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YOUTH AND SPORTS



ATMOSPHERIC CHEMISTRY

Lecture No.: 8

Organisation of study

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- 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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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)

N_2O



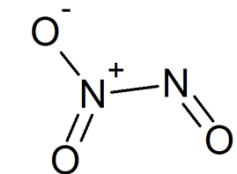
Nitric oxide

(nitrogen monoxide)

NO

Dinitrogen trioxide

N_2O_3

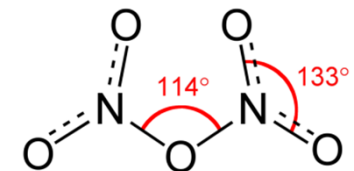


Nitrogen dioxide

NO_2

Dinitrogen pentoxide

N_2O_5



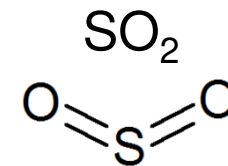
Note 1: Dinitrogen trioxide is formed only at low temperatures ($< 21\text{ }^\circ\text{C}$) by reversible reaction $\text{NO} + \text{NO}_2 \leftrightarrow \text{N}_2\text{O}_3$.

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

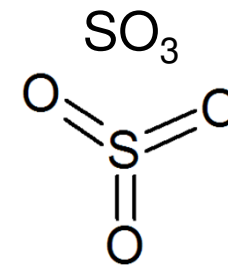
Acidic substances

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

Sulphur dioxide



Sulphur trioxide

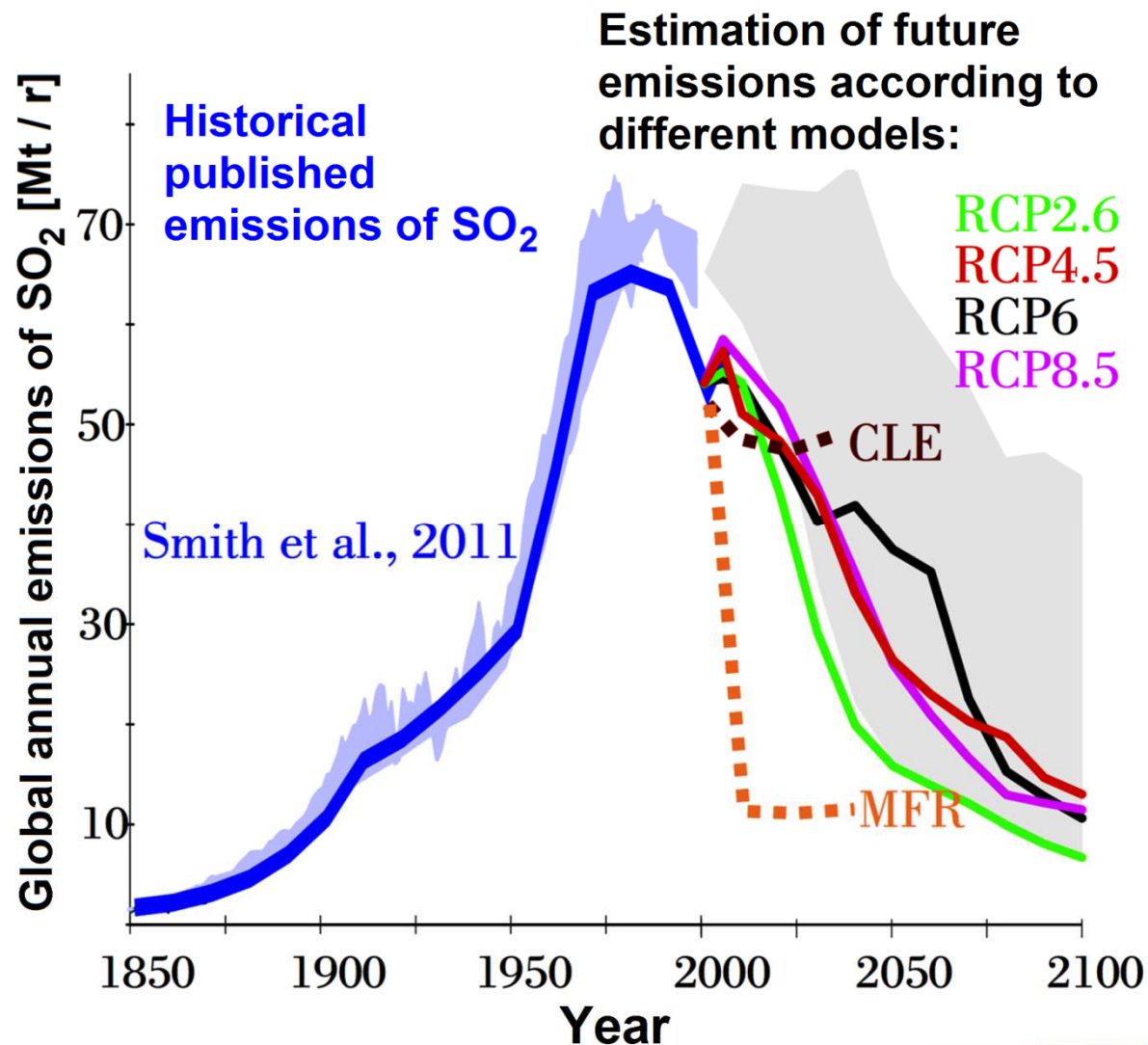


Origin of sulphur oxides emissions

- 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.).

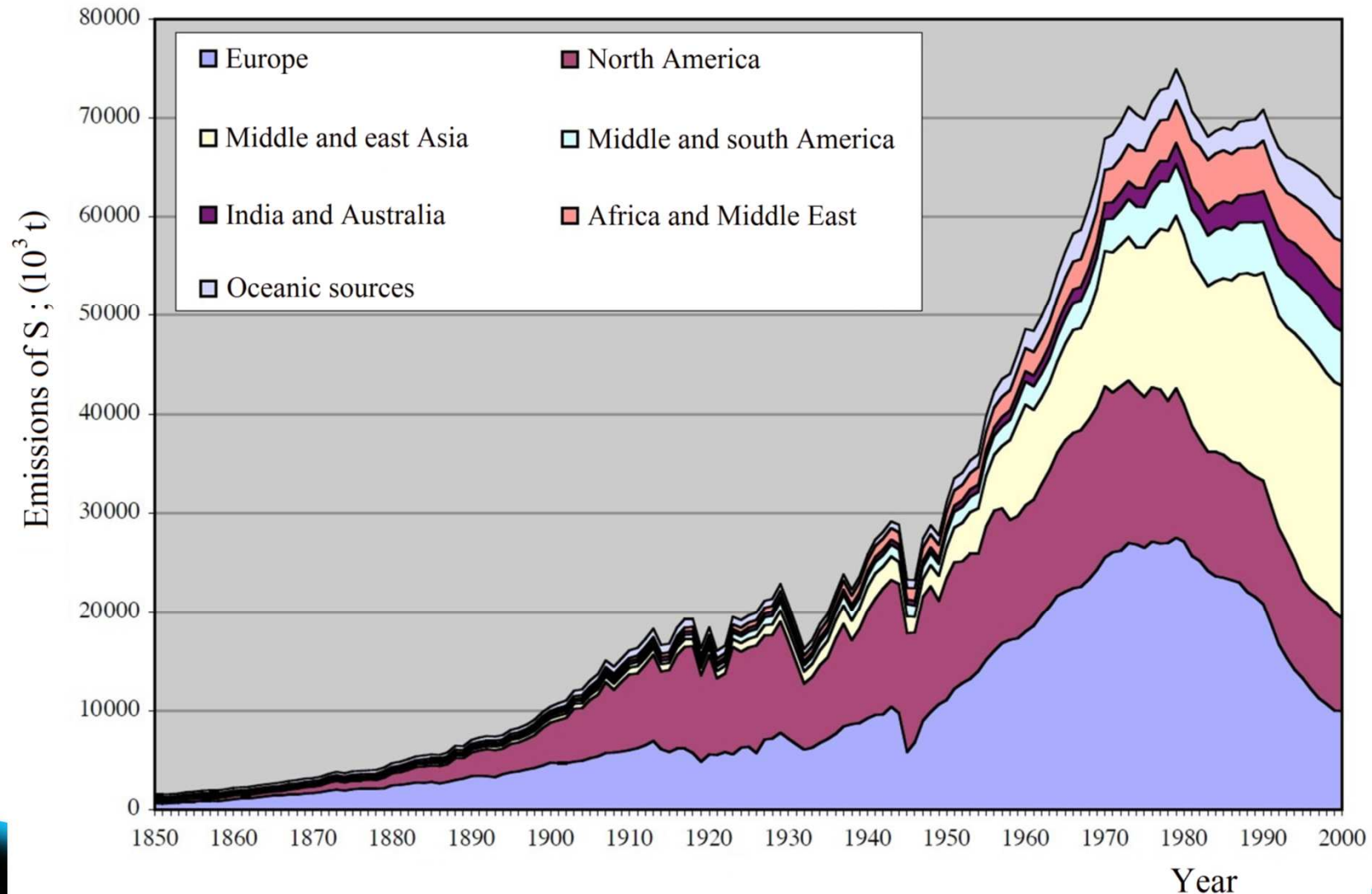
Origin of sulphur oxides emissions

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



Origin of sulphur oxides emissions

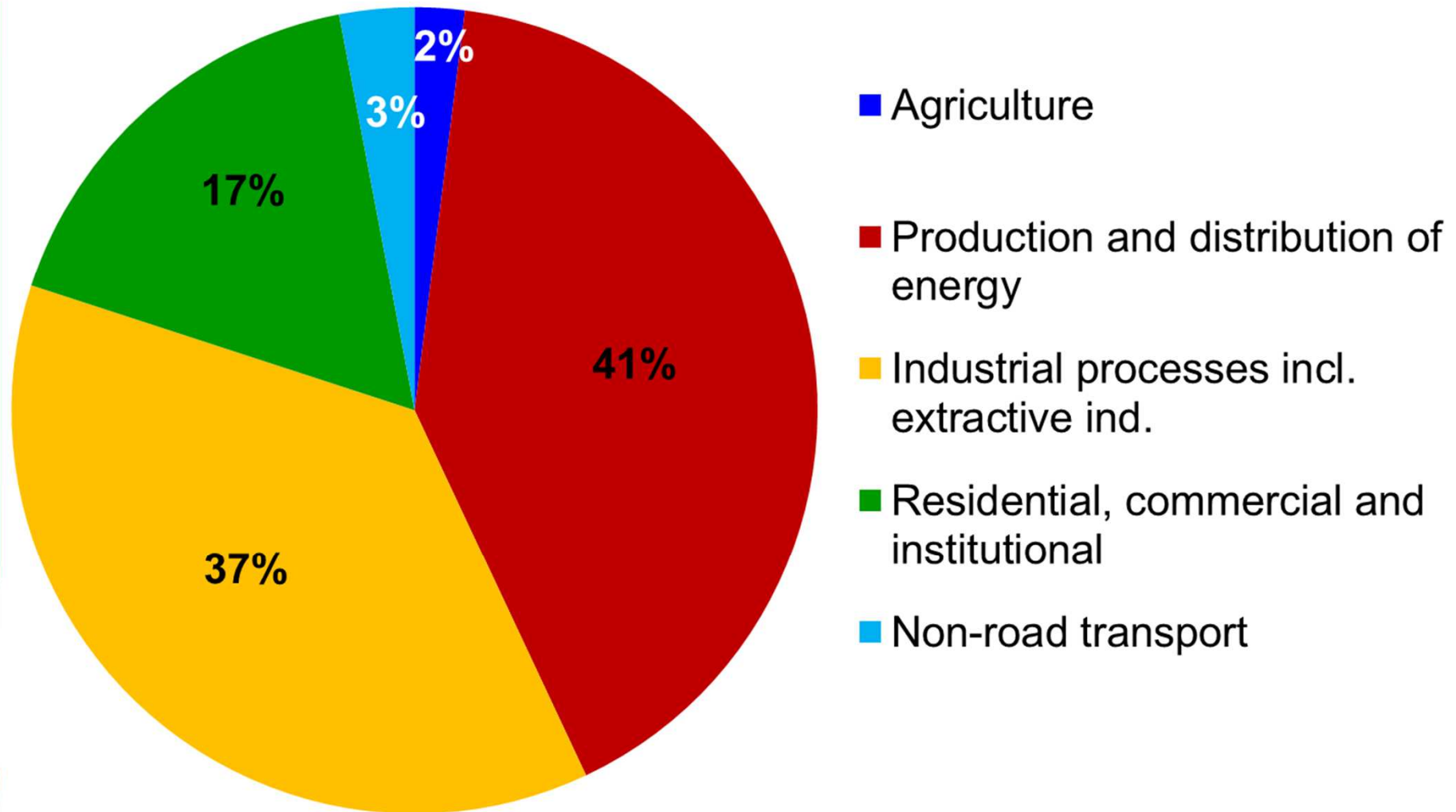
- Time-related evolution of sulphur oxides calculated for S (Source: Pacific Northwest National Laboratory)



Origin of sulphur oxides emissions

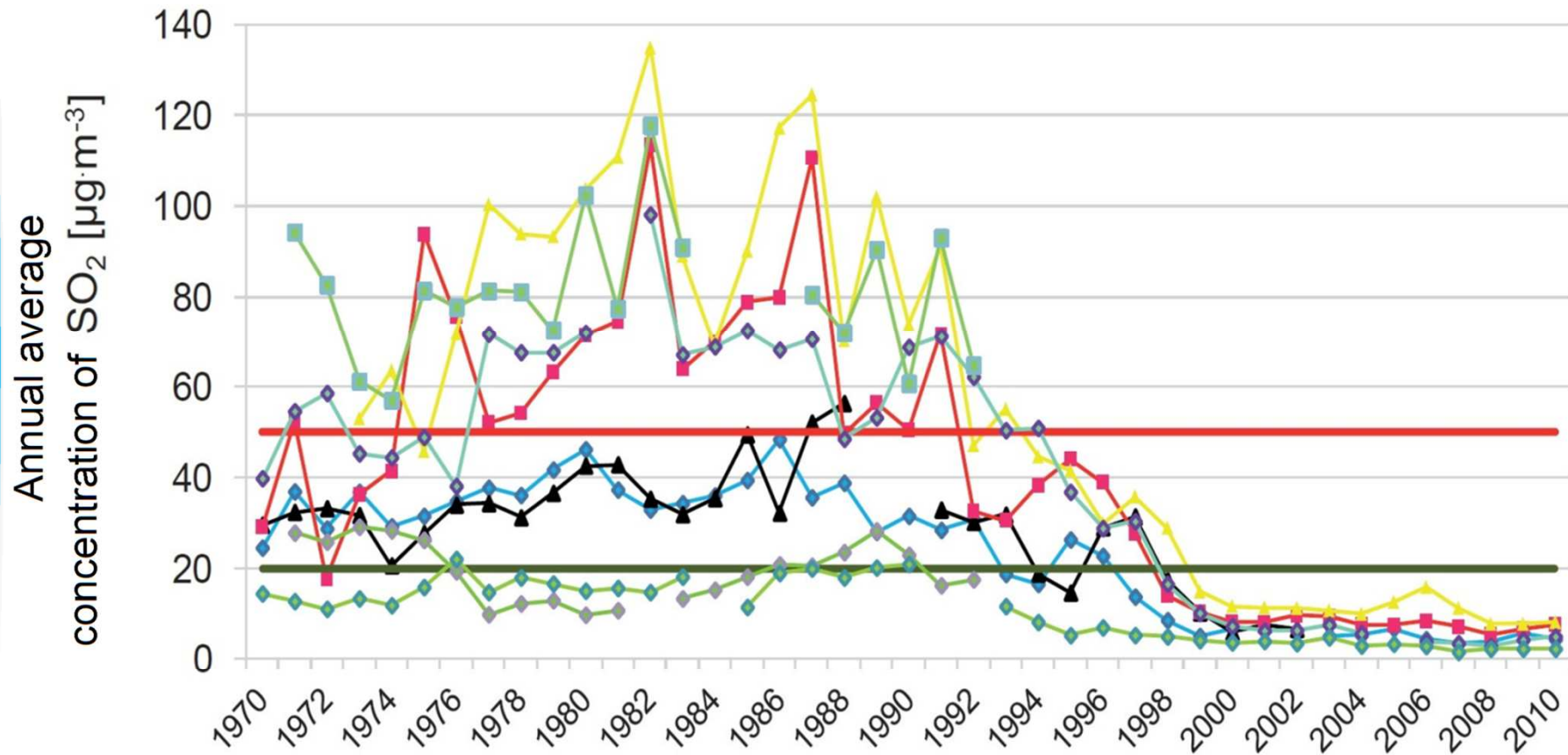
■ Distribution of SO₂ sources in EU in the year 2020

(Source: www.eea.europa.eu/publications/air-quality-in-europe-2022/sources-and-emissions-of-air)



Origin of sulphur oxides emissions

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



Monitoring station:

▲ Albrechtice/Karviná

■ Tušimice

— Imission limit for annual average concentration according to old national regulation

◆ Souš (Jizerské hory)

◆ Ostrava-Poruba

— Valid imission limit for vegetation protection

◆ Lysá hora (Beskydy)

◆ Milešovka (České Středohoří)

◆ Měděnec (Krušné hory)

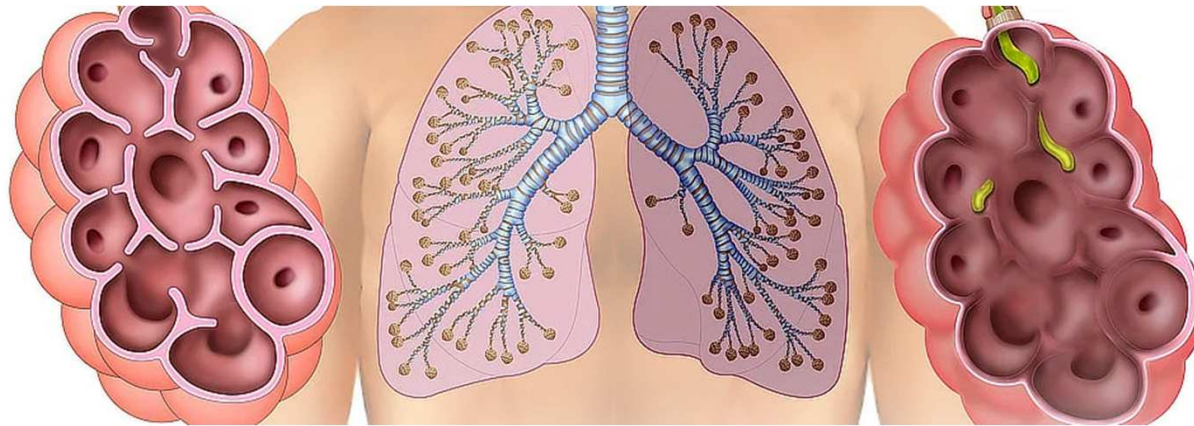
◆ Ústí n/L-Kočkov

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 ⇒ 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, acidified water seems to be clear and transparent ⇒ due to the lack of saprophytic microorganisms phytomass is not decomposed, but it is only accumulated at the bottom.

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 – Algal bloom = typical first symptom!

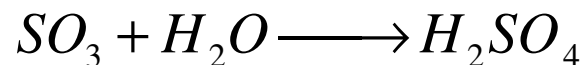
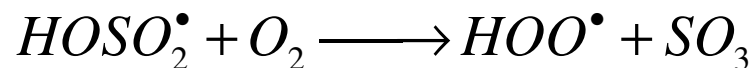
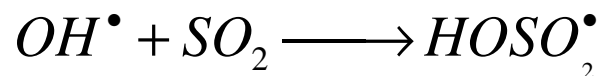


Reactions of sulphur oxides

- 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.

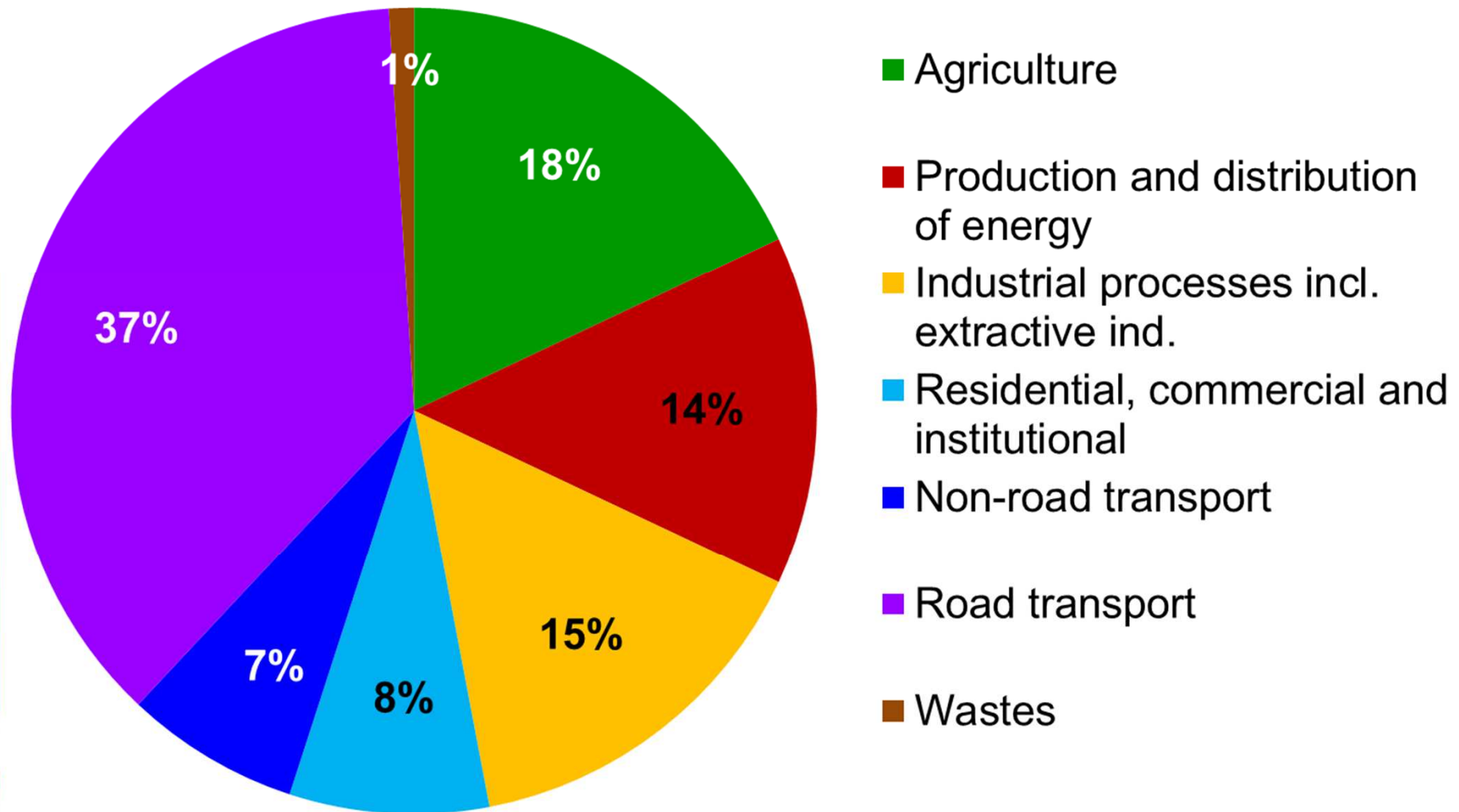
Origin of nitrogen oxides emissions

- **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

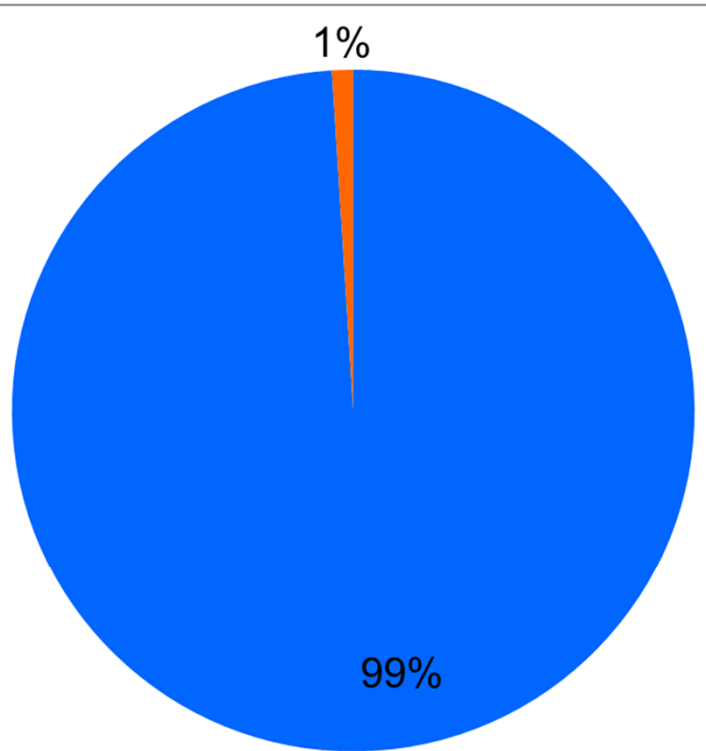
■ Distribution of sources in EU in the year 2020

(Source: www.eea.europa.eu/publications/air-quality-in-europe-2022/sources-and-emissions-of-air)



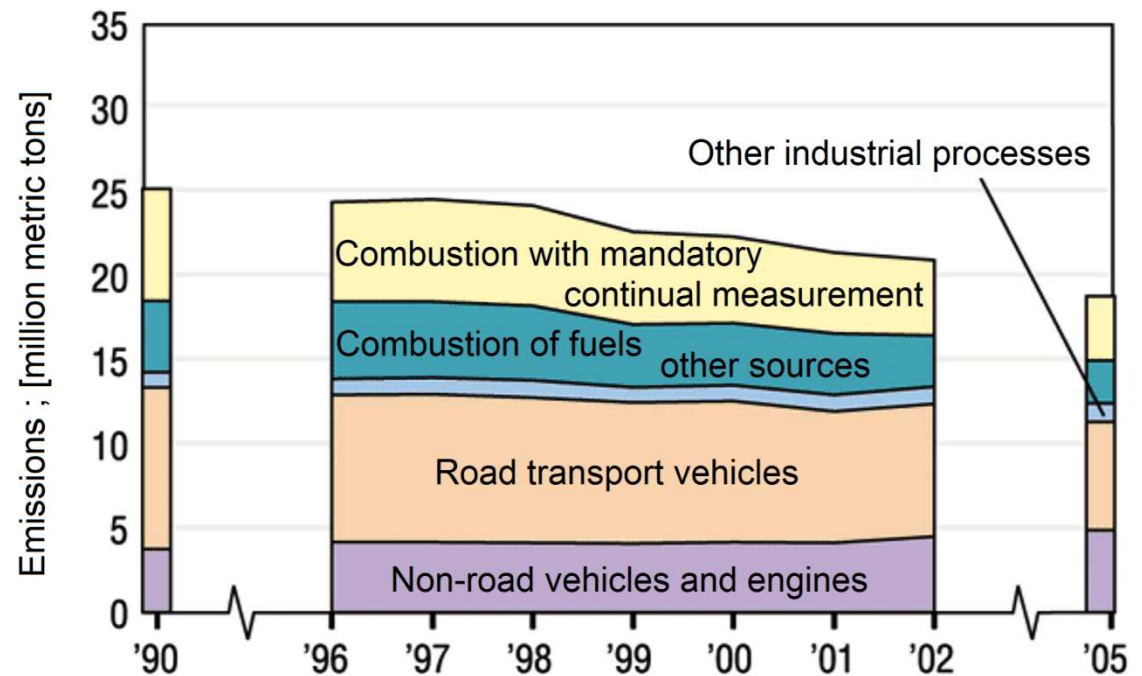
Origin of nitrogen oxides emissions

- **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

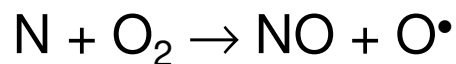
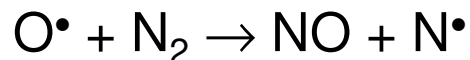
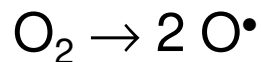
■ Basic mechanisms of NO_x formation

- 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:

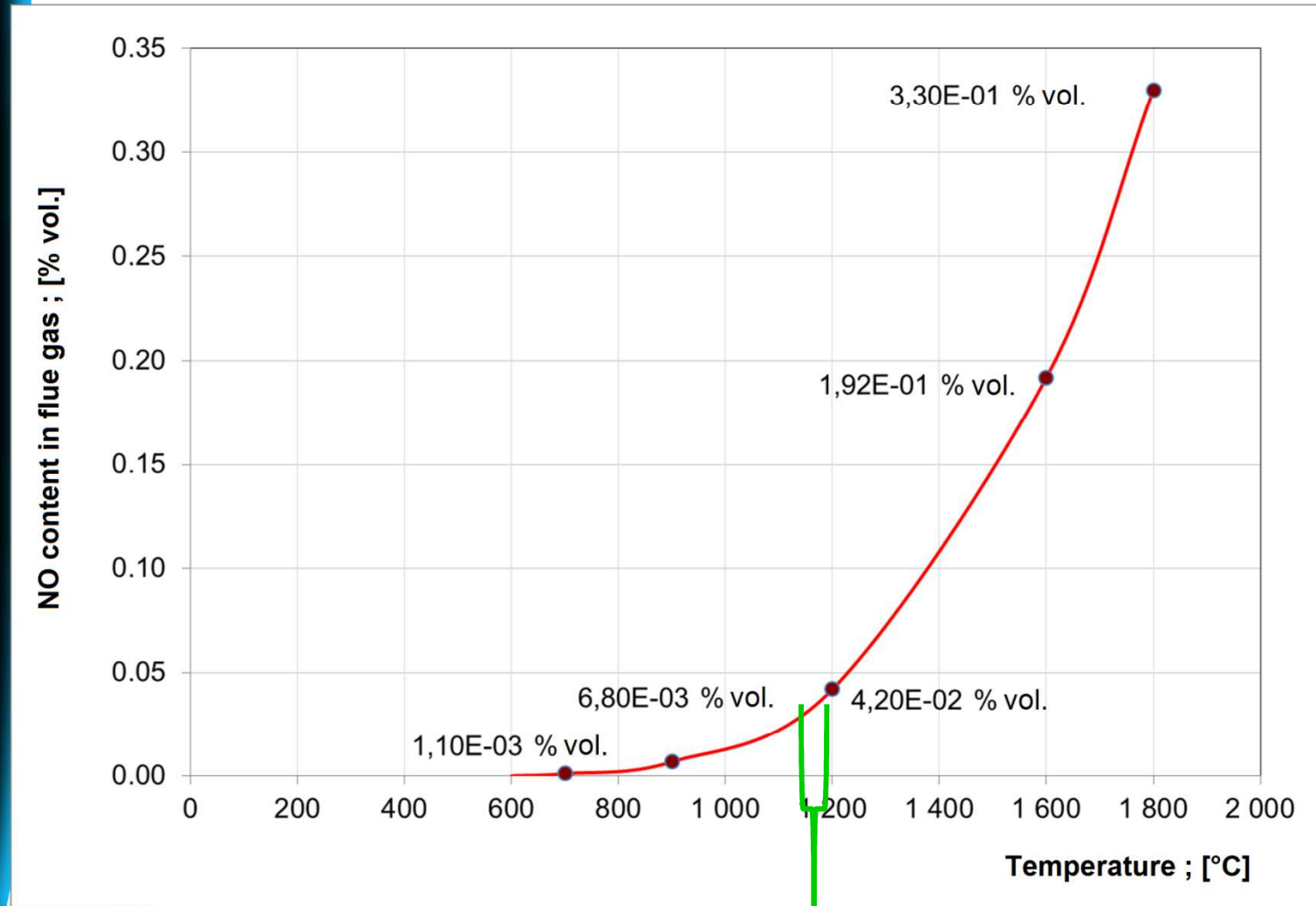
Lowering oxygen concentration (esp. in the high temperature region)

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 N₂;
- 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:

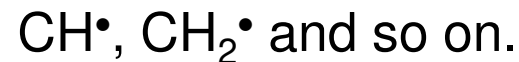
$$V = \frac{N_{\text{converted to NO}}}{N_{\text{bonded in organics}}}$$

Origin of nitrogen oxides emissions

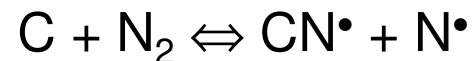
■ Prompt nitrogen oxides

- 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:

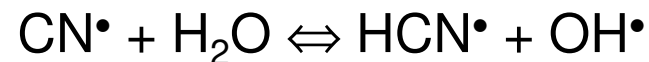
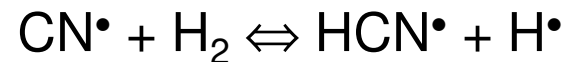
Initiation creation of hydrocarbons radicals:



Reaction of radicals with nitrogen:



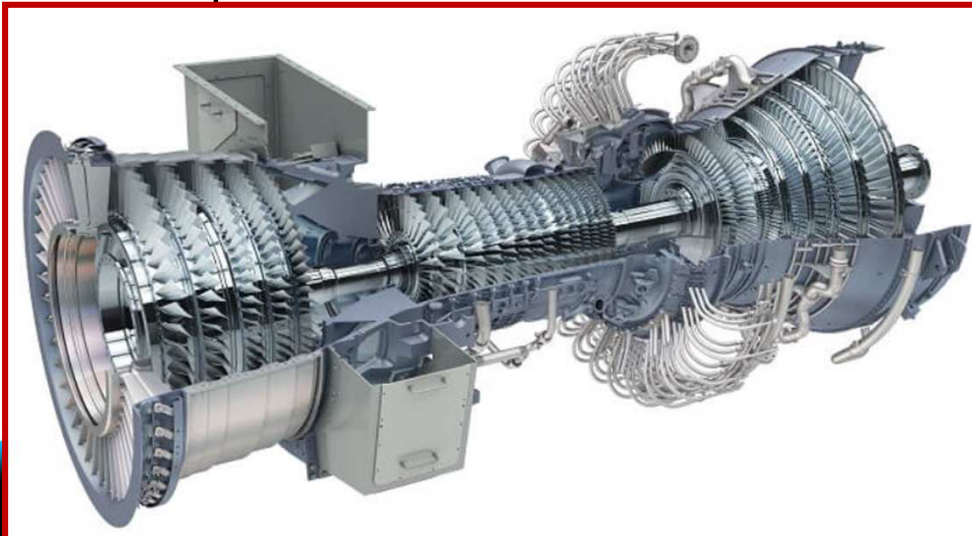
Transformation of CN[•]



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 biggest ratio of the primary NO₂ is detected in gas turbines:
$$\text{NO} + \text{HO}_2^\bullet \Leftrightarrow \text{NO}_2 + \text{OH}^\bullet$$
 - Secondarily NO is oxidised to NO₂ in the vent and stack at the temperature < 65 °C and excess of air.



Atmospheric reactions of NO_x

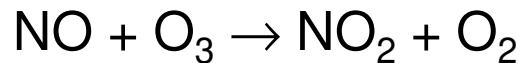
- **Homogenous reactions – reactions of the system NO-NO₂-O₃**

- The fundament of all tropospheric reactions occurring at daylight;

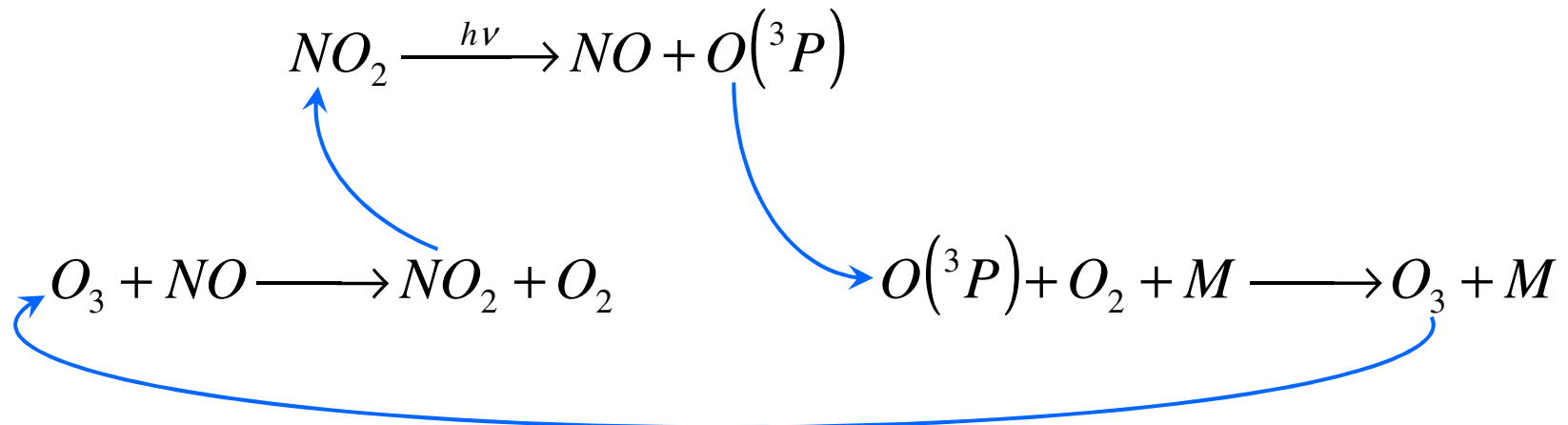
- Whereas in the flue gas vents oxidation takes part:



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:

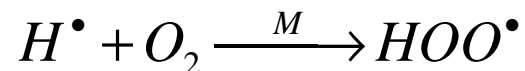
$$\frac{k_{\text{photolysis}}}{k_{\text{oxidation}}} = \frac{[NO] \cdot [O_3]}{[NO_2]} \quad [O_3] = \frac{k_{\text{photolysis}}}{k_{\text{oxidation}}} \cdot \frac{[NO_2]}{[NO]}$$

- 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:

