Department of Technologies and Installations for Waste Management

Emission and Transport of Air Pollutants

Lecture 1

Air pollution and its impact on environment and human health

1

References

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Clean, dry air components

Component	Percentage, %	
	by volume	by mass
nitrogen, N_2	78,084	75,527
oxygen, O_2	20,946	23,143
argon, Ar	0,934	1,282
carbon dioxide, CO_2	0,034	0,0456
neon, Ne	0,001818	0,00125
helium, He	0,000524	0,0000724
methane, CH_4	0,00015	0,0000775
krypton, Kr	0,000114	0,00033
wodór, H_2	0,00005	0,000348
nitric suboxide (I), N_2O	0,00003	0,000076
xenon, Xe	0,0000087	0,000039
ozon, O_3	0,000002	0,000006
nitrogen dioxide, NO_2	0,0000001	0,0000007

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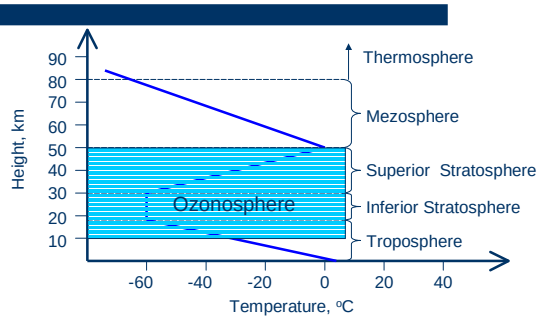
The Layers of the Atmosphere



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Sources of air pollutants

- **Natural sources**, e.g., volcanoes activity (sulfur, chlorine, ash particles), ocean spray, pollen, wildfire

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Sources of air pollutants

- **Anthropogenic sources**, e.g.,industrial, commercial, agricultural, transportation activities

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Sources of air pollutants

- **Anthropogenic sources**,

- waste deposition in landfills,

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Sources of air pollutants

- **Anthropogenic sources:**

- burning different kinds of fuel: power plants, furnaces and other types of fuel-burning heating devices, waste incinerators

CHP plant in Warsaw.

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Pollutant Emission

- **Primary gaseous pollutants:**
- sulfur compounds (e.g., SO_2, H_2S)
- nitrogen compounds (e.g., NO, NH_3)
- carbon compounds (e.g., CO, hydrocarbons HC: BaP, benzen,)
- halogen compounds (e.g., fluorides, chlorides, bromides)

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Pollutant Emission

Primary gaseous pollutants:

NO composes 95% of produced by burning of fuel NO_x

Mechanizms of NO formation:

1. **Thermal NO**
2. **By N_2O mechanizm**
3. **Fuel NO**
4. **Prompt NO**

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Pollutant Emission

1. Thermal NO – the reaction between oxygen and nitrogen in the combustion air at temperatures >1400ºC in oxidising atmospheres; dependent on the flame temperature and residence time at high temperatures; predominantly formed in the flame envelope

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Pollutant Emission

Zeldowicz mechanizm:

$$O_2 + M \leftrightarrow O + O + M$$

$$O + N_2 \xrightarrow{k_1} NO + N$$

$$N + O_2 \xrightarrow{k_2} NO + O$$

$$N + OH \xrightarrow{k_3} NO + H$$

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Pollutant Emission

2. By N_2O mechanizm: t>1200ºC, λ>1

$$N_2 + O + M \rightarrow N_2O + M$$

$$N_2O + O \rightarrow NO + NO$$

$$N_2O + O \rightarrow N_2 + O_2$$

With presence of H_2O dissociation products:

$$N_2O + H \rightarrow NO + NH$$

$$N_2O + H \rightarrow N_2 + OH$$

$$N_2O + OH \rightarrow N_2 + HO_2$$

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Pollutant Emission

3. Fuel NO – the oxidation of fuel-bound nitrogen compounds at temperatures **>750ºC**; dependent on the nitrogen content of the fuel, the amount of nitrogen evolved at high temperatures during devolatilisation, and the burner design. The burner design affects the rate of mixing between the combustion air and the volatile nitrogen. This in turn affects the degree of conversion of volatile nitrogen to NO.

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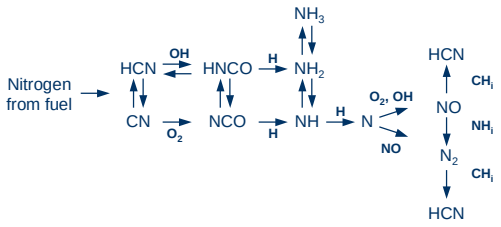
Pollutant Emission



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Pollutant Emission

4. Prompt NO – the fixation of atmospheric (molecular) nitrogen by hydrocarbon fragments in reducing atmospheres (λ<1); formed in the early part of all coal flames, in the ignition region, at t<750ºC

$$CH + N_2 \rightarrow HCN + N$$

$$CH_2 + N_2 \rightarrow HCN + NH$$

$$HCN + O \rightarrow NCO + H$$

$$NCO + O \rightarrow NO + CO$$

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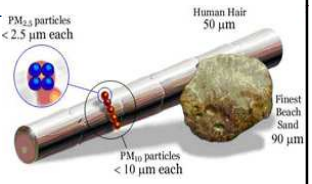
Pollutant Emission

- **Primary particulate matter:**

- air ions, with diameters much smaller than 0,1 μm
- fine particles between 0,1 – 2,5 μm
- PM_{10} - particles with diameters 10 μm or less
- Carbonaceous material, made of soot, including elemental carbon and organics



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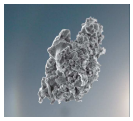
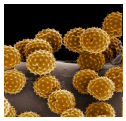
Pollutant Emission

- **Primary particulate matter:**
- Particles from automotive emission, mostly lead in the form of oxide, sulfate or bromochloride
- Particles containing light and heavy metals
- Large particles, such as **dust** and sand
- Viable particles, such as **pollen**, **micro-organisms** and insects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Pollutant Emission

- **Primary aerozols (1-100 μm)**
  - directly emitted into the atmosphere e.g.,fugitive dust

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Pollutant Emission

- **Secondary gaseous pollutants O_3:**

- Ozon is nalurally generated in the stratosphere by photochemical reaction in which high-energy solar radiation breaks the oxygen molecules, i.e.

$$O_2 + h\nu \rightarrow 2O^{\bullet}$$

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

- anthropogenic generation of O_3 is process in which NO_2 is photochemically dissociated by

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

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

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Pollutant Emission

- **Secondary gaseous pollutants NO_2:**

– is formed in combustion exhaust gases by

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

- by O_3 consumption (at night)

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

- NO – to -NO_2 conversion, in a polluted atmosphere, is dominated by the essential role of carbon - containing species

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Pollutant Emission

- **Secondary gaseous pollutants: NO_2**

The simplest carbon-containig species is CO, whose reaction with NO_x is summarized in reactions:

1. $NO_2 + h\nu \rightarrow NO + O$
2. $O + O_2 + M \rightarrow O_3 + M$
3. $O_3 + NO \rightarrow NO_2 + O_2$
4. $O_3 + h\nu \rightarrow O(^1D) + O_2$
5. $O + M \rightarrow O + M$
6. $O(^1D) + H_2O \rightarrow 2OH^{\bullet}$
7. $CO + OH^{\bullet} \rightarrow CO_2 + HO_2^{\bullet}$
8. **$HO_2^{\bullet} + NO \rightarrow NO_2 + OH$**
9. $OH^{\bullet} + NO_2 \rightarrow HNO_3$

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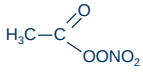
Pollutant Emission

- **Secondary gaseous pollutants PANs:**
- Peroxyacyl nitrates, or PANs
- Most common **PAN** (*peroxyacetyl nitrate*):



Hydrocarbons + O_2 + NO_2 + hν → $CH_3COOONO_2$

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Pollutant Emission

- **Secondary particulate matter:**
  - sulfates, SO_4^{2-}
  - nitrates, NO_3^-
  - organic particles

Secondary particulate matter consist mainly of fine particles (smaller than 2,5 μm).

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Pollutant Emission

- **Secondary inorganic aerosols are composed of:**
  - gas phase: NH_3, HCl, HNO_3, H_2O
  - liquide phase: H_2O, NH_4^+, SO_4^{2-}, NO_3^-,H^+, Na^+, Cl^- HSO_4^-, H_2SO_4
  - solide phase: Na_2SO_4, $NaHSO_4$, NaCl, $NaNO_3$, NH_4Cl, NH_4NO_3, $(NH_4)_2SO_4$, NH_4HSO_4, $(NH_4)_3H(SO_4)_2$

Secondary areosols consist mainly of particles in size from 0,01 μm to 2 μm.

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Secondary pollution Synergism

- **Synergy** - an effect of the interaction of the actions of two agents such that the result of the combined action is greater than expected as a simple additive combination of the two agents acting separately.

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Synergy effect

- Los Angeles smog
- California smog
- London smog
  In1952 (4000 of deaths)

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Synergy effect

- **Smog** is a kind of air pollution; the word "smog" is a portmanteau of smoke and fog. **Classic smog** results from large amounts of coal burning in an area caused by a mixture of smoke and sulfur dioxide.

  Modern smog does not usually come from coal but from vehicular and industrial emissions that are acted on in the atmosphere by sunlight to form secondary pollutants that also combine with the primary emissions to form **photochemical smog**.

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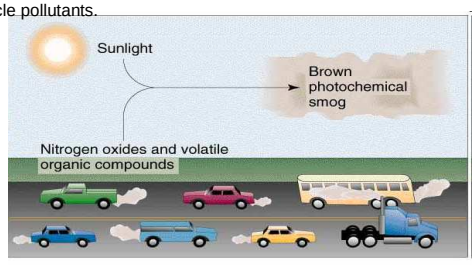
Photochemical smog

Photochemical smog, or brown haze, occurs where sunlight acts on vehicle pollutants.



(b) Photochemical smog

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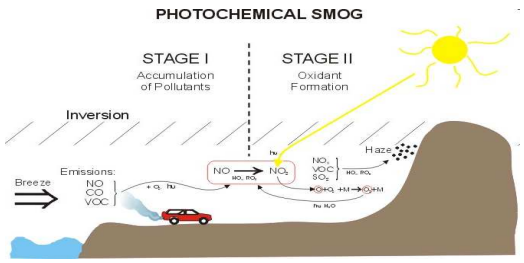
Photochemical smog



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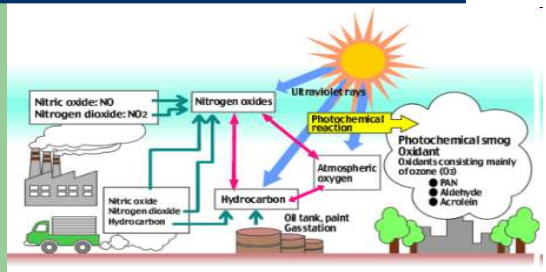
Photochemical smog



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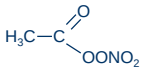
Photochemical smog

Simplified global reaction:

NO_x+ NMVOC+CO+CH_4+hν ⟶ O_3+PAN+HCHO+X

PAN (*peroxyacyl nitrate*)
– azotan nadtleno-acetylowy



HCHO - formaldehyde
X- other organic reaction products

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Acid rain – aerosol pollution

- Acid rain is caused by emissions of nitrogen, and sulfur oxides which react with the water molecules in the atmosphere to produce acids.

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Acid rain

In gas phase:

$SO_2 + OH\cdot \rightarrow HOSO_2\cdot$

$HOSO_2\cdot + O_2 \rightarrow HO_2\cdot + SO_3$

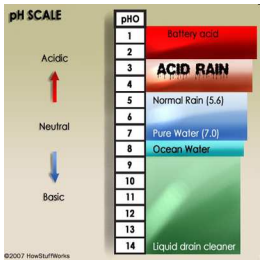
$SO_3\ (g) + H_2O\ (l) \rightarrow H_2SO_4\ (l)$

$NO_2 + OH\cdot \rightarrow HNO_3$
and
$NO_2 + O_3 \rightarrow NO_3 + O_2$
$NO_3 + HO_2\cdot \rightarrow HNO_3 + O_2$

Global reactions:

$2SO_2 + H_2O + O_2 \quad 2H_2SO_4$

$4\ NO_2 + 2H_2O + O_2 \longrightarrow 4HNO_3$



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Transport of Air Pollutants

Emissions of sulfur dioxide and nitrogen oxides react with the hydroxyl radicals and water vapor in the atmosphere to form their respective acids, which come back down either as dry acid deposition or, mixed with water, acid precipitation.

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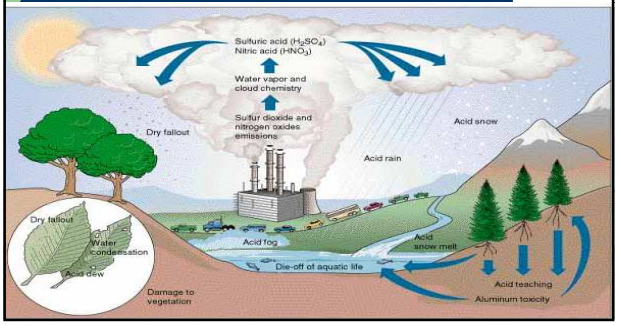
Transport of Air Pollutants



Effects of Air Pollution

- Air pollution can cause number of health hazards to human beings, animals, birds, in addition to causing number of deleterious effects on earth's atmosphere as well as vegetation and even on some buildings.
- The effects of air pollution have no limitations or country boundaries. They can extend to any adjoining country or even far off country from the country of origin.

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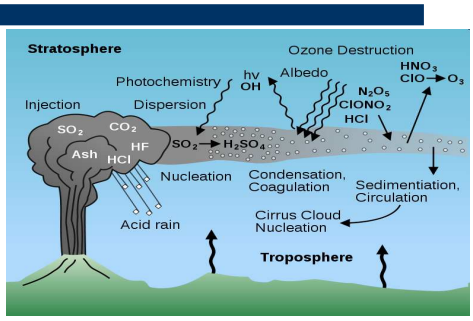
Transport of Air Pollutants

Schematic of volcano injection of aerosols and gases



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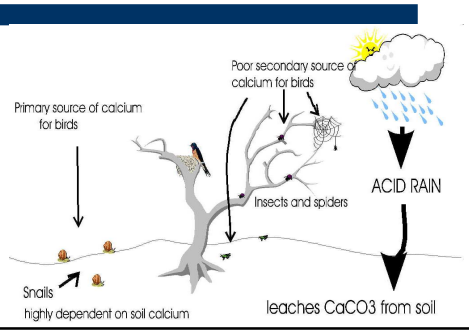
Environmenlal effects of Acid rain



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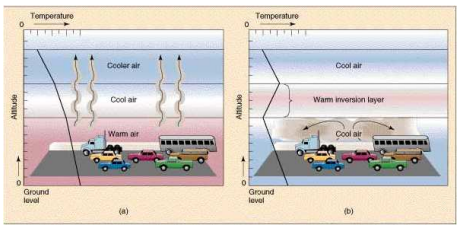
Transport of Air Pollutants

(a)Normally, air temperatures are highest at ground level and decrease at higher elevations. (b) A temperature inversion is a situation in which a layer of warmer air overlies cooler air at ground level.



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PANs impact on human health and environment

- **PANs** are powerful respiratory and eye irritants present in photochemical smog. At concentrations of only a few parts per billion they cause eye irritation. At higher concentrations they cause extensive damage to vegetation. Both PANs and their chlorinated derivates are said to be mutagenic, as they can be a factor causing skin cancer.

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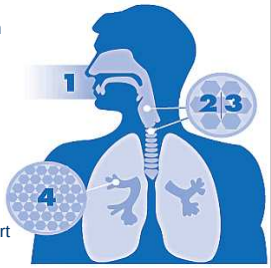
Particulate matter impact on human health

1 **Particulate matter** enters our respiratory (lung) system through the nose and throat,

2/3 The larger particulate matter (PM_{10}) is eliminated through coughing, sneezing and swallowing,

4 $PM_{2.5}$ can penetrate deep into the lungs. It can travel all the way to the alveoli, causing lung and heart problems, and delivering harmful chemicals to the blood system.



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Particulate matter impact on human health

- **Particulate matter -** California wildfires of 2008

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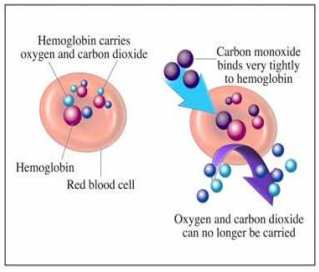
Carbon monoxide impact on human health

- **Carbon monoxide (CO)** is a colourless, odorless, tasteless, toxic gas
- Breathing CO reduces the blood's ability to carry oxygen. In severe cases, CO **can cause death**.
- It has strong affinity to combine/bind with haemoglobin in blood to form carboxyhaemoglobin, which reduces oxygen carrying capacity of blood to cause headache,nausea, asphyxiation and fainting



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PAHs

- Often, PAHs consist of three or more fused benzene rings containing only carbon and hydrogen.
- PAHs are solids with low volatility at room temperature. They are relatively insoluble in water, and most can be photo-oxidized and degraded to simpler substances.

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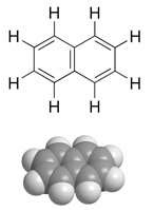
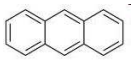
PAHs

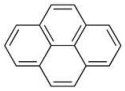
Naphthalene



Anthracene



Pyrene



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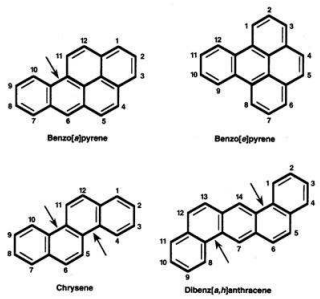
PAHs

- PAHs are a class of organic compounds produced by incomplete combustion or high-pressure processes.
- PAHs form when complex organic substances are exposed to high temperatures or pressures.



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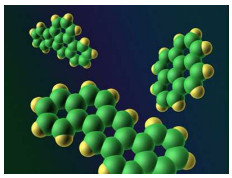
PAH's impact on human health

- Health effects from PAH's include cancer, adverse reproductive effects, lung damage, and kidney damage.



Hydrocarbon	M, g/mol	wskaźnik równoważny BaP
Benzo(a)piren	252	1
Dibenzeno(a,h)antracen	278	1,4
Benzo(g,h,i)perylen	276	1
Chryzen	228	0,26
Benzo(e)piren	252	0,05
Indeno(1,2,3,-c,d)piren	276	0,1
Fluoranten	202	0,034
Benzo(a)antracen	228	0,033

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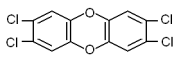
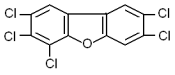
Dioxins

Dioxins occur as by-products in the manufacture oforganochlorides, in the incineration of chlorine-containing substances such as PVC (polyvinyl chloride), in the bleaching of paper, and from natural sources such as volcanoes and forest fires.



2, 3, 7, 8 – tetrachlorodibenzeno-p-dioxin (2,3,7,8 – TCDD)



2, 3, 6, 7, 8 – pentachlorodibenzeno-p-furan (2,3,6,7,8 – PCDF)

There is 75 types of dioxins and 135 types of furans

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Dioxins impact on human health

●**Dioxin**
From 2004 TCDD hasn't been concidered carcinogenic.

Chloracne on the face and neck on an herbicide production worker

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Carbon dioxide impact on GHE

- CO_2 does not show adverse effects to the earth ecology,
- More CO_2 is emitted by antropogenic processes than any other substance
- CO_2 adsorbs electromagnetic radiation at a wavelength about 15 μm, which corresponds to the maximum intensity of the earth radiation
- In the last 100 years CO_2 level in the atmospher rised, higher CO_2 in atmosphere is blame for global warming (rise in temperature).

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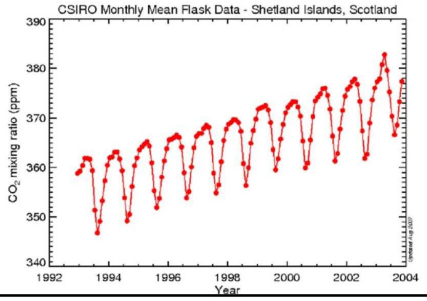
Changes of concentration of CO_2



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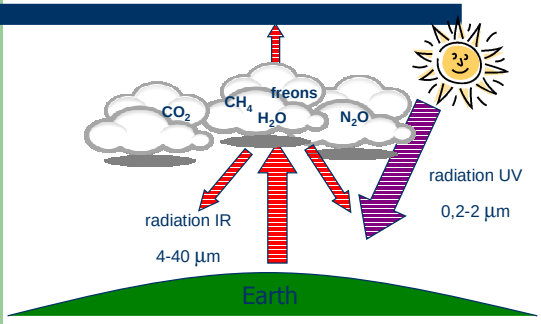
Green house effect



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Green house effect

United Nations Framework Convention on Climate Change -1992 , http://unfccc.int

Kyoto Protocol to UNFCCC– 1997:
Article 3 – The Parties included in Annex 1(Poland) shall ensure that their aggregate anthropogenic carbon dioxide equivalent emissions of the greenhouses gasses don't exceed their assigned amounts (for Poland **94%,** percentage of base year of period), with a view to reducing their overall emission of such gasses **by at least 5 per cent below 1990 levels** in the commitment period 2008 -2012.

Article 6 – Any Party included in Annex 1 may transfer to, or acquire from, any other such Party emission reduction units resulting from projects aimed at reducing antropogenic removals of greenhouse gases (**emissions trading**)

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Green house effect – Influence of gases on GHE

Gases	Gas contribution on GHE, %
H_2O (clouds, water vapour)	80-94
CO_2	2-5
O_3	2-4
CH_4	1-2
Others	1-9

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Green house effect - on the other hand

- The earth's temperature is mainly controlled by variations in solar radiation
- The effect of CO_2 increasing is a consequence of rise of earth temperature, not the opposite . Rise of earth temperature cause (with some delay) rise of released from the oceans CO_2.
- Total global emmision of CO_2 is about 2 900 mld Mg, antropogenic production is about 29 mld Mg CO_2 it is (0,02 -0,05) %,
- Homework : You tube: Great Swindle – the movie.

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Question for exam:

1. Give examples of primary gaseous and particulate matter pollutans
2. Mechanisms of NO formation, including the conditions
3. What is a synergy effect?
4. What is a london smog?
5. What is a photochemical smog/ Describe its mechanism.
6. Describe negative influence of CO on human being
7. Draw TCDD and point its adverse effect on human being
8. Give some examples of PAH.
9. Write down some reactions of acid rain formation
10. What is Green House Effect? What are arguments for and against the main influence of CO_2 on GHE?
11. What are two main resolutions of *Kyoto Protocol*?

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