



EUROPEAN UNION
European Structural and Investing Funds
Operational Programme Research,
Development and Education

MSMT
MINISTRY OF EDUCATION,
YOUTH AND SPORTS



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

The published materials are intended for students of the University of Chemistry and Technology, Prague as a study material. Some text and image data contained therein are taken from public sources. In the case of insufficient quotations, the author's intention was not to intentionally infringe the possible author(s) rights to the original work. If you have any reservations, please contact the author(s) of the specific teaching material in order to remedy the situation.

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 8

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

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

Distribution of pollutants

- Pollutants can be divided into following fundamental groups:

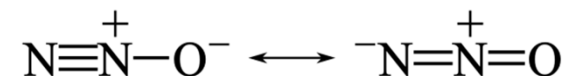
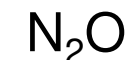
- Acidic substances
 - decrease atmospheric pH and subsequently acidify soil and water;
- Toxic substances
 - damage health of plants and animals chemically, physically or due to their radioactivity;
- Substances damaging O₃-
 - decompose the stratospheric O₃ layer;
- Greenhouse gases
 - change the balance between heat absorption and radiation from the atmosphere;
- Precursors
 - in their initial form they show no dangerous properties, but undergo changes resulting in the above mentioned properties, or allow other compounds to be transformed into dangerous substances.

Acidic substances

- Main gases having acidic reaction:

- Nitrogen oxides (NO_x)

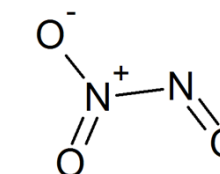
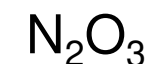
Nitrous oxide (laughing gas, azoxide)



Nitric oxide (nitrogen monoxide)



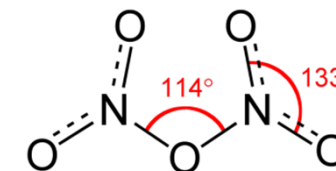
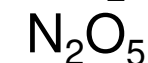
Dinitrogen trioxide



Nitrogen dioxide



Dinitrogen pentoxide



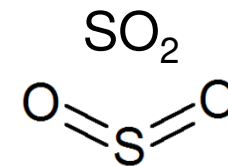
Note 1: Dinitrogen trioxide is formed only at low temperatures ($< 21\text{ }^\circ\text{C}$) by reversible reaction $\text{NO} + \text{NO}_2 \leftrightarrow \text{N}_2\text{O}_3$.

Note 2: Dinitrogen pentoxide is a crystalline substance sublimating at $t > 30\text{ }^\circ\text{C}$.

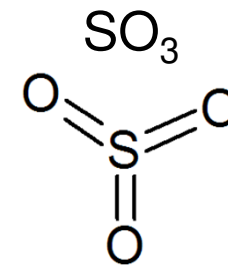
Acidic substances

- Main gases having acidic reaction:
 - Sulphur oxides (SO_x)

Sulphur dioxide



Sulphur trioxide

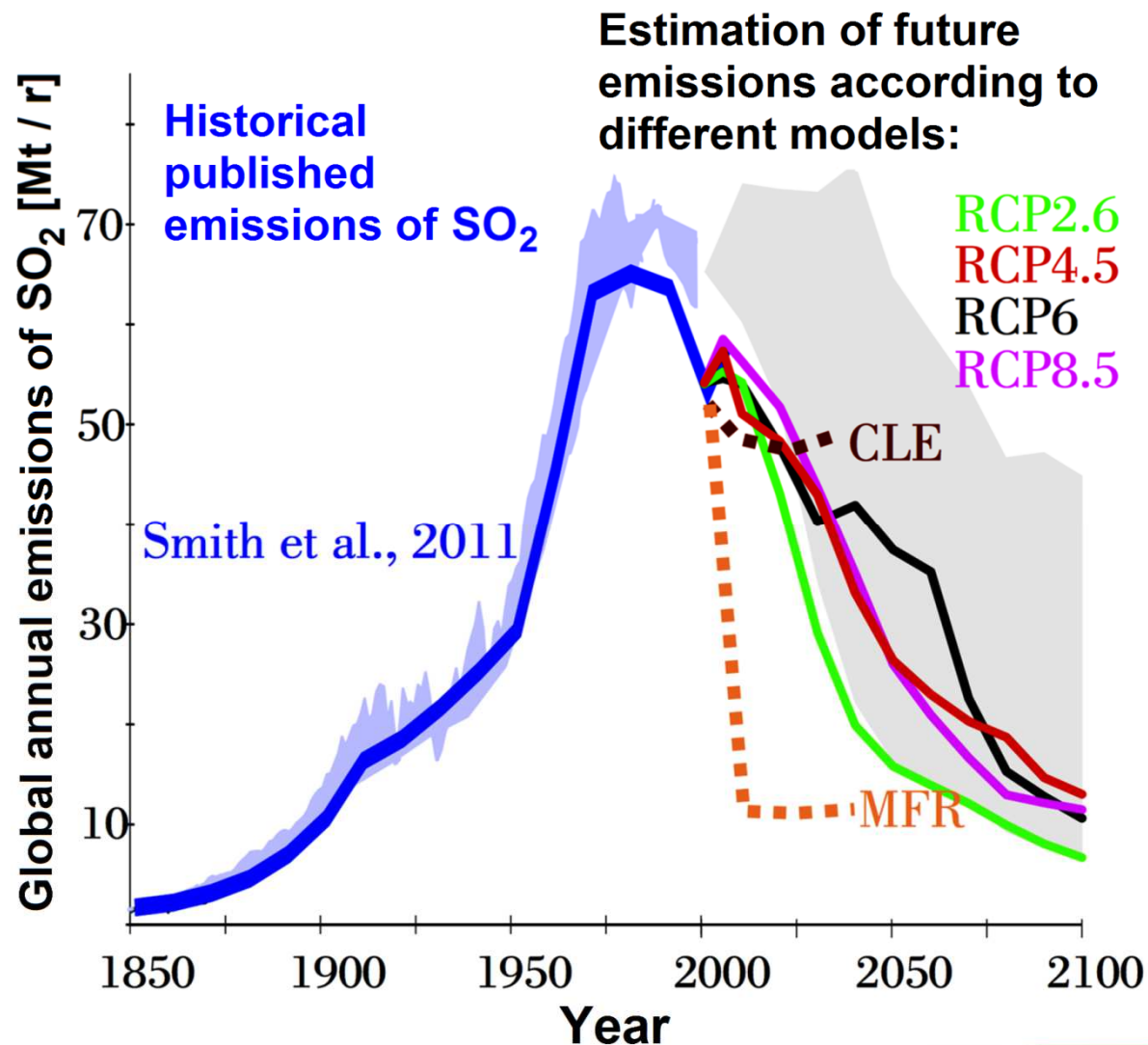


Origin of sulphur oxides emissions

- Natural sources:
 - Volcanic gases
 - In the form of sulfurous acid in mineral springs – release of vapours
- 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-sulphur liquid fuels in diesel-electric locomotives and marine ships etc.).

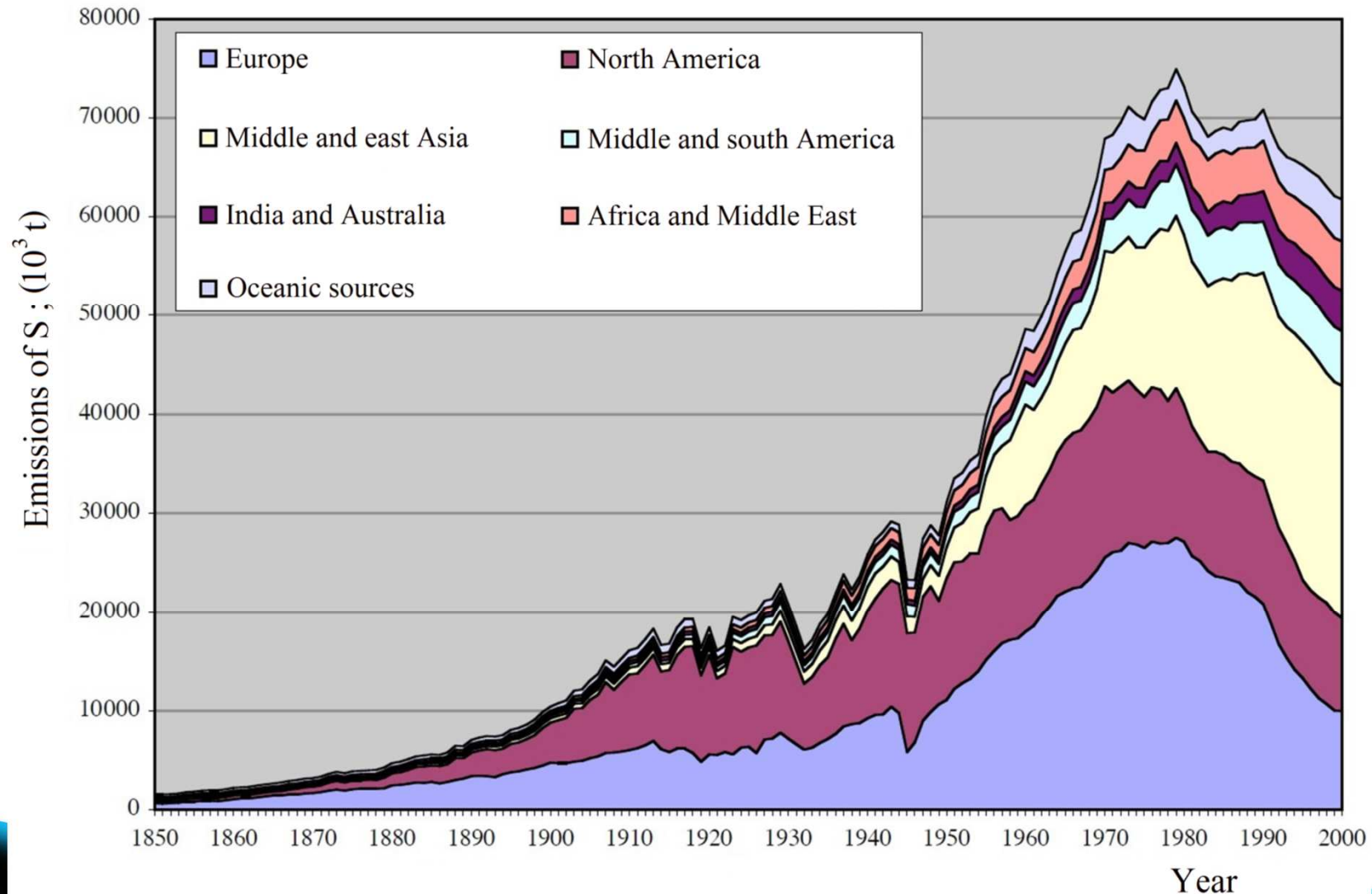
Origin of sulphur oxides emissions

- Estimated evolution of SO₂ emissions – different models (Source: Cofala et al., 2007)



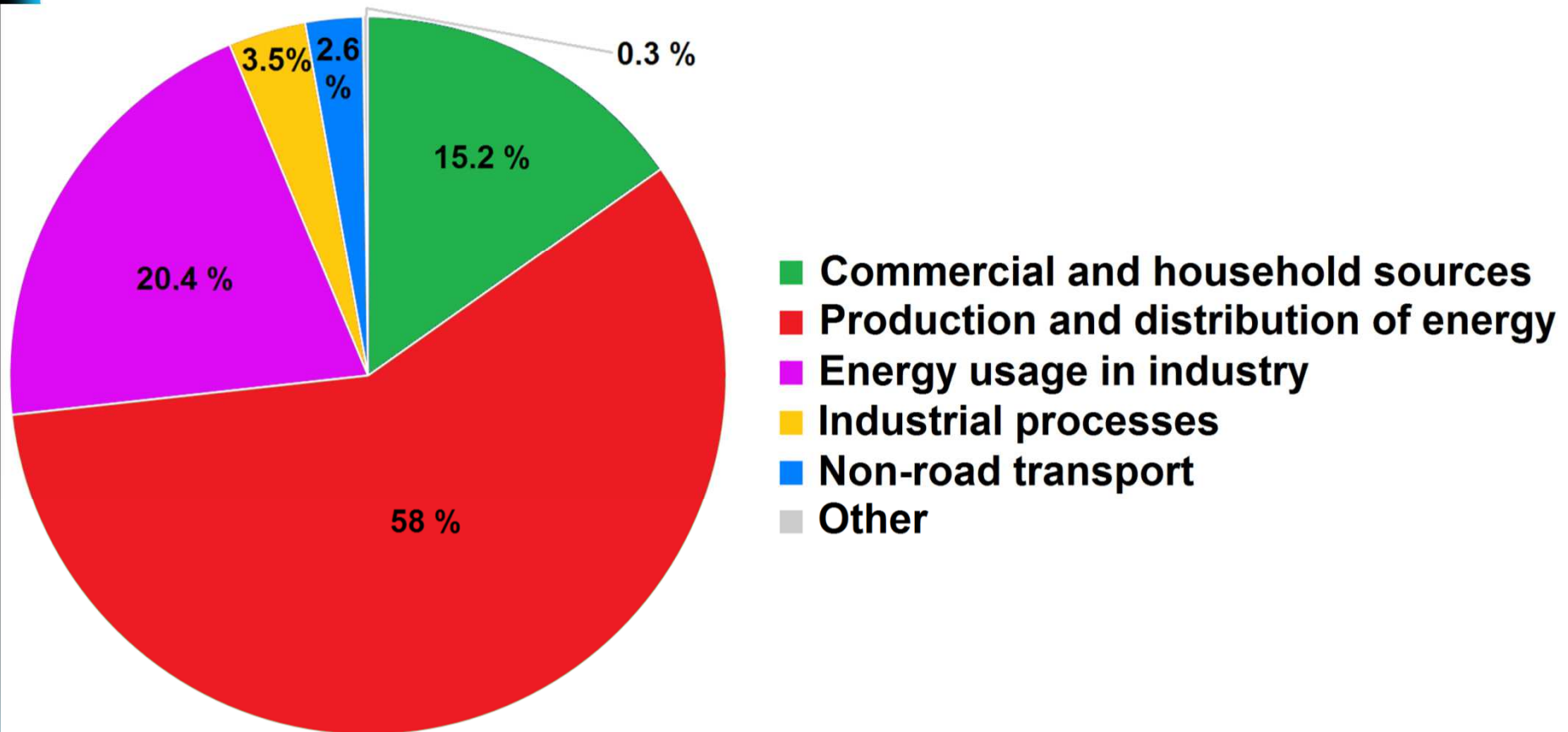
Origin of sulphur oxides emissions

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



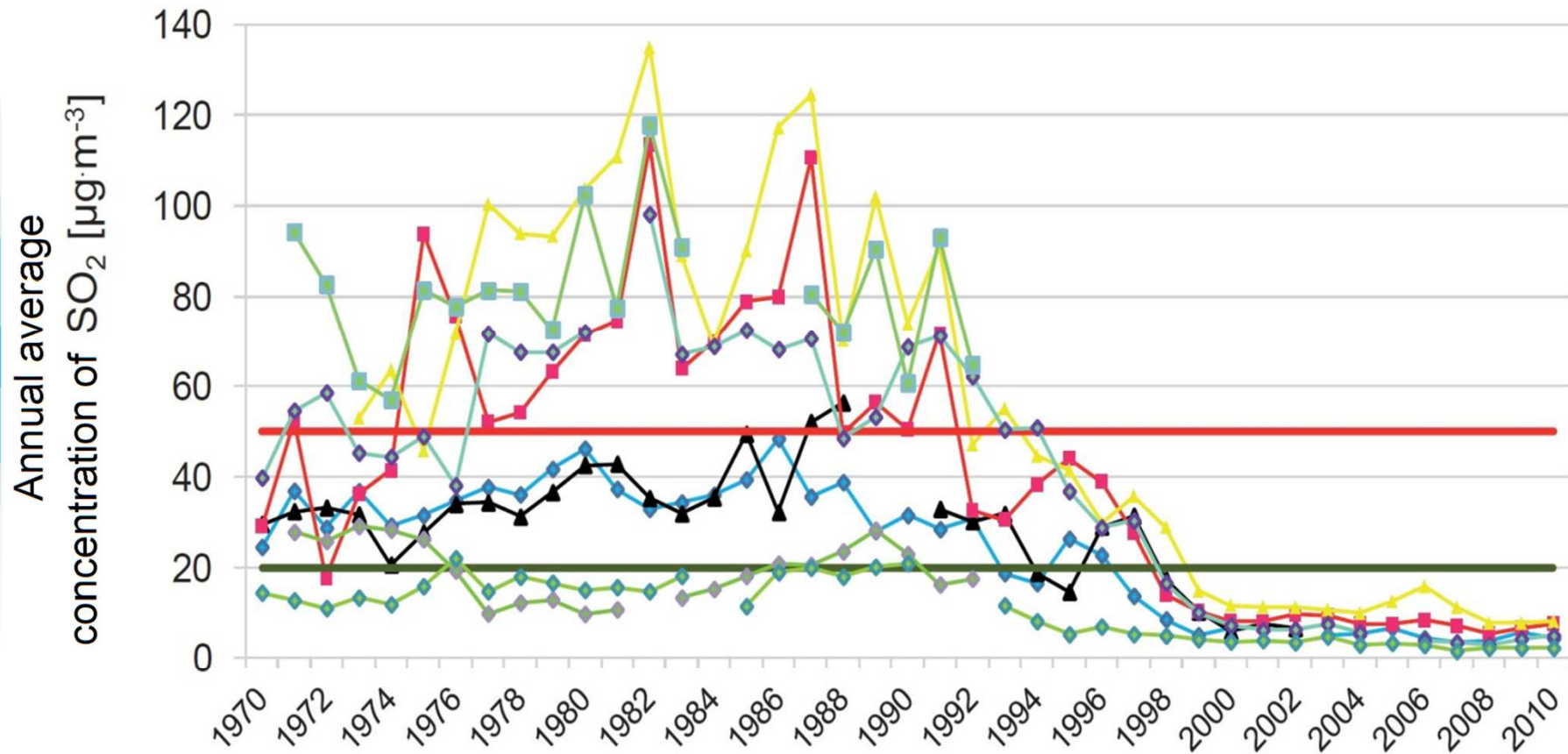
Origin of sulphur oxides emissions

- **Distribution of SO₂ sources in EU in the year 2015** (Source: EEA)



Origin of sulphur oxides emissions

- **SO₂ imissions in Czech rep. between 1971 – 2011** (Source: <http://portal.chmi.cz>)



Monitoring station:

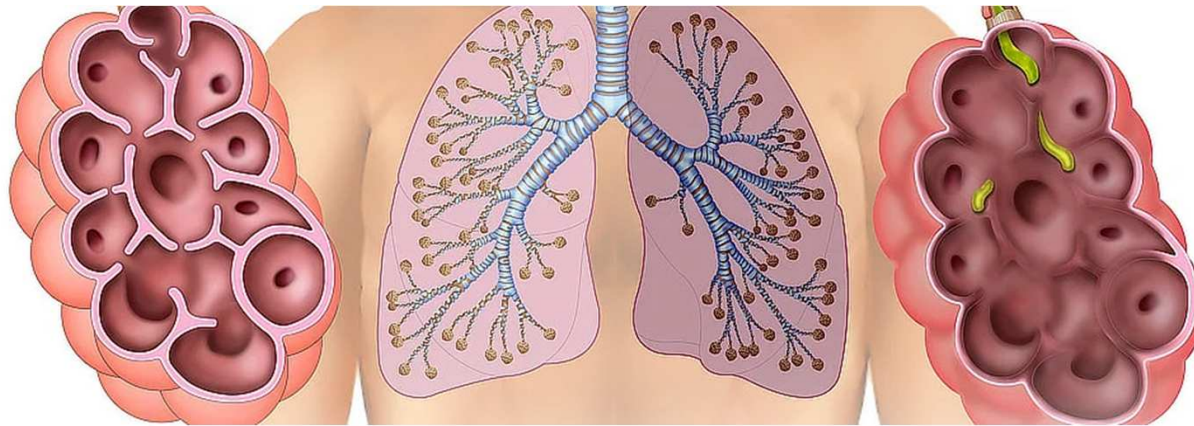
- ▲ Albrechtice/Karviná
- ◆ Souš (Jizerské hory)
- ◆ Lysá hora (Beskydy)
- Měděnec (Krušné hory)
- Tušimice
- ◆ Ostrava-Poruba
- ◆ Milešovka (České Středohoří)
- ◆ Ústí n/L-Kočkov
- Imission limit for annual average concentration according to old national regulation
- Valid imission limit for vegetation protection

Health impact of SO₂

- **Diseases caused by exposure to SO₂** (Source: WHO)
 - Short-term exposure to SO₂ emissions with duration between 5 minutes to 24 hours has a negative effect on the respiratory tract. Acute effects of the 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 diseases (asthma, chronic obstructive pulmonary disease) and circulatory system, and people otherwise weakened (e.g. combination of stress, smoking, impaired immunity, etc.);
 - Studies show a 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.

Chronic exposure by SO₂

- **Difference: asthma x emphysema** (Source: WHO)
 - Emphysema = destruction of alveoli septa (visible symptom: increased chest volume).



- Asthma = permanently narrowed bronchi



Impact of SO₂ on vegetation

- **Damaging of plants** (Source: Výzkumný ústav rostlinné výroby, v.v.i.)
 - Degradation of plant tissues due to chlorophyll decomposition;
 - Formation of diluted sulphuric acid by reacting with water aerosol;
 - Critical SO₂ concentrations, if exceeded – damage of plants:

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

* coniferous forests more sensitive

Impact of SO₂ 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 \Rightarrow Damaging of photosynthesis \Rightarrow Defoliation
- Indirect effects
 - Reaction of esp. SO_2 with H_2O and reaction of SO_3 with H_2O to form acid rains \Rightarrow 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 $\text{pH} < 5,6$
 - Formed primarily by acids of SO_x and NO_x , to a minor extent also by HCl ;
 - Main negative impact on coniferous trees;
 - Weaker effect in the Southern hemisphere.

Effects of acidic deposition

- Water acidification
 - Reducing pH of water due to acid deposition and subsequent negative processes affecting the biotope;
 - Degree of acidification is given by the 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 of the location to acidification \Rightarrow neutralisation of acidic deposition;
 - Bedrock consisting of gneisses and granite \Rightarrow 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-} and NO_3^- ;
 - Sensitive basin: incomplete neutralization with subsequent transfer of Al^{3+} , Mn^{2+} , Zn^{2+} etc. from soil into surface water.

Effects of acidic deposition

- Water acidification
 - Destruction of ecosystem due to:
 - ↳ Decrease of pH value;
 - ↳ Extraction of toxic metals (normally immobilized in rocks):
Al, Cd, Pb, Cu;
 - Death of water organisms \Rightarrow reduction of biodiversity;
 - Dominance of acidophilic species (e.g. sphagnum in wetlands)
 - Disruption of trophic degree \Rightarrow flushing out the nutrients from water and soil;
 - Paradox! Visually, acidified water seems to be clear and transparent \Rightarrow due to the lack of saprophytic microorganisms phytomass is not decomposed, but it is only accumulated at the bottom.

Effects of acidic deposition

- Water acidification – example of acidophilic organism
 - Sphagnum:
the plant species typical for acidic wetlands



Acidic deposition vs. eutrophication

- Water eutrophication – warning, often confused with acidification!
 - Process of enrichment of water by nutrients, especially N and P;
Natural eutrophication = flushing out of 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^- , $\text{P}_2\text{O}_7^{4-}$) 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 water, esp. at the bottom where the 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 with varying density and blocking exchange of O_2)

Acidic deposition vs. eutrophication

- Water eutrophication: first symptom = algal bloom

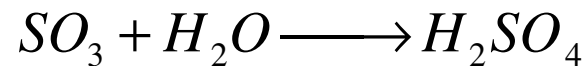
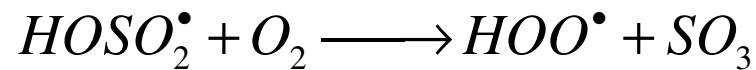
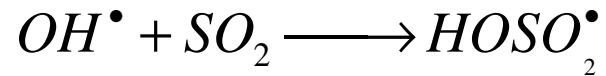


Reactions of sulphur oxides

- Sulphur oxides – mostly anthropogenic / sulphur in reduced form – mostly biogenic
- Biogenic forms of sulphur emitted in atmosphere (especially):
 - Carbon disulphide CS_2
 - Hydrogen sulphide H_2S
 - Carbonyl sulphide COS
 - Dimethyl sulphide $(\text{CH}_3)_2\text{S}$
 - Dimethyl disulphide $\text{CH}_3\text{-S-S-CH}_3$
- Reactions of reduced forms of sulphur
 - The first phase is the reaction with OH^\bullet , following sequence of reaction is not fully mapped, but it leads to oxidation to SO_2
 - SO_2 is either oxidized very slowly : $2\text{SO}_2 + \text{O}_2 \rightarrow 2\text{SO}_3$
 - Or it again reacts with hydroxyl radical, afterwards to H_2SO_4 .
The mechanism is demonstrated on the following slide.

Reactions of sulphur oxides

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



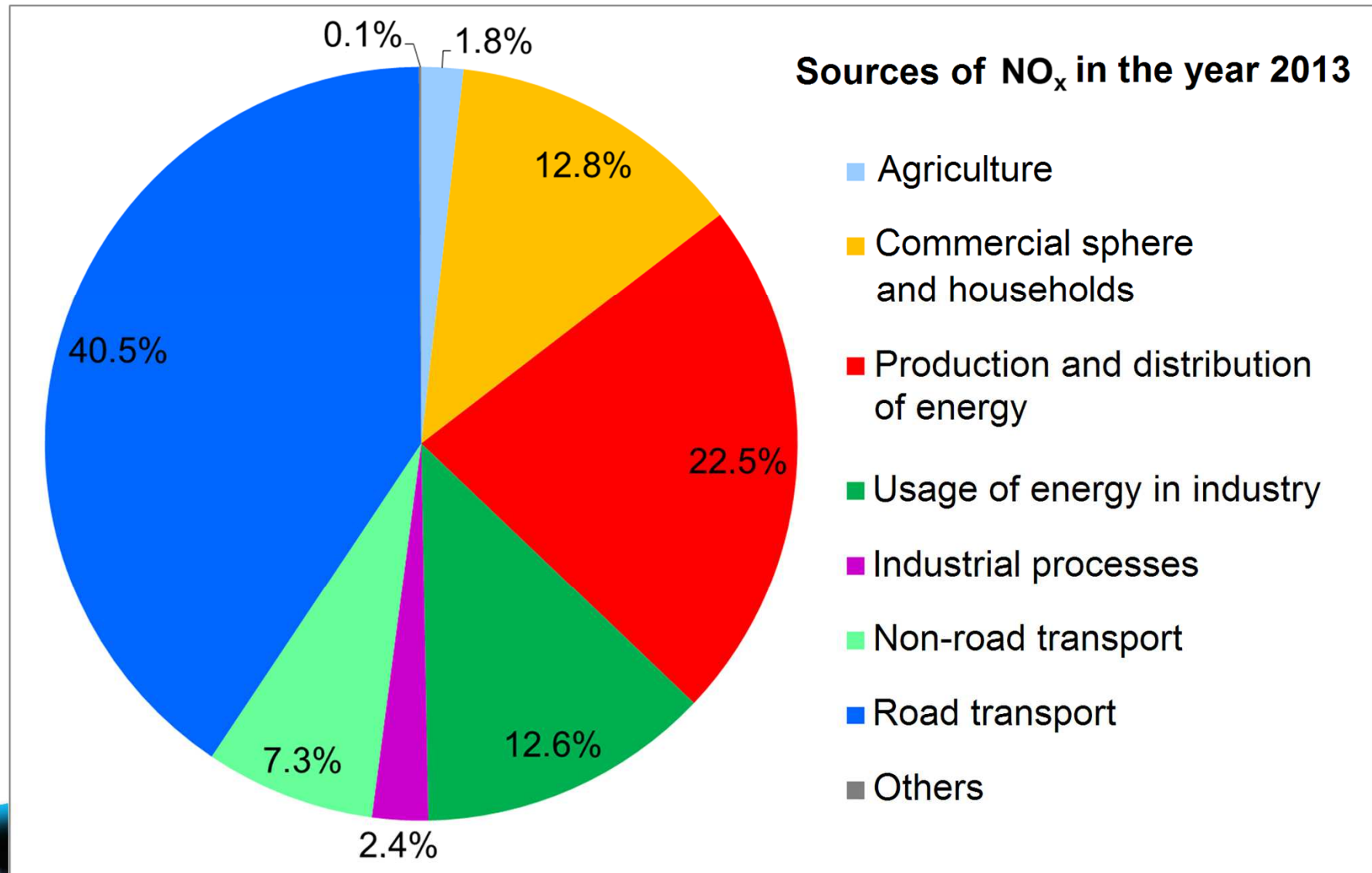
- Possibility of excitation by UV radiation
 - SO_2 in lower troposphere is only oxidized and photodissociation does not take part;
 - SO_2^* loses excessive energy by its transfer to inert substances \Rightarrow SO_2 therefore does not undergo photooxidation.

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 on average 3 % per year);
 - Warning: concentrations in municipal air decreased more slowly than the officially declared progress of emissions reduction in member countries (i.e. the real emissions are higher);
 - In power industry the decrease is significant due to introduction of low-emission burners, scrubbers, SCR, SNCR and partial transition from coal to natural gas;

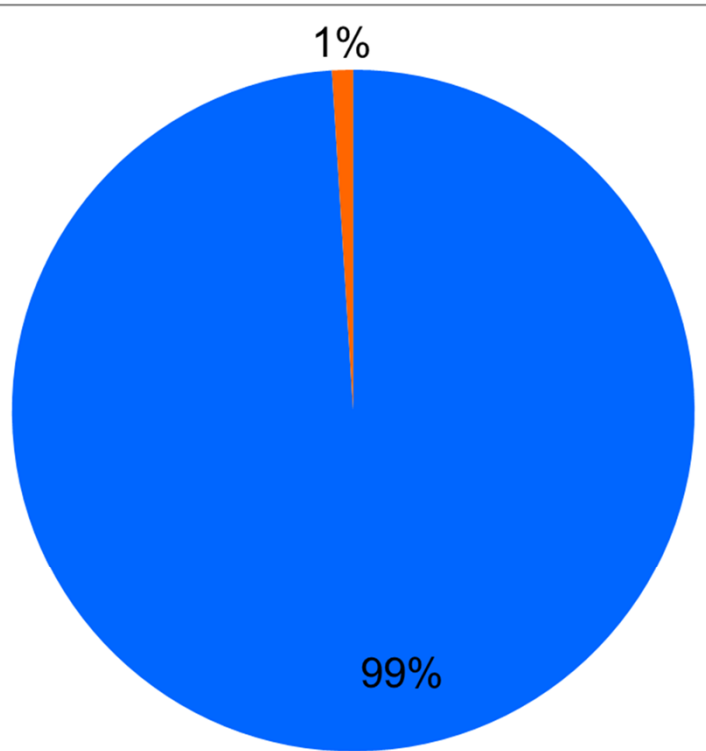
Origin of nitrogen oxides emissions

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



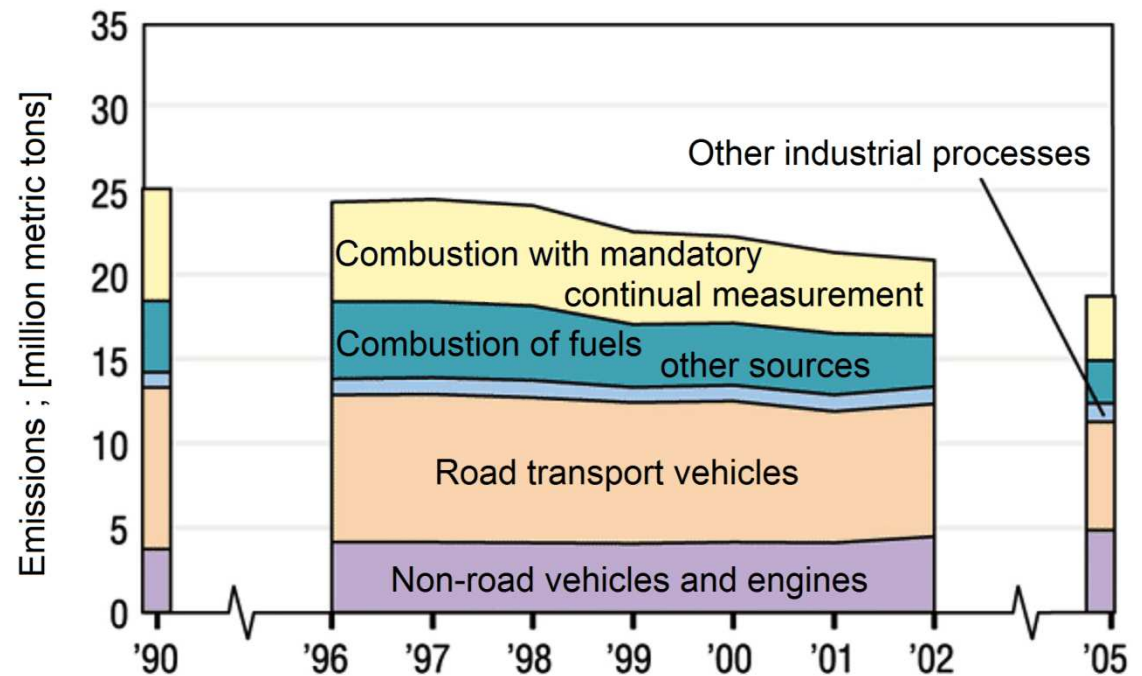
Origin of nitrogen oxides emissions

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



Ratio between NO_x sources in the U.S.A. in 2005

- Anthropogenic
- Biogenic



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 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;
 - High NO₂ concentrations cause lethal pulmonary edema with latency up to 72 hours. N₂O reduces hemoglobin concentration in blood.
 - Changes in lung functions due to exposure to NO₂ in healthy persons > 4 mg/m³, asthmatics ≥ 0.2 , children 0.09 – 0,5 mg/m³.

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 that is important as greenhouse gas; less important gases are N_2O_3 and N_2O_5 ;
- In practice the sum is re-calculated to NO_2 ;
- The NO_x formation especially in energetic processes (combustion), during nitric acid production and during incineration in diesel engines;
- During combustion processes, the formation of NO dominates (90 – 99 %), the second in order is NO_2 (for liquid fuels 1 – 10 % of the total, for solid fuels 1 – 5 % of the total).
- Secondarily in the smoke plume above the stack a part of NO is oxidized to NO_2 ;
- During water vapour 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

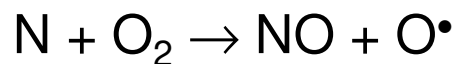
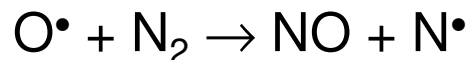
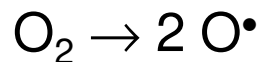
■ Basic mechanisms of NO_x formation

- Generating NO_x is conditioned by high temperatures, with the exception of several industrial chemical processes;
- 3 mechanisms participate in NO_x formation during the incineration of fuels:
 - High-temperature NO_x
 - Fuel NO_x
 - Prompt NO_x
- Among chemical processes the most important role is played by nitric acid manufacture ⇒ see N₂O release in the lecture about GHGs;

Origin of nitrogen oxides emissions

■ High-temperature mechanism

- Oxidation of atmospheric N₂ at high temperatures (especially during combustion of all types of fuels);
- The reaction rate depends on temperature, concentration of nitrogen, concentration of oxygen and upon the residence time;
- The necessary condition is reaching the temperature of oxygen dissociation: O₂ → 2O•;
- The critical temperature for a fast increase of the reaction rate is approximately 1200 °C;
- The mechanism of oxidation is radical-based, however it may vary according to individual specific conditions;
- Example: Incineration of coal with excess of air:



Origin of nitrogen oxides emissions

■ High-temperature mechanism

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

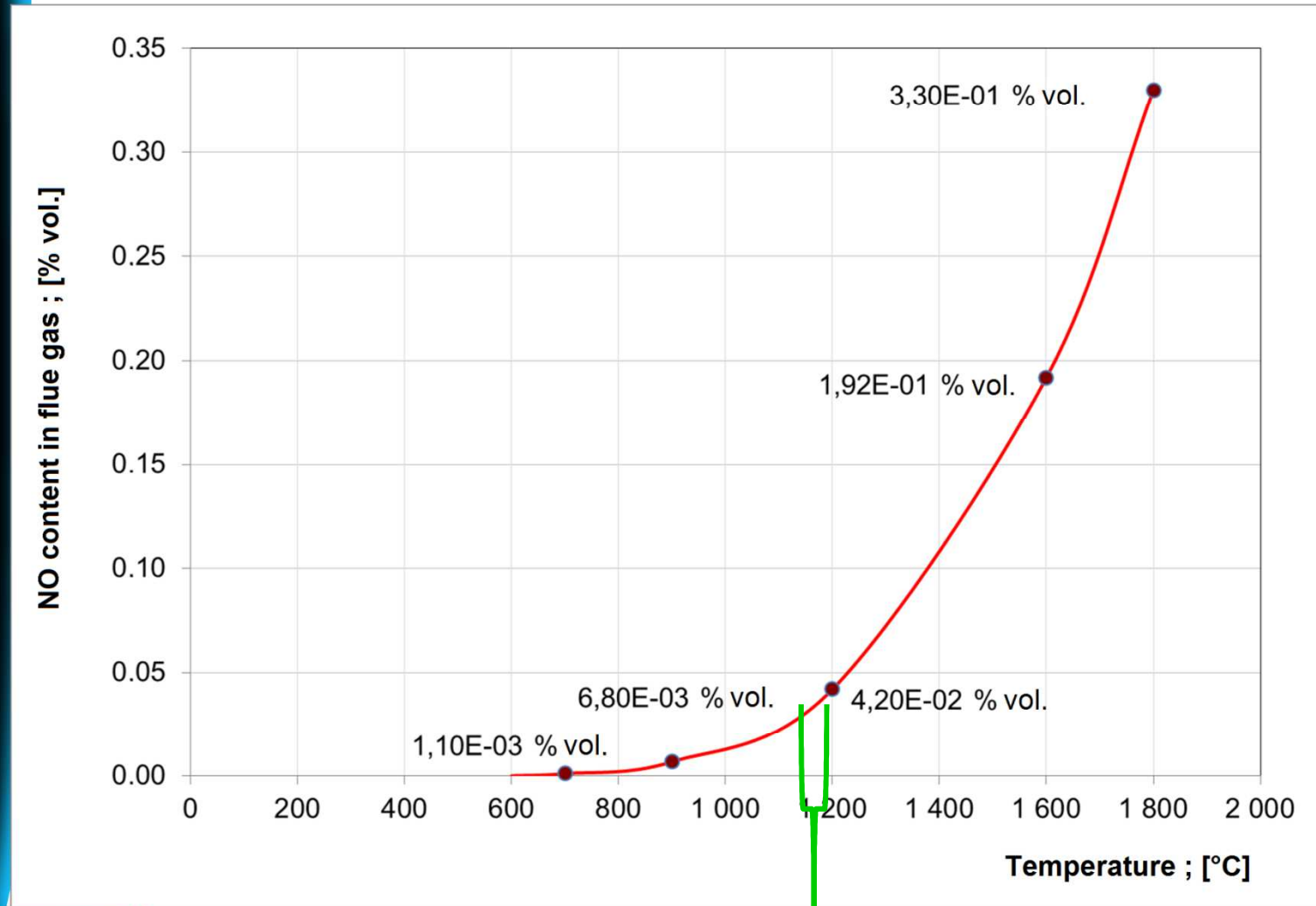
Lowering oxygen concentration (esp. in the high temperature region)

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- temperature mechanism

Origin of nitrogen oxides emissions

■ Fuel nitrogen oxides

- Formation from nitrogen contained in the fuel;
- The reaction requires high temperatures;
- Only the 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), the following particles then enter the reaction: N–H, N–C and $-C\equiv N$;
 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:

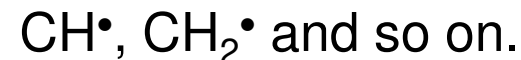
$$V = \frac{N_{\text{converted to NO}}}{N_{\text{bonded in organics}}}$$

Origin of nitrogen oxides emissions

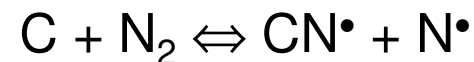
■ Prompt nitrogen oxides

- Less frequent mechanism of NO formation;
- Oxidation of air N₂ inside thin zone at the border of flame;
- The mechanism is conditioned by presence of gaseous hydrocarbons;
- The principle discovered by Fenimore:

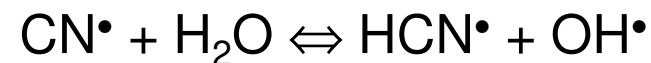
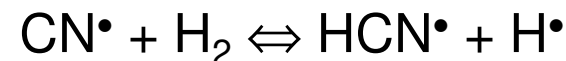
Initiation creation of hydrocarbons radicals:



Reaction of radicals with nitrogen:



Transformation of CN[•]

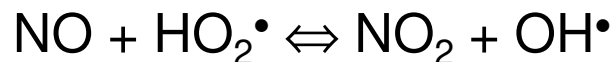


Oxidation of HCN[•] to NO (complicated mechanism depending on conditions).

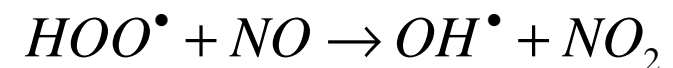
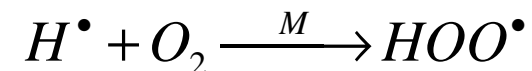
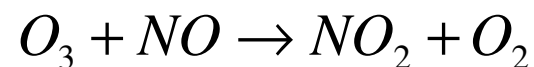
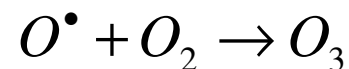
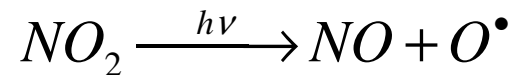
Origin of nitrogen oxides emissions

■ Primary, secondary and tertiary formation of NO₂

- NO₂ is produced by oxidation of NO;
- In standard burners NO₂, primarily generated inside the combustion chamber, represents max. 10 % of all NO_x;
- Primary production is determined by shock cooling of flue gas;
- The highest ratio of the primary NO₂ is detected in gas turbines:

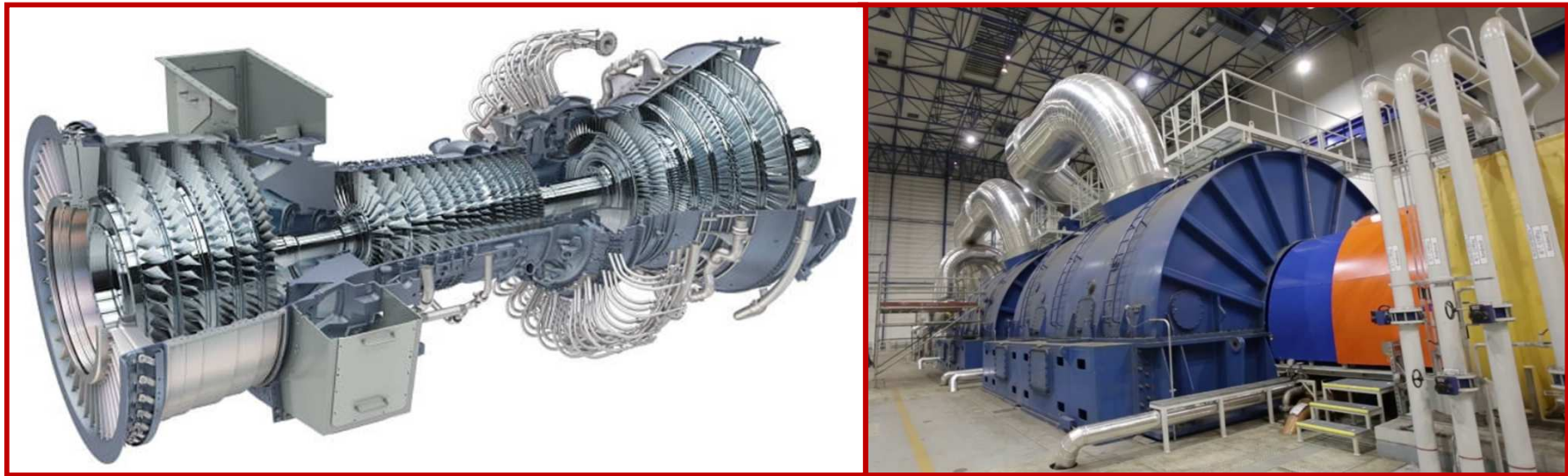


- Secondarily NO is oxidised to NO₂ in the vent and stack at the temperature < 65 °C and excess of air.
- Tertiary NO is converted into NO₂ in the outer environment by photochemical reactions in the outer atmosphere and influences the formation of tropospheric ozone:



Origin of nitrogen oxides emissions

- **Primary NO₂ formation**
 - The highest ratio of the primary NO₂ is detected in gas turbines:
(due to very rapid cooling of exhaust gases)



Atmospheric reactions of NO_x

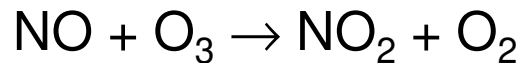
- **Homogenous reactions – reactions of the system NO-NO₂-O₃**

- The fundament of all tropospheric reactions occurring at daylight;

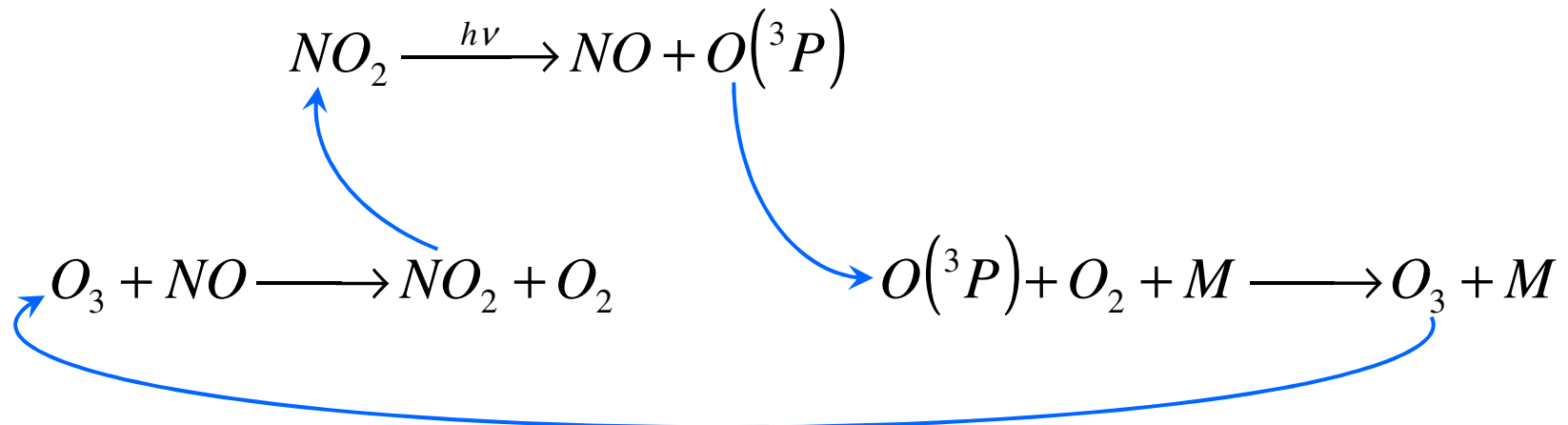
- Whereas in the flue gas vents oxidation takes part:



in the free atmosphere, the reaction with O₃ is kinetically preferred:



- When exposed to the sunlight the following cycle occurs:



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

Atmospheric reactions of NO_x

■ Homogeneous reactions – reactions of system NO-NO₂-O₃

- Photodissociation $NO_2 \xrightarrow{h\nu} NO + O(^3P)$ very fast \Rightarrow under zenith solar radiation 40° and decay halftime of NO₂ < 2 min
- oxygen atom in the base state O(³P) reacts with molecular oxygen also instantly;
- Regeneration reaction of a part of NO to NO₂ called “titration” also very fast;
- Result of the above cycle is the equilibrium between photodissociation of NO₂ and oxidation of NO by ozone.
- The photostationery state is established and is defined by the ratio of rate constants of photolysis of NO₂ and oxidation of NO:

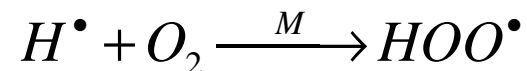
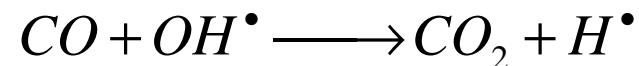
$$\frac{k_{\text{photolysis}}}{k_{\text{oxidation}}} = \frac{[NO] \cdot [O_3]}{[NO_2]} \quad [O_3] = \frac{k_{\text{photolysis}}}{k_{\text{oxidation}}} \cdot \frac{[NO_2]}{[NO]}$$

- Equilibrium concentration of ozone is given by ratio of NO₂ and NO concentrations.
- At night only oxidation of NO by ozone occurs, without subsequent photolysis of NO₂. (Details: photochemical smog)

Atmospheric reactions of NO_x

■ Homogeneous reactions – reactions of system CO-NO_x

- CO is released into the atmosphere by incomplete incineration and hydrocarbon oxidation;
- CO is low reactive but it can form a hydroperoxyle radical by reacting with a hydroxyle radical:



- The hydroperoxyle radical reacts subsequently with NO (see tertiary formation of NO₂) and regenerates hydroxyle radical.



- During a day NO₂ undergoes photodissociation as described in previous slides
- The termination reaction of all the cycles above is:

