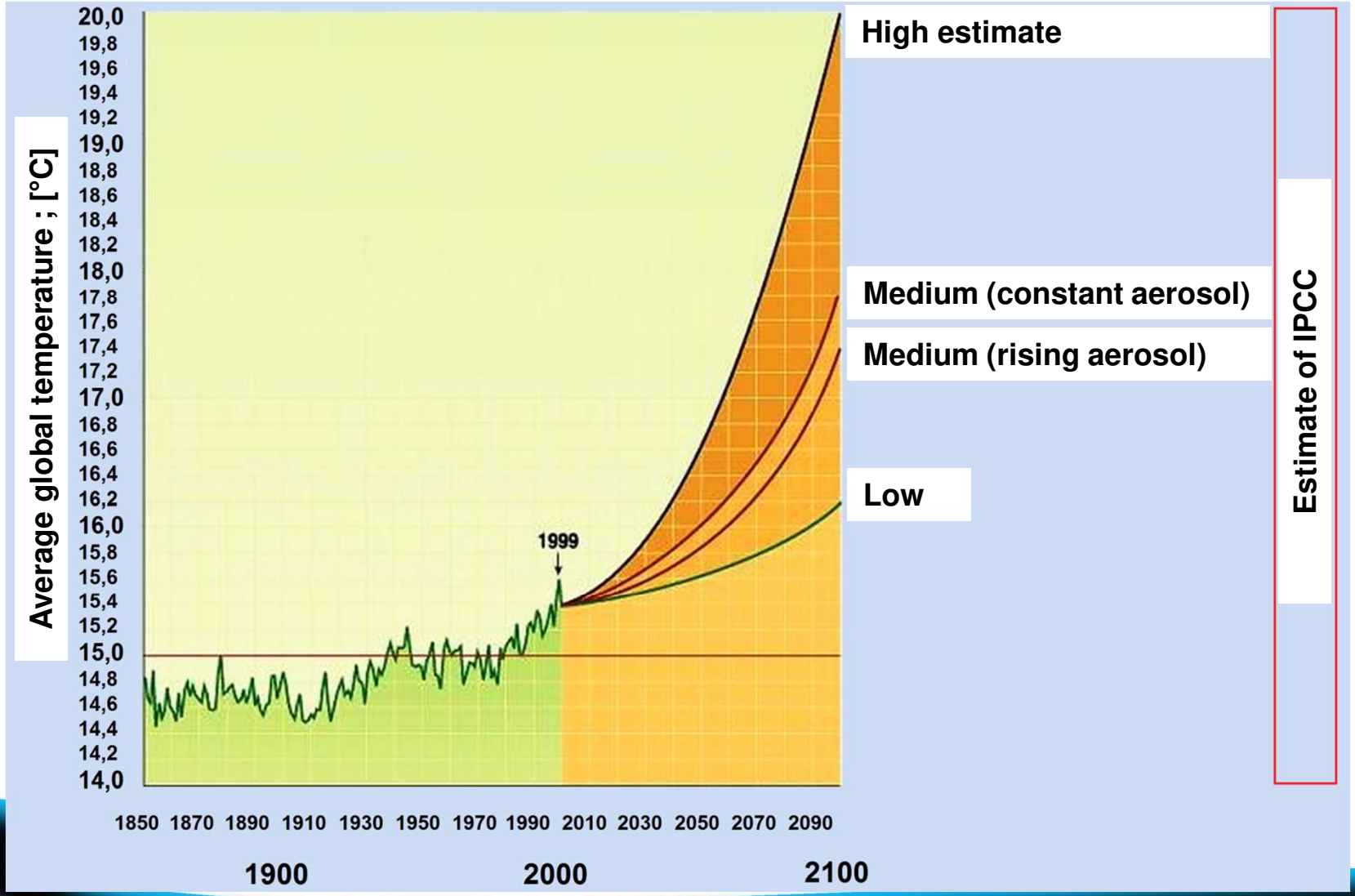
  (Source: Gomes; Carbon Dioxide Capture and Sequestration)

  - 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 CO_2 concentration was changing.
  - The rise of CO_2 concentration in the atmosphere corresponds to only 55 % of total anthropogenic emissions $\Rightarrow$ Natural mechanisms are still able to absorb 45 - 50% of the CO_2 produced by human activities.
  - Retention capacity of the oceans is about 1.7 Gt (CO_2)/year (in total retained about 38,000 Gt (CO_2);
  - Retention capacity of the forests is around 1.4 Gt (CO_2)/year;
  - Based on that, scenarios of temp. variations have been prepared.

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 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 CH_4 emissions in total: 80 %;
  - Ratio between anthropogenic and natural emissions:

    Anthropogenic: 60 %

    Natural: 40 % (½ are wetlands)

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 ⇒ **<u>negligible importance!</u>**

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** into CO_2 by means of numerous reactions: (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 into hydroperoxymethane, which is gradually transformed into formaldehyde)

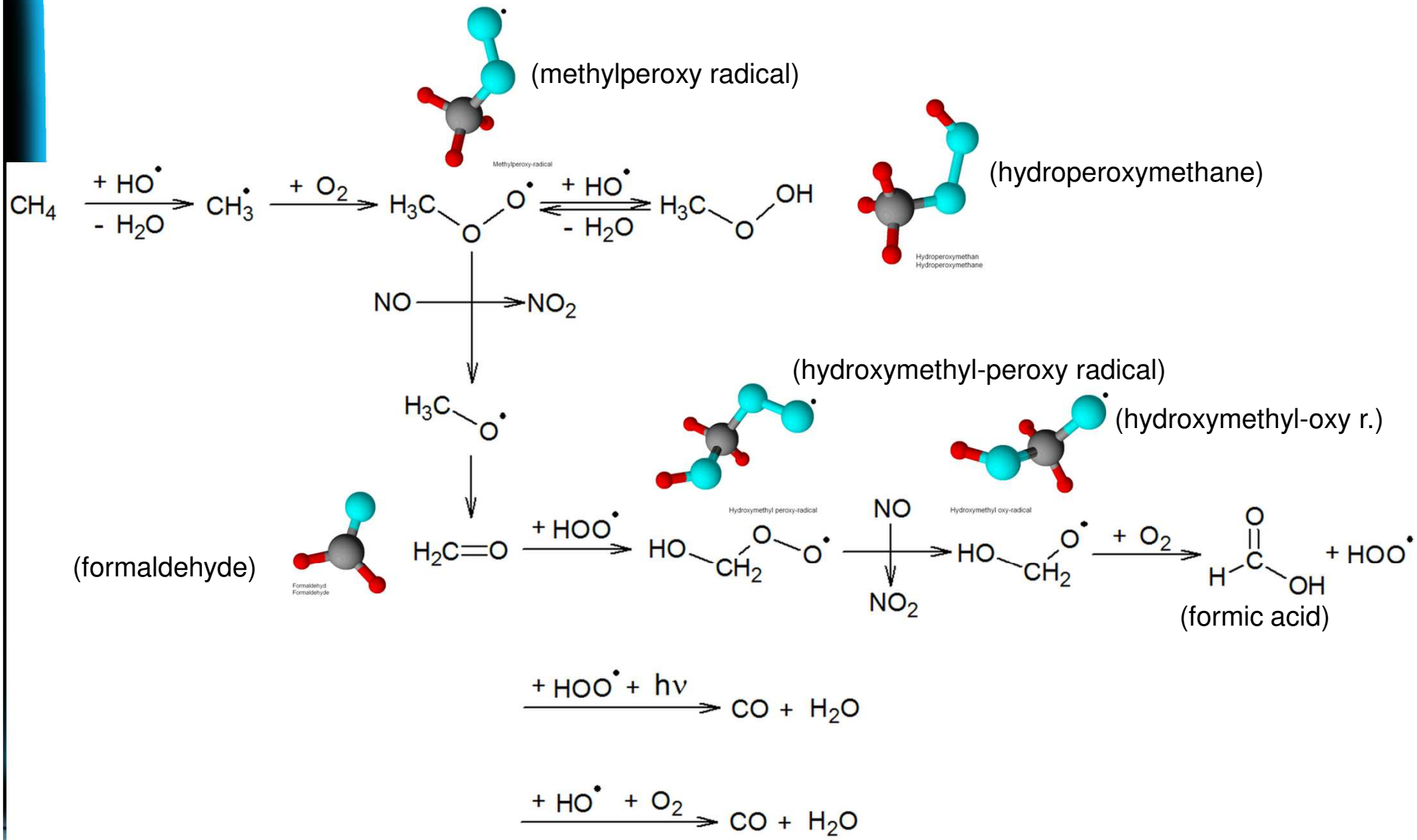
$$CH_3O_2^{\bullet} + HO_2^{\bullet} \longrightarrow CH_3OOH + O_2$$

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

$$CH_3O^{\bullet} + O_2 \longrightarrow HCHO + HO_2^{\bullet}$$

Environmental issues of CH_4

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



Environmental issues of CH_4

- Lifetime and decay of CH_4 in the air (Source: http://www.irz.cz/repository/latky/methan.pdf)
  - Reaction with $OH^{\bullet}$ 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. 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, 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

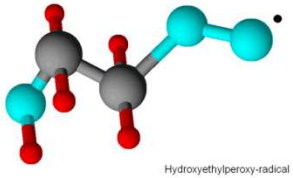
The ratio of the last two mechanisms grows together with the number of C atoms in the initial hydrocarbon chain in favour of alkyl nitrate.

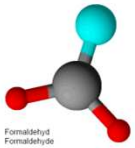
Environmental issues of C_xH_y

- 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

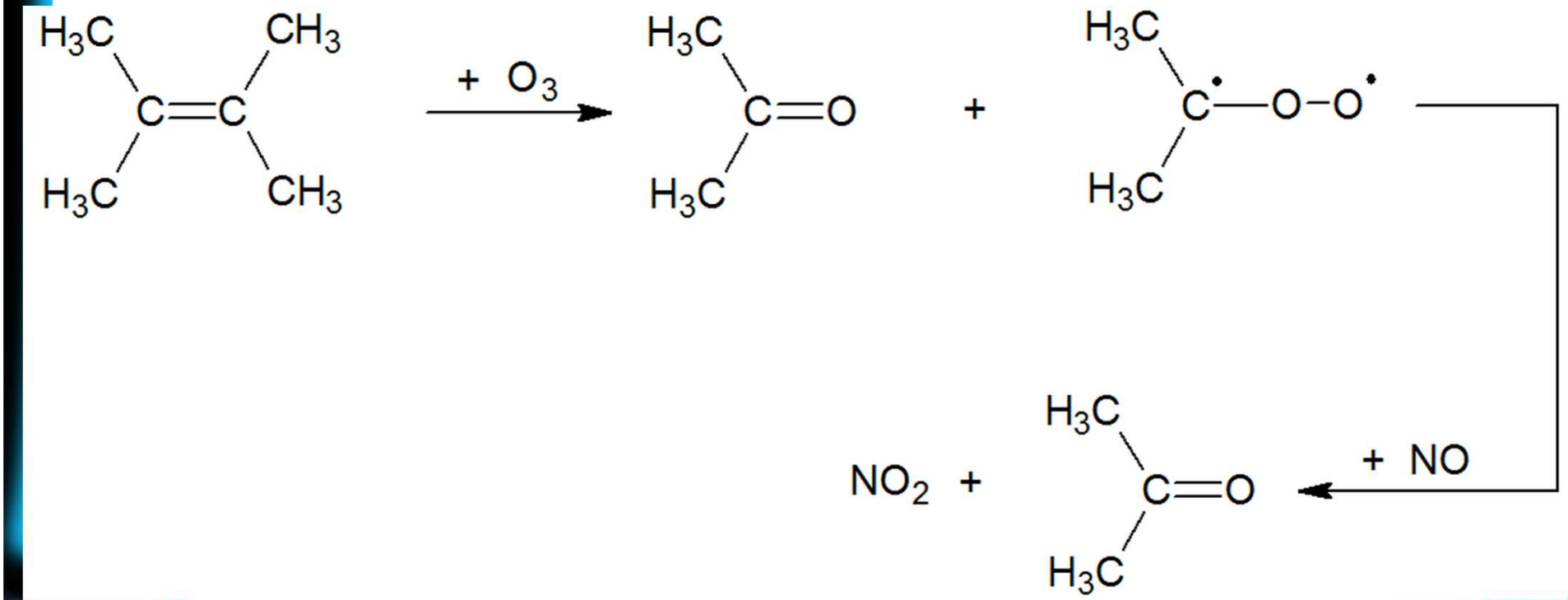
- Transformation of alkenes – Addition of HO• onto double bond, followed by oxidation





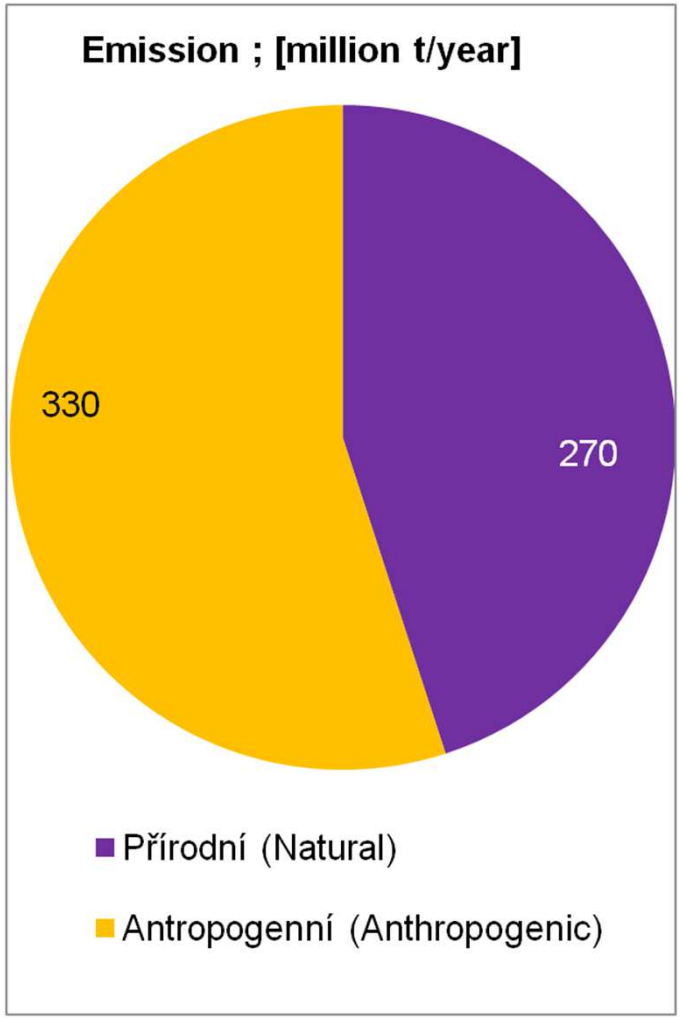
Environmental issues of C_xH_y

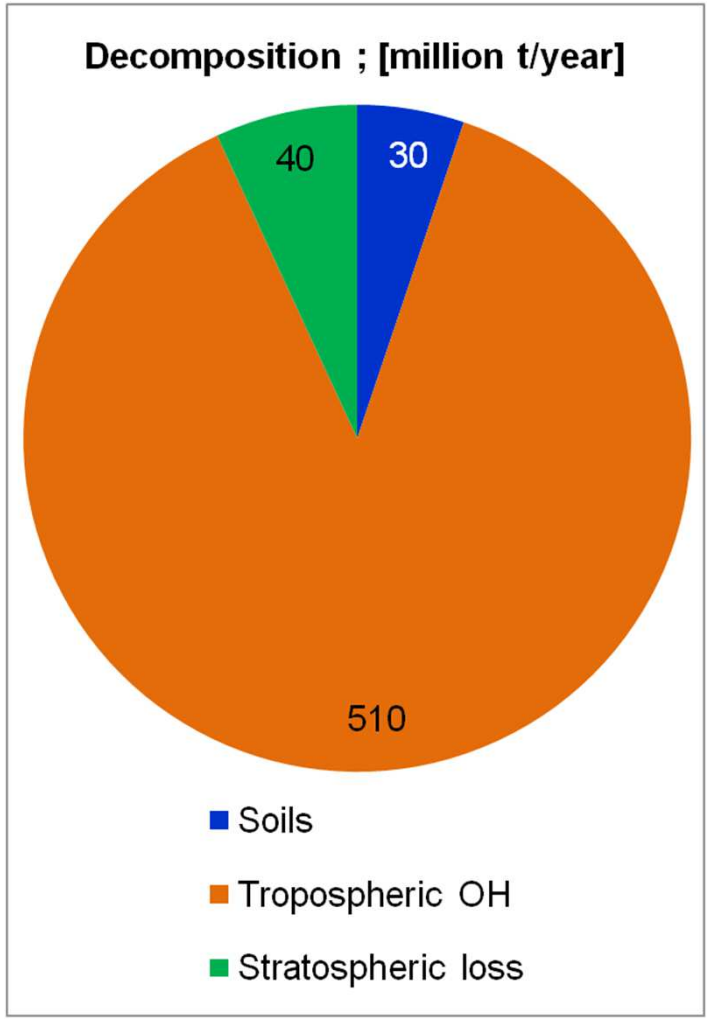
- Transformation of alkenes – reaction with O_3 → Crieg radicals
  - Crieg alkylperoxyl biradicals – strongly oxidative ⇒ oxidize NO to NO_2, NO_2 to NO_3^- (see chapter acid deposition), SO_2 to SO_3 etc.;
  - Double bond of the alkene is cleaved to form aldehyde (or ketone) and alkylperoxyl biradical,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



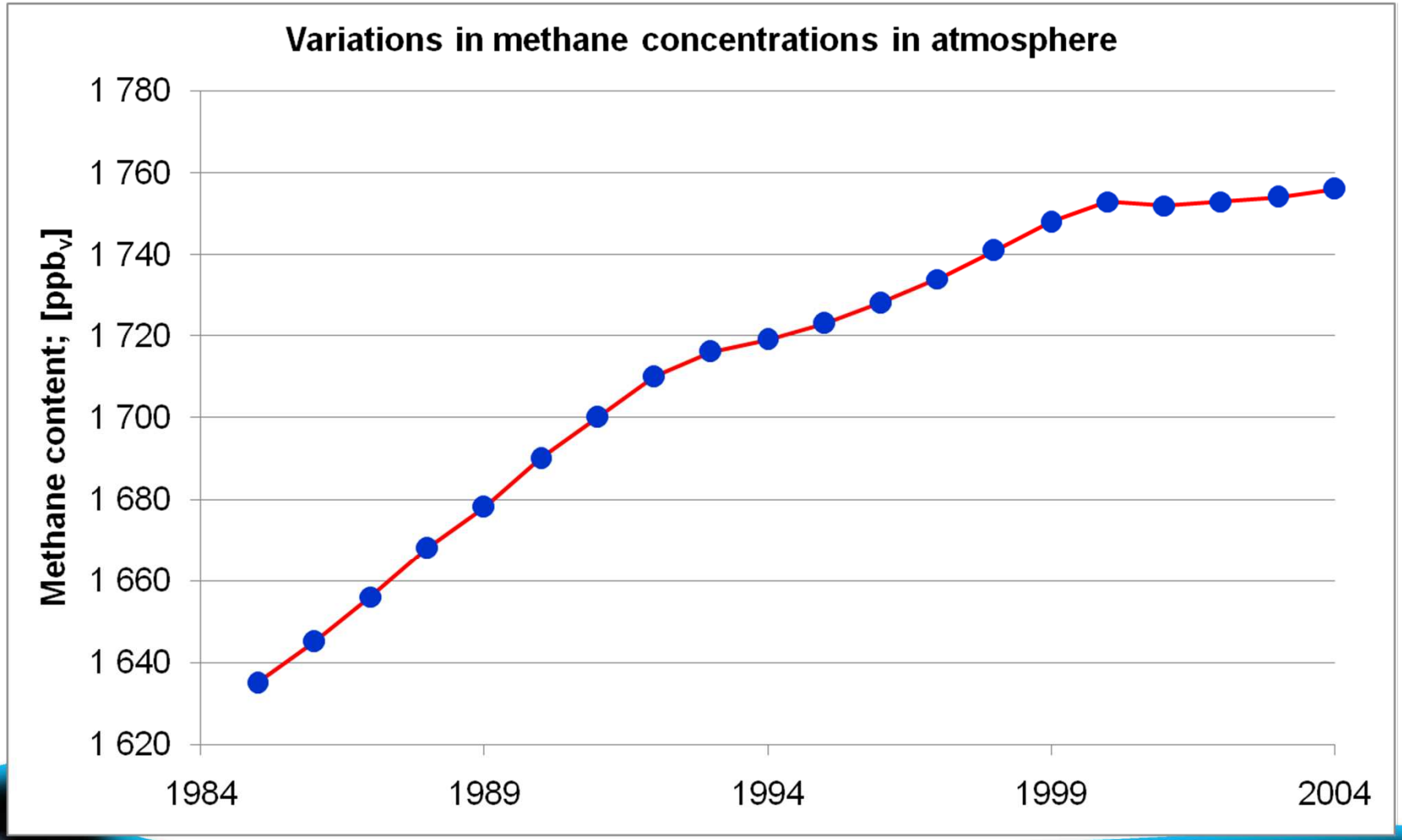


Overall misbalance + 20 mil. t/year

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 of the group of nitrogen oxides: nitrogen monoxide NO, dioxide NO_2, azoxide N_2O, N_2O_3 and N_2O_5;
- **Formation of N_2O** (Source: IPCC)
  - N_2O 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.; N_2O max. 3.10^{-6} % vol.)

    In fluidized bed combustors significantly higher N_2O 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(N_2O) = 298

    according to US EPA 310

    presently EU ETS in conformity with EPA 310;

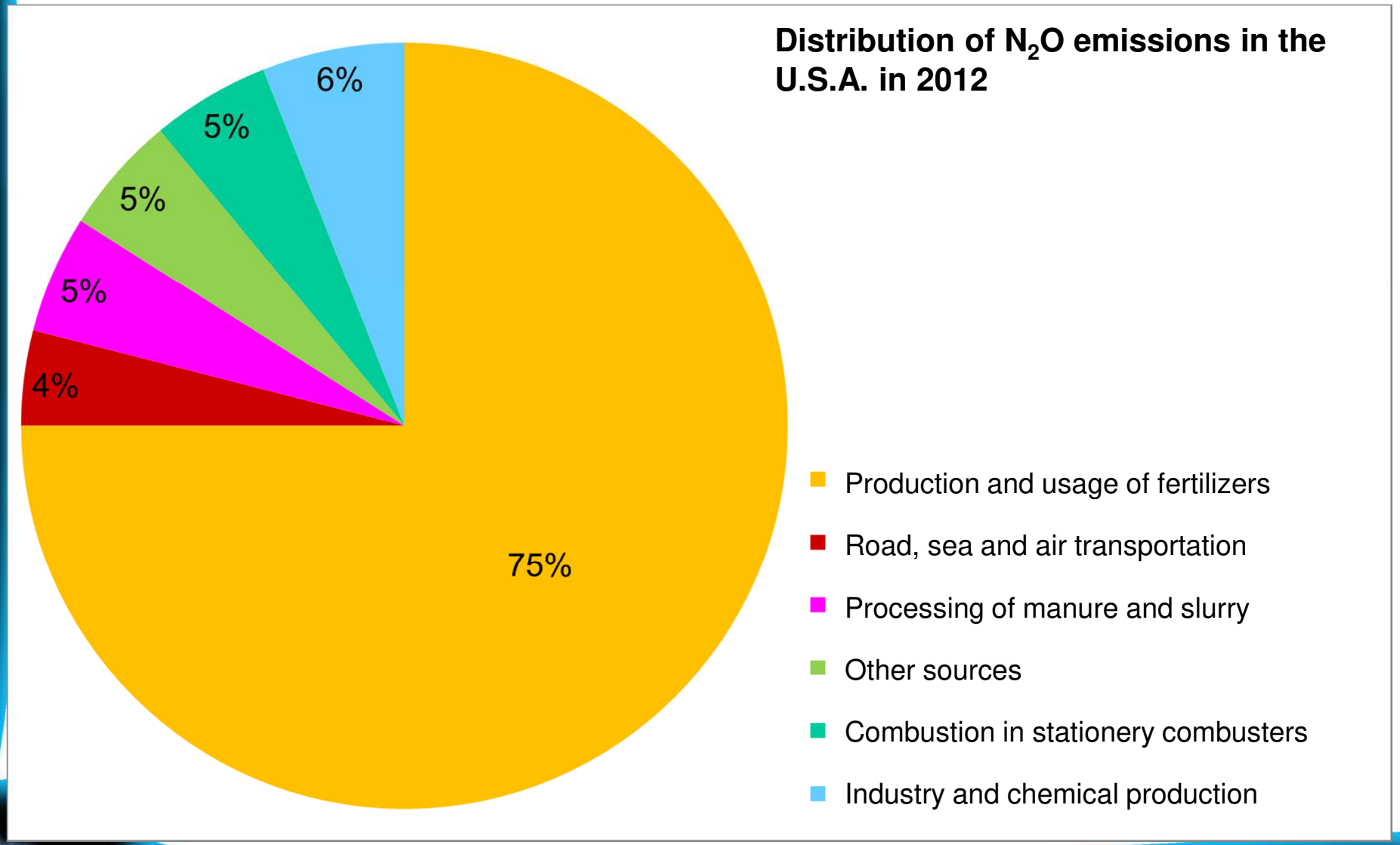
Environmental issues of N_2O

- **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: metabolised 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 $\Rightarrow$ 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 $\Rightarrow$ comparable with operation of 80.10^6 personal cars!

Environmental issues of N_2O

- **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 NO_2 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 NH_3

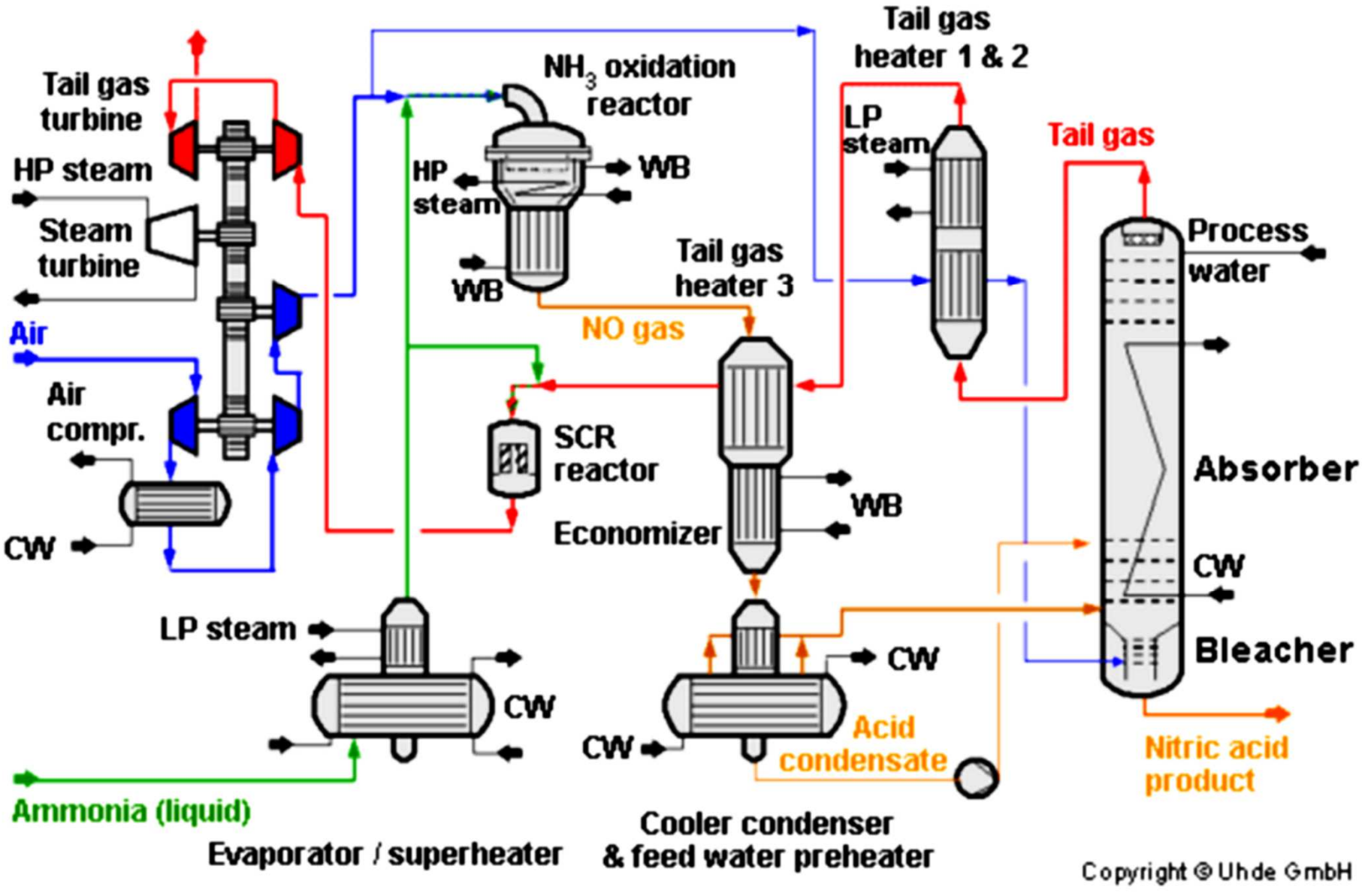
    Secondary catalyst – high temperature decomposition of N_2O

    Tail gas reduction catalyst

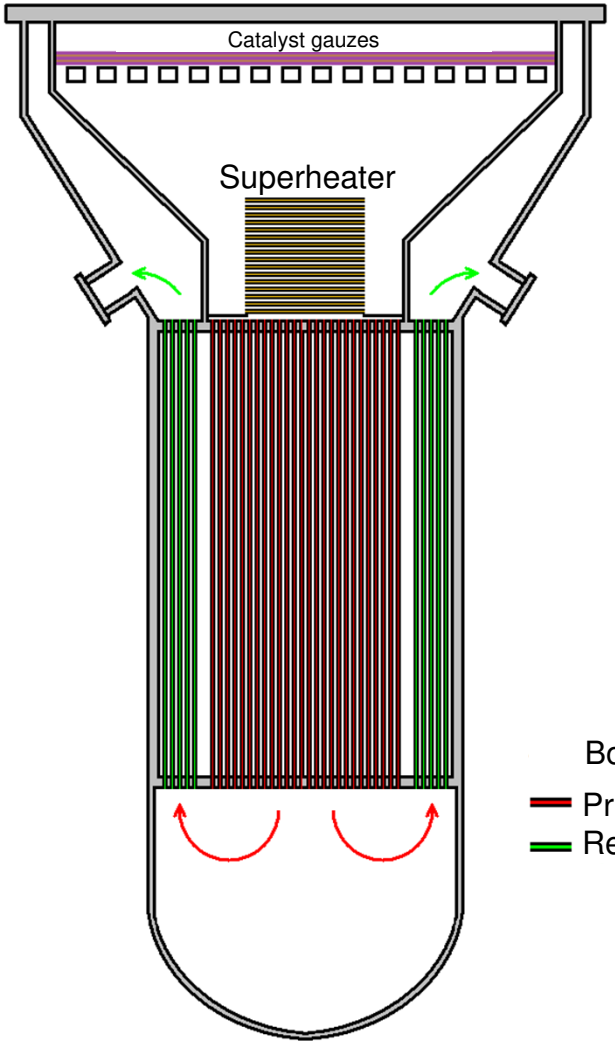
Environmental issues of N_2O

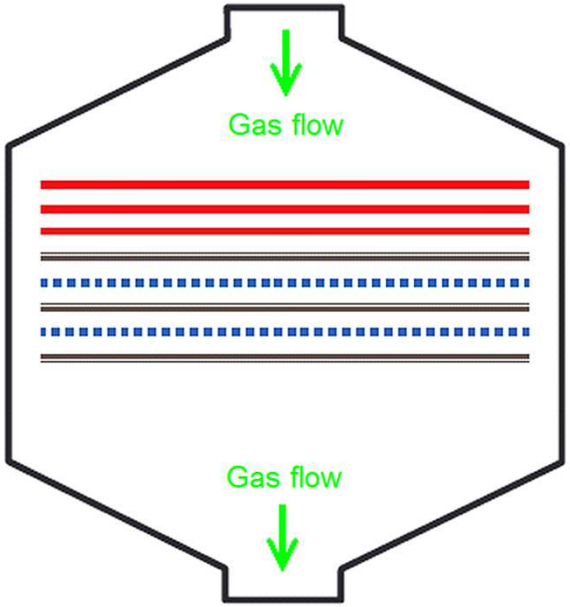
- **Main emission source – nitric acid manufacture**
- **Czech constructor of NA plants – Chemoprojekt, a.s.**
- **Typical parameters of recent installations:**
  - Nominal production capacity 660 – 1 500 $t_{100\%\ HNO3}$/day;
  - Adjustable performance scale 70 – 110 % of nominal capacity
  - Concentration of produced 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





Oxidation gauzes PtRh

Steel separation screens
Catchment gauzes Pd
Catchment gauzes Pd

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