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# **EVIRONMENTAL EFFECTS OF FOSSIL FUEL COMBUSTION**

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#### Environmental effects of fossil fuel combustion

Fossil fuel which include, natural gas, petroleum, shale oil and bitumen are the main source of heat and electrical energy. All these fuels contain beside major constituents (carbon, hydrogen, oxygen) other materials as metal, sulfur and nitrogen compounds. During the combustion process different pollutants as fly ash, sulfur oxides (SO<sub>2</sub> and SO<sub>3</sub>), nitrogen oxides (NO<sub>x</sub> = NO<sub>2</sub> + NO) and volatile organic compounds are emitted. Fly ash contain different trace elements (heavy metals) Gross emission of pollutants is tremendous all over the world. These pollutants are present in the atmosphere in such conditions that they can affect man and his environment.

Air pollution caused by particulate matter and other pollutants not only acts directly on environment but by contamination of water and soil leads to their degradation. Wet and dry deposition of inorganic pollutants leads to acidification of environment. These phenomena affect health of the people, increase corrosion, destroy cultivated soil and forests. Most of the plants, especially coniferous trees are not resistant to sulfur and nitrogen oxides. Following longer exposure leaves wither and fall. Widespread forest damage has been reported in Europe and North America regions. Many cultivated plants are not resistant to these pollutants either especially in the early period of vegetation.

The mechanisms of pollutants transformation in atmosphere are described by environmental chemistry. An important role in these transformations plays photochemistry.  $SO_2$  and  $NO_x$  are oxidized and sulfuric and nitric acids are formed in presence of water vapors, fog and droplets.

Other problem discussed connected with human activities is emission of volatile organic compounds to the atmosphere. These emissions cause stratospheric ozone depletation, ground level photochemical ozone formation, toxic or carcinogenic human health effects, enhancing the global greenhouse effect, accumulation and persistence in environment.

Wet flue gas desulfurization (FGD) and selective catalytic reduction (SCR) can be applied for flue gas treatment and SO<sub>2</sub> and NO<sub>x</sub> emission control.

#### Ekologiczne skutki spalania paliw kopalnych

Paliwa kopalne (węgiel, ropa naftowa, gaz, łupki bitumiczne) są głównymi źródłami energii cieplnej i elektrycznej. Wszystkie te paliwa, poza głównymi składnikami, jak: węgiel, wodór czy tlen, zawierają także związki metali, siarki i azotu. Podczas procesu spalania zanieczyszczenia takie, jak: pył, tlenki siarki (SO<sub>2</sub> i SO<sub>3</sub>), tlenki azotu (NO<sub>x</sub> = NO + NO<sub>2</sub>) oraz lotne związki organiczne emitowane są do atmosfery. Emitowane pyły zawierają różne pierwiastki śladowe, m.in. metale ciężkie. Zanieczyszczenia te obecne są w środowisku w takich ilościach, że mogą wpływać na zdrowie człowieka i stan środowiska naturalnego.

Powodują one, poza zanieczyszczeniem atmosfery, również zanieczyszczenie gleby i wód, prowadząc do ich degradacji. Mokry i suchy opad zanieczyszczeń nieorganicznych prowadzi do zakwaszenia środowiska, powodując erozję, niszcząc ziemie uprawne oraz lasy. Większość roślin, szczególnie drzew iglastych, nie jest odpornych na działanie tlenków azotu i siarki i powstających z nich kwasów. W rezultacie dłuższej ekspozycji liście żółkną i opadają. Szerokie w zasięgu zniszczenia lasów dotknęły regiony Europy i Ameryki Płn.

Mechanizm przekształcenia zanieczyszczeń w atmosferze jest opisywany przez chemię atmosfery. Ważną rolę odgrywa tu fotochemia. Utleniane  $SO_2$  i  $NO_x$  w obecności pary, mgieł i kropelek wody tworzą kwasy azotowy i siarkowy.

Innym problemem jest emisja lotnych zanieczyszczeń organicznych w procesie spalania. Powodują one niszczenie ozonu stratosferycznego i tworzenie się warstwy ozonu na powierzchni Ziemi. Koncentrowanie tych zanieczyszczeń w środowisku potęguje efekt cieplarniany, a także wywołuje toksyczne i kancerogennne skutki zdrowotne.

Gazy spalinowe mogą być oczyszczane przy użyciu selektywnej redukcji katalitycznej oraz przy zastosowaniu różnych metod odsiarczania.

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#### **1. FOSSIL FUEL SOURCES**

Fossil fuel includes coal, natural gas, petroleum, shale oil, and bitumen. They all contain carbon and were formed as a result of geological processes from the remains of organic matter produced by photosynthesis hundreds and millions years ago.

A man used coal for a long time as fuel to generate, first heat, and after that electric energy. In the production of heat and energy its three variations are used: peat, lignite, and bituminous coal. Peat deposition is the first step in coal formation. Dried peat burns readily with a smoky flame and a characteristic odor. Vast beds occur in Europe, North America and northern Asia but are worked only where coal is deficient. In Ireland millions of tons of peat are consumed annually. Russia, Sweden, Germany and Denmark also produce and use considerable quantities, and peat is used locally in England and Scotland.

Lignite occupies a middle position between peat and bituminous coal. World production of lignite in 1992 was 308 million tons, of which Germany (mostly the eastern part) reached 135 mln tons, Russia - 130 mln (CIS - 135 mln), Czech Republic and Slovakia - 60, Poland - 67, Greece - 51, Romania - 38, Turkey - 45, Bulgaria - 28, 1-2% of world production - Spain, Hungary, India, Thailand, North Korea. Lignite is mostly extracted in open pits, at which the thermal-electric power stations are located. In countries which do not possess the supplies of bituminous coal there also exist underground mines of this coal. Lignite is characterized with large content of ash, moisture and often sulfur. Considerably better fuel is bituminous coal (combustible value in a moist and ash-free state is ca. 24 MJ/KG).

Deposits of bituminous coal and of anthracite exist mostly in Carboniferous and Permian formations. The area of the greatest accumulations of Carboniferous coal is the Euro-American province, stretching from eastern parts of South America across Europe to West Asia. The share of supplies of this province is over 22% supplies of bituminous coal of the world. The area of the land of Gondwana, which stretches embracing central and eastern Asia, Australia, South Africa and South America is characterized by the occurrence of Permian carbons. The share of supplies of this province is about 17% of supplies of bituminous coal and of lignite of the world. Less significant economic meaning have the supplies of bituminous coal of Mesozoic age (upper Triassic period, Middle Jurassic period, Lower and Upper Cretaceous period) and Tertiary period.

Geologic resources of bituminous coal together with anthracite are  $772.5 \cdot 10^9$  tsf. balance resources  $492.5 \cdot 10^9$  tsf. Greatest quantity of geologic supplies occur in Asia (71%), of balance supplies in Asia (44%) and in America (26%).

Bituminous coal and anthracite are extracted in 40-45 countries by ca. 20,000 mines mostly underground with different degree of gas hazard. Is it greatest in mines of bituminous coal and of similar types. The hazard is due to the susceptibility of coals to self-ignition in underground excavations. In China the excavation is performed in little mines organized in cooperatives.

World production of bituminous coal in 1992 was 3179 mln tons, of which China - 1000, USA - 607, CIS - 489, India - 213, South Africa - 177, Australian - 180, Poland - 132, GB - 83, Germany - 66, 1-2% of world production is reached by Canada, North Korea, below 1% - Colombia, South Korea, Spain, Indonesia, Czech Republic, France, etc.

# 2. ENERGY DEMAND AND AIR POLLUTION

At the moment when coal was used to produce heat, for warming flats and for cooking, in greater municipal agglomerations disadvantageous influence of its combustion on environment was observed. Americans may think smog was invented in Los Angeles. Not so. In fact, and Londoner coined the term "smog" in 1905 to describe the city's insidious combination of natural fog and coal smoke. Smog in London predates Shakespeare by four centuries. Until the 12th century, most Londoners burned wood for fuel. But as the city grew and the forests shrank, wood became scarce and increasingly expensive. Large deposits of "sea-coal" off the northeast coast provided a cheap alternative. Soon, Londoners were burning the soft, bituminous coal to heat their homes and fuel their factories. Sea-coal was plentiful but it didn't burn efficiently. And lot of its energy was spent making smoke, not heat. Coal smoke drifting through thousands of London chimneys combined with clean natural fog to make smog. If the weather conditions were right, it would last for days. Early on, no one had the scientific tools to correlate smog with adverse health effects, but complaints about the smoky air as an annoyance date back to at least 1272, when King Edward I, on the urging of important noblemen and clerics, banned the burning of sea-coal. Anyone caught burning or selling the stuff was to be tortured or executed. The first offender caught was summarily put to death. This deterred nobody. Of necessity, citizens continued to burn sea-coal in violation of the of law, which required the burning of wood few could afford. Sadly, the problem of wood shortage exists nowadays. The one important renewable resource, fuel wood, which supplies 20 or even 30 per cent of energy in some rural economies, is running out and there is a world shortage. It is ironic that the first fuel resource to run into really short supply will be a "renewable" resource. The effect of this shortage on hundreds of millions of inhabitants of sub-Saharan Africa is to reduce even further their subsistence level lifestyle.

The combustion of coal in household furnaces, the so-called low emission, is still the nightmare of many municipal agglomerations. Such furnaces do not use modern technologies of combustion or cleanings of fumes, what is possible in case of large professional power stations.

Inventions of Edison, who also started in 1882 first power station of direct current, introduced mankind into the era of electricity. Already after the first world war people began building heat and power generating plants in USA, Western Europe and Soviet Union. It should be mentioned, that the first water power station became erected in Lauffen in 1891 and the first nuclear power station in Colder Hall, GB in 1956.

World demand for energy increased in the course of last two hundred years average by 2.3% a year. Today the electric energy constitutes about one third of energy used on a global scale. Figure 1 presents the demand for energy per person throughout the history.



Fig.1. Individual energy consumption. The service sector includes teaching, trade, office work, etc. (Adapted from UNESCO Courier).

If the whole world could be brought up to Western Europe's living standard, which requires for its maintenance about 6 tones of coal equivalent per person per year (that is 6 kW electric fires burning day and night for each of us) then the world's proved fossil fuel resources, coal, oil and gas, would last for just 17 short years. As it is, there are  $31.4 \times 10^{21}$  Joules of proved renewable fossil fuels reserves (coal 20.3, oil and gas 11.1); at current rates of demand of  $400 \times 10^{18}$  Joules per annum the resources will last for 80 years. Nuclear energy could transform the situation if we choose to use it. As it is, every year we burn fossil fuel that took a million years to form so that in some 200 years, starting in the middle of the last century, we will have burnt all the fossil fuel formed during the history of the world. There is currently a glut of fossil fuels but as the developing world industrializes and its economies expand, that glut could quickly become and famine in the second decade of the next century (25 years away).

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#### **3. COMBUSTION AND POLLUTANTS FORMATION**

The major constituents of fossil fuels are carbon, hydrogen, and oxygen, with lesser amounts of other materials such as metal compounds (sulfides and oxides). Oil and coal contain sulfur in the form of sulfurous amino acids:



and other compounds i.e.: ethyl mercaptane ( $C_2H_5SH$ ). Coal, besides the above compounds, contains other inorganic sulfur compounds as pyrite sulfides and sulfates ( $Fe_2(SO_4)_3$ , MgSO<sub>4</sub>, CaSO<sub>4</sub>, etc.). For coal half the sulfur is in an organic and the rest in an inorganic form.

The actual quantities of sulfur compounds depend both on the fuel type and on the source. Thus, the sulfur content in oil and coal can vary between less than 1% to 5%. Natural gas, as pipeline gas, has had the sulfur compounds removed, as they corrode pipelines.

Claus process is most often used:

$$2H_2S + 3O_2 \rightarrow 2H_2O + 2SO_2 \tag{1}$$

$$2H_2S + SO_2 \rightarrow 2H_2O + 3S \tag{2}$$

and elemental sulfur can be obtained, the process is a source of raw sulfur i.e. in France and Canada. During combustion of fossil fuel, the hydrogen and carbon compounds are oxidized with the evolution of energy.

$$C + O_2 \rightarrow CO_2 + 93.0 \text{ kcal/mol} (395 \text{ MJ/mol})$$
 (3)

$$H_2 + 1/2O_2 \rightarrow H_2O + 68.3 \text{ kcal/mol} (287 \text{ MJ/mol})$$
 (4)

If insufficient oxygen is present for complete oxidation of the carbon, some of the carbon dioxide formed may react, to give the monoxide:

$$C + CO_2 \rightarrow 2CO - 410 \text{ kcal/mol} (172 \text{ MJ/mol})$$
(5)

or some of the carbon may react with less oxygen:

$$C + 1/2O_2 \rightarrow CO + 26.4 \text{ kcal/mol} (111 \text{ MJ/mol}).$$
 (6)

This shows that when combustion occurs with insufficient oxygen, much carbon monoxide is produced, and the overall heat release is far less than when complete combustion is achieved.

During incomplete combustion of oil or coal, volatile organic compounds that are complex hydrocarbons can be driven off, and these form one component of smoke, particularly from small domestic furnaces. In larger furnaces the volatile, which are highly combustible, are ignited by radiation and convection from the hot walls of the furnace, and are burned to carbon dioxide and water.

#### 3.1. Formation of sulfur oxide

The minor constituents of the coal and oil, sulfur and nitrogen, also form oxides during combustion. For sulfur:

. . . . . .

(9)

$$S + O_2 \rightarrow SO_2$$
 (7)

and to a lesser degree in the flame

$$SO_2 + O^* \to SO_3 \tag{8}$$

and also

ļ

$$\stackrel{\text{\tiny 2-1}}{\longrightarrow} \text{SO}_2 + 1/2\text{O}_2 \rightarrow \text{SO}_3 + 85 \text{ MJ}$$

In fact, in the normal flame SO<sub>3</sub> only represents about 1% of the total sulfur oxides. Although SO<sub>3</sub> is the stable of forms at lower temperatures, the rate of formation, without catalyst present, is so slow as to be insignificant, while at flame temperatures, the dioxide is more stable. Nitrogen oxide (NO) is also formed during combustion. In part this is from nitrogen in the fuel, of which according to different experiments, between 18% and 80% is oxidized; the rest is due to reactions with atmospheric nitrogen in the flame and post-flame regions.

#### 3.2. Formation of nitrogen oxides

Nitrogen contained in fuel is a component of volatile and stable organic compounds. During the heating of coal-dust at the temperature below 1000 K first weakly bonded aliphatic compounds are emitted. After degassing of 10-15% of the initial mass of coal in degassing products the nitrogen compounds begin to appear. They include mainly ammonia (NH<sub>3</sub>), molecular nitrogen (N<sub>2</sub>) and vestigial quantities of oxide nitrogen (NO). In temperature 1000 -1200 K the thermal tars decay begins. At ca. 1100 K the bonds of aromatic rings producing nitric compounds burst mostly prussic acid (HCN), NH3, N2. The quantity of emitted nitric compounds increases with temperature, with the speed of degassing and with the diminution of dimension of grains of coal-dust. During degassing of volatile parts up to 70% of nitrogen contained in fuel is released (including ca. 40% in the form of N<sub>2</sub> and up to 10% in the form of NH<sub>3</sub> and HCN). In temperature ca. 1800 K the total degassing of nitrogen compounds contained in coal takes place. Nitric compounds released during pyrolysis react through a series of indirect reactions to NO, NO<sub>2</sub>, N<sub>2</sub>O or N<sub>2</sub>. Depending on circumstances of combustion, i.e. at low concentrations of oxygen in fumes, there can also occur reactions of NO reduction. During combustion of coal-dust a considerable quantity of nitrogen contained in fuel stays in constant residues after degassing, i.e. in coke and soot. The quantity of nitrogen remaining in coke increases together with decreasing the temperature of combustion and with the excess of air. Nitrogen combined with coke is degassing slower than when it is in volatile parts. In time of burning of coke nitrogen undergoes significant degassing and simultaneous oxidizing to NO. The quantity of oxides of nitrogen produced from nitrogen combined in coke may constitute ca. 20-30% of the total quantity of NO produced in the process of combustion. Also amino compounds NH come into being. Free active coke has reductive properties of NO. Similar quantities of oxide of nitrogen are formed from nitrogen fixed in soot particles. Particles of soot also have reductive properties of NO. The speed of their reductive reactions is greater than the speed of NO reaction with the surface of coke. It should be stressed that only part of nitrogen contained in coal (10-20%) can become transformed into fuel NO<sub>x</sub>. In case of liquid fuels and gas-fuels a greater part of fuel nitrogen undergoes of conversion to NO<sub>x</sub>.

The formation and reduction of fuel nitrogen oxides can be illustrated by the following reactions:

$$RNH_2 + 1/2O_2 \rightarrow NO + H_2 \tag{10}$$

$$NH_3 \xrightarrow{c} 1/2N_2 + 1/2H \tag{11}$$

$$NO + CO \xrightarrow{c} 1/2N_2 + CO_2$$
(12)

$$HCN + 2NO \rightarrow 1/2N_2 + CO_2 + 1/2H_2$$
(13)

The production process of thermal nitrogen oxides is proceeded by molecular nitrogen from air used for combustion. In temperatures above 1300°C in a zone rich in oxygen a partial dissociation of its molecules reacting with nitrogen follows:

$$N + O_2 \rightarrow NO + O$$
 (14)

$$0 + N_2 \rightarrow NO + 0 \tag{15}$$

In a zone rich in fuel the hydroxide radicals occur which are also responsible for the formation of nitrogen oxide.

$$N + OH \rightarrow NO + H$$
 (16)

With the increase of temperature of combustion above 1570 K the rate of reaction creating NO<sub>x</sub> clearly increases.

Prompt nitrogen oxides are produced in the presence of hydrocarbons of which in a zone with little contents of oxygen free radicals are formed:

$CH + N_2 \rightarrow HCN + N$	(17)
	( )

 $C + N_2 \rightarrow CN + N$  (18)

 $CN + H_2 \rightarrow HCN + H$  (19)

 $CN+H_2O \rightarrow HCN + OH$  (20)

$$HCN, CN + O \rightarrow NO + R \tag{21}$$

Prompt nitrogen oxides formation is less important than thermal and fuel oxides formation processes in the case of coal combustion.

#### 3.3. Emission of organic compounds

It is a widely accepted fact that the organic component of coal actually consists of two structures. The main one is a macromolecular insoluble three-dimensional lattice whose structure involves aromatic and hydroaromatic units bound with ether and thioether chains and short alkyl bridges. The second constituent consists of particles representing low and medium molecular weight, usually soluble in organic solvents. This molecular component is assumed to contain varying distribution of aliphatic hydrocarbons, hydroxylated polycyclic aromatic compounds and heterocyclic compounds.

If hydrocarbons are not totally oxidized during combustion, a variety of substances can appear in the exhaust gas e.g. alcohols, aldehydes or organic acids. Hydrocarbons can be oxidized to carbon dioxide and water via stable oxidation states (methanol, formaldehyde, formic acid, carbon monoxide etc) which are are also possible emissions components. During incomplete combustion or insufficient mixing of fuel and air in the flame, part of the fuel can escape unburned along with exhaust gas. In contrast, if there is a lack of air, thermal decomposition (pyrolysis) can set in. This decomposition process either takes place via the reaction of partial oxidation or it leads to the formation of new hydrocarbons not originally contained in the fuel. This is a path through which aromatic (e.g. benzene, toluene, xylenes and polycyclic aromatic hydrocarbons (PAH)), some of which are known to be carcinogenic are formed. In the first stage of PAH formation addition of smaller aliphatic compounds and cyclization into hydroaromatic hydrocarbons into fully aromatic hydrocarbones takes place. Finally the formation of larger polycyclic aromatic hydrocarbons from smaller ones follows (Fig. 2). The PAH family of hydrocarbons consists of molecules containing two or more fused six-carbon aromatic rings. Two common members of the group are naphthalene and benzol(a)pyrene with two and five fused rings, respectively.



Fig. 2. Possible mechanisms for the formation of PAHs during combustion.

The degree of emission of Volatile Organic Compounds (VOC) in the combustion process depends on its conditions. Considerably higher concentrations of VOC are emitted from furnaces used by the communal/social sector typically operating low-capacity heating plants. In large power stations the combustion process is constantly monitored, besides it is run at higher temperatures.

Research of the coal combustion process conducted in many centres for different combustion conditions has shown that among the emitted pollutants many organic compounds of low boiling point occur: benzene, toluene, aldehydes, phenols, aliphatic compounds  $C_5$ - $C_{20}$ , furanes, dioxins and significant amounts of PAH, just to mention a few.

PAH can also be contained in the matrix fossil fuel: oil or coal. At medium temperatures (approx. 200°C) and under increased pressure PAH can be formed from biological material constituting exploitable fossil deposits. Although the process following this path is rather slow, comparably large quantities of polycyclic compounds can be formed. These compounds are released unchanged or undergo certain transformations during the combustion of coal or oil. Their emission with flue gases from a coal-fired power plant amounts to 30-930 mg/m<sup>3</sup>, from municipal waste incineration plant - 17-2700 mg/m<sup>3</sup>, bonefire - 2800-173,000 mg/m<sup>3</sup>. Particularly large quantities are released during tobacco smoking, reaching the value 0.8-2.0  $\mu$ g/g tobacco.

Below is some emission data for selected countries:

Source	Quantity (ktons/y)		
	USA	Sweden	Norway
Residential heating combustion (wood, coal, oil, gas)	1380	132	62.5
Waste incineration (municipal plants, bonefires, forest fires, agricultural waste)	1150	3.5	13.7
Power generation (coal, oil, peat)	401	13	1.3

Organic pollutants occur in both solid phase (adsorbed and associated by ash) and gaseous vapor phase. Distribution of these pollutants between ash and gaseous state depends on the type of furnace and combustion condition. Generally it can be assumed that approx. 20-30% of pollutants exist in adsorbed and ash-associated forms. It has been observed that two- and threering hydrocarbons prevail in gaseous phase while the four- and five-ring ones are present in the solid matter (ash).

Organic pollutants which have a long environmental residence time are generally called persistent organic pollutants (POPs). These include polycyclic aromatic compounds and a host of chlorinated\_organic compounds. PAHs feature strong UV and visible light absorption. It leads to photochemical modification and transformation of these substances. PAHs in clear water with high oxygen concentration exposed to sunlight have half-life shorter than an hour (e.g. benzeno(a)pyrene of then order of 1 year). For PAHs with lower molecular weight the half-life is much shorter in sediment water but much longer in the first described conditions. In the first case photolytic degradation and biodegradation in the second case take place. On the other hand PAHs deposited in the soil or water undergo biological degradation by microorganisms. Combustion processes involving chlorine are the source of dioxins as well. Dioxins, or PCDD, (polychlorinated dibenzo(1-4)dioxins) are widely distributed in relatively low concentrations in the atmosphere, soil, sediments, plants, animals and in humans.

For example the 2,3,7,8-tetrachlorodibenzo(1,4)dioxin has the following structural formula:



Other halogenoderivatives formed in the combustion process are polychlorinated dibenzofurans (PCDFs).

Combustion sources produce a variety of PCDD and PCDF congener profiles. Even for a single source, the profile will vary with the fuel used and the combustion temperature. Combustion sources include municipal waste incineration plants, coal-fired power plants and others.

Dioxins associated with particulates from combustion processes may reside in the atmosphere for considerable periods. For dioxins and PCDFs phototransformation of vapor phase material is quite important. As for reaction of OH radical with dioxins, an estimate of the tropospheric lifetime is approx. 7 hours of specific nature. One of the most important of those processes in the action of biological barriers resulting in selective bioaccumulation which protects living organisms against excessive concentration of chemical elements. The action of biological barriers is, however, of limited effectiveness.

#### 3.4. Emission of fly ash

Boiler installations burning pulverised fuel emit fly ash. With respect to its particle size, solid particles in the air can be divided into the following two categories:

- macroscopic particles ( $\phi > 1\mu m$ ) formed by comminution
- colloidal particles ( $\phi < 1 \mu m$ ) formed in the process of condensation.

Macroscopic particles in turn, can be divided into the further two groups:

- precipitating particles ( > 20 μm)
- suspended (non-precipitating particles) (  $< 20 \ \mu m$ ).

The non-precipitating particles is capable of forming stable aerosols, such as two-or three-phase fogs.

Particles of dust and ash, as well as molecules of gases, become condensation nuclei facilitating formation of fog. This is the reason why in heavily industrialized areas fogs occur with several times higher intensity than in other ones.

Very often fly ash is a source of trace elements (heavy metals). Usually three groups of this type pollutants, originating from human activity, are distinguished. they constitute severe environmental hazards:

- 1. the elements of very high degree environmental hazard: Cd, Pb, Cu, Hg, Zn, Sn, Cr,
- 2. the elements of high degree of potential threats: Bi, U, Ba, Mn, Ti, Fe, Se, Te,
- 3. the elements of medium degree of environmental hazard: F, Ni, As, V, Al, W, B, Br, Co, Be, Rb, Li, Ge, Cs.

Transfer of each of those elements to a higher link of the food chain is effected by various processes.

# **4. GROSS EMISSION OF POLLUTANTS**

The mass of pollutants formed during combustion of 1 ton of coal (of the sulfur content 0.5%) or equivalent, in terms of fuel capacity, quantities of oil and gas is shown in the following list:

Fuel type pollutant	SO <sub>2</sub> /kg/	NO <sub>x</sub> /kg/	Fly ash /kg/
Coal	12.3	2.4	5.4
Fuel oil	3.8	1.7	0.4
Natural gas	-	2.4	0.1

The intensity of emission of sulfur oxides from any fuel depends on the content of pure sulfur in that particular fuel. Combustion of 1 kg sulfur leads to formation of 2.0 kg SO<sub>2</sub> or approx. 3.1 kg  $H_2SO_4$ . The higher the content of pure sulfur in the fuel burnt, the more of these compounds are emitted, practically in the form of SO<sub>2</sub> whose percentage reaches as much as 98%.

Other pollutants, such as carbon and nitrogen oxides, can also be extremely harmful for the natural environment. Combustion of 1 kg nitrogen produces as much as  $3.3 \text{ kg NO}_2$  or about 4.5 kg HNO<sub>3</sub>. Burning of 1 kg coal produces about 3.7 kg carbon dioxide. A man excretes 1 kg CO<sub>2</sub> during his 24-hour respiration.

A 1000-MW heat/electricity generation station burns 9.000 tons coal daily. Assuming that the coal contains approx. 20% of ash, the station produces, within 24-hour operation, about 1.600 tons of solid furnace waste and about 400 tons  $SO_2$ , 55 tons  $NO_2$  and 27,000 tons  $CO_2$ .

Annually the station uses up 23.3 million tons of coal while the figures characterizing emission of pollutants are 580,000, 50,000, 20,000 and 10 millions tons, respectively. Figure 3 presents waste generation for the 700 MW power block equiped in air pollution control installations.

Combustion of fossil fuels is unfortunately, the most important source of air pollution. Among the processes in which fuel is used for energy (electricity and heat) production coal burning plays a leading role. Burning fossil fuel is and will be a main source of energy for a long time. In the year 1995 the power installed based on the coal fired boilers was equal to 870 GW, oil fired boilers 435 GW, while the total world power installed was equal to 2900 GW. According to the predictions the total is likely to increase to 5400 GW by the year 2020, including 1836 GW installed in power stations using coal and 648 GW in oil fired power stations.

When burning fossil fuels air polluting substances such as particulate,  $SO_2$ ,  $NO_x$ , volatile organic compounds (VOC) and others are generated. Exemplary flue gas composition are presented in Table 1.

	Hard coal	Lignite
Pollutants	ppm	
SO <sub>2</sub>	350-1700	100-2700
SO <sub>3</sub> /SO <sub>x</sub>	~0.01	~0.01
NO <sub>2</sub>	200-1600	100-500
NO <sub>2</sub> /NO <sub>x</sub>	~0.05	~0.05
HCI	30-125	12-60
HF	5-60	0.3-2.6
СО	300-680	-
VOC (mg/m <sup>3</sup> )	-	-
particulate (mg/m <sup>3</sup> )	500-3500	1500-2500
Carrier gas	vol %	
N <sub>2</sub>	70-80	60-78
CO <sub>2</sub>	11-15	11-15
O <sub>2</sub>	4-7	4-7
H <sub>2</sub> O	3-8	8-24

Table 1. Concentrations of pollutants in flue gases from different sources



Fig. 3. Mass flows and flue gas composition of the 700 MW power plant block.

Carbon dioxide (CO<sub>2</sub>): 16% = 310 g/m<sup>3</sup>; Oxygen (O<sub>2</sub>): 6%, Nitrogen oxides (NO+NO<sub>2</sub>): 0.04% = 650 mg/m<sup>3</sup>  $\xrightarrow{DENOX}$  200 mg/m<sup>3</sup>; Sulfur dioxide (SO<sub>2</sub>): 0.1% = 2000 mg/m<sup>3</sup>  $\xrightarrow{FGD}$  ca. 200 mg/m<sup>3</sup>; Nitrogen (N<sub>2</sub>): 77.5%; Particles: ca. 6.5 g/m<sup>3</sup>  $\xrightarrow{ESP}$  ca. 10 mg/m<sup>3</sup>. These data give an idea concerning possible pollutant concentrations, they vary from one fuel to another e.g. for lignite as high  $SO_2$  emissions as 5500 ppm are observed. Even if concentration of pollutants is low, the global emission is very high for the volume of flue gases emitted. In the case of hard coal volumetric rate of gas flow (per MW of heat capacity) is in the range 1000-1500 m<sup>3</sup>/h (gas temperature 393-473 K), lignite - 1550-2200 m<sup>3</sup>/h. Incineration of one ton of municipal solid waste incineration produces 4200 m<sup>3</sup> (505 K).

Worldwide emission of SO<sub>2</sub> from coal fuel power stations only reaches about 55 millions metric tons annually: 17.5 in the US, 7 in China, 6, 6 in CIS, 3.6 in Germany, 1.9 in Poland 2.2 in Bulgaria and 1.3 Turkey. Emission from domestic and industrial furnaces which use coal as an energy carrier must be added this these numbers. One should remember however that total emission is much higher and for example in the case of China is equal to 22,000 kt/year.

Emission of  $NO_x$  (recalculated as nitrogen) produced fossil fuel combustion including engines is equal to 21 millions tons (N) annually.

VOC emissions from combustion (without traffic) reach almost 0.2 million tons annually in the US only. The total emission of this pollutant in GB you equal to 1.8 million tons and 2 million tons in France in 1989.

# **5. POLLUTANTS IN ATMOSPHERE**

Air pollutants are those substances-gases, mists, and particulate aerosols-which are present in the atmosphere in such concentrations that they can adversely affect man and his environment. Most of these substances-sulfur dioxide, nitrogen oxides, and many others - are naturally present in the atmosphere in low (background) concentrations. They are produced in nature, as well as from sources, and generally the natural background concentrations are such as to be harmless, they may play anthropogenic vital part in the natural cycles of growth and decay. Unusually high natural concentrations do occur; examples being methane and hydrogen sulfide from geothermal sources, but these are exceptional circumstances. So when we refer to air pollutants we think of those in relatively high concentrations (compared with background values) which result from the chemical and biological processes used by man. Most notables among these are fuel combustion - for heating, cooking, and industrial processing - and the generation of electricity.

The natural (background) levels of the naturally occurring gases and their estimated residence times are given in Table 2.

The residence time is the average time during which the substance remains in the atmosphere before being adsorbed he the earth's surface, or interacts in the atmosphere, being rendered harmless.

The Earth's atmosphere consists of several layers extending from the Earth's surface to outer space. However, the part of the atmosphere that affects weather and climate, and in which most air pollutants are emitted and dispersed, is just a thin layer, from the surface up to a height of 10 to 15 km, called the troposphere. (If the Earth were the size of an apple this layer would be less than the thickness of its skin). Above the troposphere lies the stratosphere, between 15 and 50 km above the Earth's surface. The stratosphere is rather isolated from the weather in the troposphere because vertical transfers between these two layers are very slow. The stratosphere holds the ozone layer (at a height of 20 to 40 km), which protects the Earth from the sun's ultraviolet radiation, an essential feature of the Earth's atmosphere for the continuing sustenance of life. The so-called "mixing layer" of the atmosphere is generally turbulent, varying in depth with meteorological conditions, ranging from a few hundred meters to about 2 km. Pollutants released into this layer are thus effectively dispersed into a larger volume of air within a few hours, including some transfer to higher levels of the troposphere. If turbulence in the mixing layers is impeded, pollutants accumulate in an even smaller volume, giving rise to high concentrations ("smog"). This occurs when winds speeds are low and when the Earth's surface temperature is lower than the air above (a temperature inversion). Contrary to the troposphere, where average on temperature decreases with, the inversion layer (typically 100 to 300 m in depth) is characterized by a temporary increase, of temperature with height, with weak wind and slow mixing, and practically no exchange with the overlying background troposphere.

Gas	Chemical symbol	Concentration	Calculated residence time
Principal gases		<u></u>	
Nitrogen	N <sub>2</sub>	78.0	continuous $(10^6 y)^2$
Oxygen	O <sub>2</sub>	20.9	continuous $(10^3 y)^2$
Argon	Α	0.93	continuous
Carbon dioxide	CO <sub>2</sub>	$0.032^{b} (0.035)^{1}$	$2-4$ years $(50-200y)^2$
Trace gases		······································	
Permanent gases		(ppm)	
(nonreactive)			
Helium	He	5.2	about 2 million years
Neon	Ne	18	continuous
Krypton	Kr	1.1	continuous
Xenon	XE	0,086	continuous
Reactive gases			
Carbon monoxide	CO	0.1	$0.5 \text{ years } (0.4 \text{ y})^2$
Methane	CH₄	1.4	4-7 years $(7-10y)^2$
Nonmethane			
Hydrocarbons	"HC"	<1x10 <sup>-3</sup>	?°
Nitrous oxide	N <sub>2</sub> O	0.25	4 years $(130y)^2$
Nitric oxide	NO	$0.2 - 2.0 \times 10^{-3}$	5 days
Nitrogen dioxide	NO <sub>2</sub>	$0.5 - 4 \times 10^{-3}$	several days
Ammonia	NH3	$6-20 \times 10^{-3}$	$7 \text{ days } (3d)^2$
Hydrogen sulfide	H₂S	$0.2 \times 10^{-3}$	2 days
Sulfur dioxide	SO <sub>2</sub>	$0.2 \times 10^{-3}$	$4 \text{ days } (3d)^2$
Chlorine	Cl <sub>2</sub>	$3-15 \times 10^{-3}$	several days
Iodine	$I_2$	$0.4-4 \times 10^{-3}$	?
Hydrogen fluoride	HF	0.08-18x10 <sup>-3</sup>	?
Hydrogen	$H_2$	0.58	?
Ozone	O <sub>3</sub>	0-0.05	about 60 days (tropospheric,
			weeksmonths; stratospheric,
			months) <sup>1</sup>

Table 2. Composition of dry air in the lower troposphere (free of water vapor)

<sup>\*</sup> This is the atmospheric background concentration, and not the concentrations found in polluted areas. When a range of concentrations is given, it indicates that these have been measured by different workers at different places.

<sup>b</sup> Minimum concentration of  $CO_2$  measured away from centres of population. In population centres  $CO_2$  concentrations vary from about 0.034% to 0.035%.

<sup>e</sup>Little is known about the residence time of the gas.

<sup>1</sup> W. Strauss: Formation and control of air pollutants. In: [Ref. 12]., pp. 170-212.

<sup>2.</sup> [Ref. 8].

Air pollution caused by particulate matter and other pollutants not only acts directly on environment but by contamination of water and soil leads to their degradation. Wet and dry deposition of inorganic pollutants leads to acidification of the environment (Fig. 4). These phenomena affect health of the people, increase corrosion, destroy cultivated soil and forests. Most of the plants, especially coniferous trees are not resistant to the action of sulfur and nitrogen oxides. Following longer exposure leaves wither and fall. Widespread forest damage has been reported in most Central and Eastern European countries as well in northeastern USA and Canada. Many cultivated plants are not resistant to these pollutants either especially in the early period of vegetation.

Air pollution grows as a result of the increase of population density and human requirements. It is composed of various solid, liquid and gaseous substances which, when introduced to the atmospheric air, cause different harmful interference's.

These days the relatively cleanest air can be found over the surface of seas and oceans. In comparison, the ambient air of villages is 10 times more polluted, in small town - 35 times, while in big cities the factor is as high as 150. Under some specific circumstances, the urban atmosphere can be polluted even 4000 time more than the air over seas.

In many cases pollutants are deposited over the territory of a different country than emitted. Therefore this is a global problem being a subject of international treaties. This is the reason why in most countries all over the world emission standards have been introduced.

# 6. POLLUTANTS TRANSFORMATION IN ATMOSPHERE

The mechanisms of pollutants transformation in atmosphere are described by environmental chemistry. The processes are rather complicated, some not perfectly clear so the reaction schemes differ from source to source. The pathways depend on many conditions (e.g. darkness, sunshine, air humidity or presence of dust or water droplets, presence of other pollutants).



Fig. 4. Mechanism of acidic rain formation.

An important role in the process mechanism plays photochemistry. Photochemical reactions concern molecules which absorb highly energetic light in the region 300-700 nm. A simplified scheme of these reactions is given in Table 3. Direct photoxidation is insignificant in the case of  $SO_2$  conversion in the air. More important is oxidation through photochemically formed radicals.

$A \xrightarrow{h\nu} A'$	$SO_2 \xrightarrow{h\nu} SO_2$ .	activation
$A^{+} \rightarrow A + h\nu$ $A^{+} + M \rightarrow A + M$		fluorescence deactivation
$A' \rightarrow B + C$	NO <sub>2</sub> $\xrightarrow{h\nu}_{290-430 \text{ nm}}$ NO <sup>+</sup> + O <sup>+</sup>	dissociation
$A^+ + B \rightarrow C + \dots$	$O_2 \xrightarrow[<242 \text{ nm}]{h\nu} O' + O'$	direct reaction

Table 3. Photochemical reactions in atmospheric air

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The most important reaction is the one with OH radicals. Hydroxyl radical is produced through different secondary photochemical reactions:

$$H + O_3 \rightarrow OH + O_2 \tag{22}$$

$$NO_2 + NO + H_2O \rightarrow 2HNO_2 \xrightarrow{h\nu} 2NO + OH$$
 (23)

$$CH_3O_2 \rightarrow CH_2O + OH$$
 (24)

An important role in the  $SO_2$  oxidation process plays  $OH_2$  radical as well, which can be formed in reactions:

$$OH + O_3 \rightarrow O_2 + HO_2 \tag{25}$$

$$CH_3 + O_2 \rightarrow CH_2O + HO_2 \tag{26}$$

In liquid phase this radical could be produced, by a Fenton type reaction (metal ion/ $H_2O_2$ ).

Conversion of  $SO_2$  in water droplets e.g. fog. cloud, rain snow or adsorbed water layer plays much more important role that previously described "dry" reaction. The first physical step is  $SO_2$  dissolution in water. The solubility is temperature dependent and in equilibrium depends on  $SO_2$  partial pressure. The oxidation of  $SO_2$  in the water solution is accelerated by catalyst e.g. magnesium, iron, copper ions with are always present in trace concentration (Table 4).

Gas phase	Liquid phase (droplets, clouds, adsorbed layer)
Direct	Pure water
1. $2SO_2 + O_2 \xrightarrow{hv} 2SO_3$ 2. chain reaction $SO_2 \xrightarrow{hv} SO_2^{-1}$ $SO_2^{-1} + SO_2 \rightarrow SO_3 + SO$ $SO_2^{-1} + O_2 \rightarrow SO_3 + O$ $SO_2^{-1} + O_2 \rightarrow SO_3 + O$ $SO_2^{-1} + O_2 \rightarrow SO_3$ $O_2^{-1} + O_2 \rightarrow SO_3$ $O_2^{-1} + O_2^{-1} \rightarrow SO_3$	chain reaction $SO_2 + H_2O \rightarrow SO_2 \cdot H_2O$ $SO_2 \cdot H_2O \rightarrow HSO_3^- + H^+$ $HSO_3^- \xrightarrow{h\nu} HSO_3$ $HSO_3 + O_2 \rightarrow HSO_5$ $HSO_5 + HSO_3^- \rightarrow HSO_3 + HSO_5^-$ $HSO_5^- + HSO_3 \rightarrow 2HSO_4^-$ $HSO_5 + HSO_3 \rightarrow end$
Radical	Catalyzed (Mn, Fe, Cu)
$SO_2 + OH + M \rightarrow HOSO_2 + M$ $SO_2 + HO_2 \rightarrow OH + SO_2$ $SO_2 + RO_2 \rightarrow RO + SO_3$	$xSO_{2} + Mn^{2+} \rightarrow [Mn(SO_{2})_{x}]^{2+}$ $HSO_{3}^{-} \xrightarrow{h\nu} HSO_{3}$ $HSO_{5} + HSO_{3} \rightarrow end$

#### Table 4. Sulfur dioxide oxidation pathways

Another pollutant emitted NO is oxidized and transformed into nitric acid by the ways presented in Table 5. The first pathway is of small importance and NO in the atmosphere is mainly oxidized by ozone. Above listed reactions are more complicated when hydrocarbons or pollutants are present in the air. Presence of  $NO_x$  and hydrocarbons enhance oxidation of  $SO_2$ .

The third problem discussed here connected with human activities is emission of volatile organic compounds to the atmosphere. The main sources are: vehicle exhaust, evaporation of petrol vapors, solvent usage, industrial processes, oil refining, land filled wastes, food manufacture, agriculture and fossil fuel combustion. This emissions cause: stratospheric zone depletion, ground level photochemical ozone formation, toxic or carcinogenic human health effects, enhancing the global greenhouse effect, accumulation and persistence in the environment.

Table 5. NO	transformation	pathways
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Oxidation
$2NO + O_2 \rightarrow NO_2$ $NO + O_3 \rightarrow NO_2 + O_2$
Dissociation
$NO_2 \xrightarrow{h\nu} NO + O$ $O + O_2 + M \rightarrow O_3 + M$ $O_3 + NO \rightarrow NO_2 + O$
Acid formation
$\begin{array}{ccc} O_3 + NO_2 \rightarrow NO_3 + O_2 \\ NO_3 + NO_2 \rightarrow N_2O_5 \\ N_2O_5 + H_2O \rightarrow 2HNO_3 \end{array}$

Particularly under the influence of solar radiation, in the atmosphere OH radicals are present in significant concentrations.

Peroxy radicals (HO<sub>2</sub> or RO<sub>2</sub>) are formed in reactions:

$$OH + CO \rightarrow CO_2 + H$$
 (27)

(1)  
 
$$H + O_2 \rightarrow H_2O$$
 (28)

$$OH + RCH_3 \rightarrow H_2O + RCH_2$$
(29)

$$RCH_2 + O_2 \rightarrow RCH_2O_2 \tag{30}$$

These radicals cause NO oxidation:

$$NO + RCH_2O_2 \rightarrow NO_2 + RCH_2O$$
(31)

and RO (or OH) radicals are reformed. Thus oxidizing agents (peroxide radicals) are formed from hydrocarbons without the RO(OH) radicals being used up in the process. The chain reaction is observed. This leads to ozone formation (Fig. 5).

Alkenes (olefins) are particularly effective in ozone formation. However, also aromatic hydrocarbons can have quite high ozone formation potential. When NO<sub>2</sub>/NO ratio increases under intensive solar radiation, such situation leads to higher ozone concentration and photochemical smog of Los Angeles type is formed. Peroxide compounds may be formed  $(RCH_2O_2 + NO_2 \rightarrow RCH_2OONO_2, RCOO + NO_2 \rightarrow RCOONO_2, RCOO_2 + NO_2 \rightarrow RCOO_2NO_2)$ . Irritant peroxyacetyl nitrate  $(PAN, CH_3 COO_2 NO_2)$  is the most stable and present in photochemical smog.



Fig. 5. Diagram illustrating ozone formation from NO<sub>2</sub> with hydrocarbons contributing.

# 7. ATMOSPHERE AND ITS ROLE

The atmosphere plays a major role in the global processes supporting life on Earth. Photosynthesis, a process which uses up carbon dioxide and produces oxygen, takes place there. The atmosphere also plays an important physical role as a heat reservoir. Heat absorbed by the atmosphere during daylight hours is released overnight, helping to maintain balanced temperature. Without the atmosphere, the Earth's surface temperature would rise very high when bathed in sunlight, but fall very low in the dark.

The oxygen contained in the atmosphere is absolutely necessary for maintaining the life of organisms using it for their metabolism processes. Gases show infinite mutual solubility and that is why all gaseous pollutants emitted in the course of human communal and industrial activity become constituents of the air. Together with the air we and other living creatures breath they get into the lungs where can be either directly absorbed or captured accumulated on small particles of dust (Fig. 6). A significant role in emission of gaseous and solid pollutants plays the process of combustion of fossil fuels.



Fig.6. Particle deposition in the different areas of the respiratory tract in dependence of the mean diameter of the particles.

According to the relevant data collected in the 70's, 27% of human-produced pollutants were an effect of operation of heat & electricity production stations. Considering the fact that many industrial processes are based on energy production by means of combustion of fossil fuels (e.g. metallurgy), it becomes clear that this particular manner of energy generation constitutes the greatest hazard to the natural environment. Global amounts of pollutants emitted by electropower station of capacity exceeding 1000 MW are shown in Table 6. The main components of gases produced during combustion of coal are nitrogen, carbon dioxide, water vapor and oxygen remaining after combustion. Depending on the composition of coal, conditions of the combustion process and flue gas purification installations used other gases and pollutants formed in the process can be SO<sub>2</sub>, SO<sub>3</sub>, NO, NO<sub>2</sub>, CO, HCl, NH<sub>3</sub>, fly ash and a wide range of compounds and elements occurring in trace amounts.

Pollutants	Organic fuel - fired power plants		
	coal*)	fuel oil**)	gas
	$2,3 \cdot 10^{6}$	1,57 · 10 <sup>6</sup>	1,9 · 10 <sup>9</sup>
	Mg/year	Mg/year	m <sup>3</sup> /year
Non-radioactive, Mg/y,			
sulfur oxides	$138 \cdot 10^{3}$	$98 \cdot 10^{3}$	1,6
nitrogen oxides as NO <sub>2</sub>	$20,9 \cdot 10^3$	$21,8 \cdot 10^3$	$12,2 \cdot 10^{3}$
carbon monoxide	21	9	traces
higher aromatic hydrocarbons	210	680	-
aldehyde	50	120	30
fly ash	$4,5 \cdot 10^{3}$	730	450
Radioactive, Ci/y			
Ra <sup>226</sup>	$17,2 \cdot 10^{-3}$	$0,15 \cdot 10^{-3}$	-
Ra <sup>228</sup>	18,8 · 10 <sup>-3</sup>	0,15 10-3	-

 Table 6. Annual emission of pollutants from 1000 MW electropower stations using combustion of fossil fuels

\*sulfur content 3.5% (15% sulfur remains in the ash); ash content 9%; flue gas purification degree 97.5%.

\*\*sulfur content 1.6%; ash content 0.05%.

These pollutants are emitted to the atmosphere where, due to various transport processes, are frequently carried over long distances, undergo many chemical and physical transitions and then precipitate and deposit in the soil or surface waters. For some pollutants, their residence time in the atmosphere can be very long.

Most of pollutants are discharged into the boundary layer (Fig. 7) which is the thin layer of the atmosphere in contact with the earth's surface where the airflow is frequently turbulent because of surface roughness. Many pollutants, especially the larger particulates (1-10  $\mu$ m) remain in the boundary layer but gases and smaller aerosol particles (<5  $\mu$ m) are transferred into the troposphere zone above by vertical movements in thermal plumes, storms and flow over mountains. Temperature of air falls with altitude in troposphere up to tropopause where the temperature gradient is reversed up to around 50 km. Tropopause occurs at around 6-8 km at the poles and 17 km at the equator. Troposphere is the zone of the greatest significance to living organisms.

The temperature in troposphere lowers with altitude to reach approx. -56°C at its upper boundary. Water content in troposphere is far from being constant because the bulk of water evaporated from lands, seas and oceans is highly changeable. Also cloud cover and level of precipitation change depending on atmospheric circulation tendencies. Almost all of water vapor in the atmosphere is contained in troposphere. The water contained in atmosphere in its various forms, such as clouds, droplets of rain, fog, aerosols along with a number of pollutants (metal ions, among others) play a major role in the chemistry of atmosphere.

The role of these heterogeneous reactions mustn't be neglected in spite of the fact that the volumetric fraction of droplets in a cloud is very small, of an order of  $10^{-6}$ - $10^{-7}$  while the volumetric fraction of clouds in troposphere is approx.  $5 \cdot 10^{-2}$ . This applies, in particular, to oxidation of sulfur dioxide and formation of acid rains.



Fig. 7. Regions of the atmoshere.

The stratosphere is the next zone above the troposphere (Fig. 8) and it consists mainly of  $N_2$ ,  $O_2$  and water, with some O and ozone. Since tropopause is characterised by low temperature, water condensation and formation of ice crystals occurs there. Very small water content in stratosphere in the form of ice crystals is reflected by the phenomenon of formation of the so-called pearly clouds at altitudes of approx. 20-25 km. The lower layer of stratosphere is almost perfectly isotermic. Rapid growth of temperature occurs higher, starting from an altitude of about 25 km, at the base of the ozone layer. It is the UV absorption that causes continual growth of temperature. Ozone concentration in the middle part of this layer equals to 10 ppm. Despite the low concentration, ozone is capable of absorbing UV of the wavelength range between 200 and 330 nm. Ozone is a highly reactive and unstable substance, but it persists in the stratosphere due to low air pressure which in this zone varies in the range of 0.1-0.001 atm. This means that the mean free path between collisions is quite long there thus reducing the probability of intermolecular reactions. This also explains why in the more remote from the earth's surface spheres (mesosphere, thermosphere) such highly reactive particles as  $O_2^+$ , NO<sup>+</sup> and O<sup>+</sup> can survive even though they would not exist close to the surface for any significant time. These species absorb short wavelength solar radiation and play a role similar to ozone in maintaining life on earth.

Pollutants do not normally enter mesosphere. The transport of atmospheric pollutants depends on the height they reach in the atmosphere, their particle size in case of dust, and climatic factors. Little transfer of air and pollutants occurs between the northern and southern hemispheres in the troposphere, but some transfer occurs between the troposphere and the stratosphere near the equator and in other places. Explosions and volcanic eruptions inject some pollutants directly into the stratosphere. Gaseous pollutants tend to remain in the stratosphere for a long time because of the lack of washout.



Fig. 8. The major zones of the Earth's atmosphere.

# 8. EFFECT OF POLLUTANTS ON HUMAN HEALTH AND ENVIRONMENT

Pollution of the atmospheric air in many different ways affects both living organisms and inanimate objects. The resulting damages are of either direct or indirect character.

The direct damages result from the action of toxic substances on living organisms. The indirectly inflicted ones are caused by absorption and dispersion of sun rays, losses of UV radiation, air ionisation, formation of fog favouring condensation of pollutants etc.

The research into these effects conducted so far has established that air pollution in cities and large industrial centres causes increased occurrence of many diseases, such as rickets in children, various lung diseases (mainly TB), bronchitis and anthracosis. Besides, the pollution is an important factor contributing to increased number of cases of lung cancer, eye diseases, circulatory problems and belatedness of children's growth. Belatedness of mental development can be assigned to increased content of certain heavy metals, particularly lead, in the food consumed by children.

Depending on their specific action on living organisms, the air pollutants can be divided into several categories:

- substances irritating mucous membranes of the respiratory tract and eyes, also capable of causing inflammation. This group comprises mostly compounds of acidic character, such as H<sub>2</sub>SO<sub>4</sub>, HCl, HF, CH<sub>3</sub>COOH, NOx and others;
- substances causing asphyxiation, making respiration and gas exchange in blood difficult or even impossible. The most notable among them is carbon monoxide, a compound binding blood haemoglobin and inhibiting normal intake of oxygen through lungs. Another example is SO<sub>2</sub> to which recently reported cases of infants' death in England and Germany are attributed. Sulfur dioxide typically causes respiratory problems and laryngitis while NO<sub>2</sub> is responsible for formation of smog, and the combined action of the two compounds results in increased excretion of phlegm;
- drug-like poisons affecting the nervous system. This group embraces hydrocarbons, esthers, alcohols, organic halogenoderivatives, amines, etc.;
- poisons causing disturbances in nutrition processes at the cellular level. Various metal compounds belong to this group, such as mercury vapors and organic compounds, organic compounds of lead, arsenic and copper;
- carcinogenic substances such as polycyclic aromatic hydrocarbons and their derivatives, e.g. 3,4-benzopyrene, aromatic amines, nitrosamines etc.;
- substances in the form of dust harmful to lung by inhalation. The most dangerous are dusts containing free silica (SiO<sub>2</sub>) which dissolves in bodily fluids and causes decomposition of protein-based substances; asbestos dust is a most talked-about example;
- gaseous substances of highly unpleasant odour; some may even be harmless to organisms but create a feeling of utter discomfort. Examples are thiols and organic derivatives of hydrogen sulphide which can be smelled in concentrations as low as 0.0003 mg/kg.

Pollution of atmospheric air caused many disastrous effects in the past. Some authors report a 5-day period of very thick smog persisting on the River Mose in Belgium, in 1930. The smog caused death of 63 people who suffered rapid cessation of heart functions. Many more were more or less seriously ill. The severe pollution affected also domestic animals. Respiratory problems occurring in cattle forced the farmers to put down many animals.

In 1952 in London, during a 4-day period of fog containing toxic substances about 4000 people died and many thousands suffered from serious diseases. In 1956, about 1000 deaths were reported for the same reason.

In 1945 in Los Angeles thick smog persisted for 100 days. The smog contained many detrimental compounds, such as sulphur oxides, nitrogen oxides and aldehydes (Table 7).

Pollutant	Highest permissible concentration [mg/kg]		
	Warning	Alarm	Danger
Nitrogen oxides	3.0	5,0	10.0
Ozone	0.5	1.0	1.5
Sulfur dioxide	3.0	5.0	10.
Carbon monoxide	100.0	200.0	300.0

Table 7. Highest permissible concentrations of air pollutants in Los Angeles

Contaminants emitted to atmosphere in the form of gases, smokes and dusts always inflict damage upon vegetation, particularly forests being its main constituent. The effects of industrial air pollutants on trees usually manifest themselves in serious disturbances in the plants' physiology. Forests react in a particularly strong manner to air pollution consisting of dusts and gases, mainly because forest areas favour concentration of industrial contaminants. The effects of the pollutants are of direct nature when damage is done to the above-ground parts of plants, usually their assimilation organs i.e. leaves and needles. Indirect harmful influence of air pollution occurs through the soil. Dust can be especially detrimental to plants as its particles tend to clog plants' "breathing" pores thus impeding gas exchange and absorption of solar radiation by chlorophyll. This, in turn, decreases the rate of CO<sub>2</sub> assimilation which weakens the trees and makes them lose their leaves. Tissues of the trees exposed to such influence show increased concentration of sulfides and sometimes certain heavy metals (Cu, Pb, Zn). Such processes are particularly pronounced during prolonged periods of drought.

 $SO_2$  affects the water circulation system within a plant. As a result, plant's tissues suffer damages, the rate of photosynthesis and chlorophyll content become significantly lower. In consequence, growth of the tree is retarded or even comes to a complete halt. Often single trees or the whole tree stand in the area perish. High concentration of  $SO_2$  causes burns of leaves, sprouts or branches putting a quick end to the affected tree. Sulfur dioxide penetrates the leaves' tissues and reacts with the compounds contained in chloroplasts. It also binds iron (Fe) thus eliminating the process of photosynthesis. The  $SO_2$  toxicity threshold, e.g. for the spruce, is very low and equals approx. 0.01 mg per one m<sup>3</sup> of air.

Mass death of coniferous as well as deciduous trees occurs most frequently during the winter time when one-year sprouts which have not lignified to a degree sufficient to allow them to withstand low temperatures and which carry too much water freeze and die.

Excess of nitrogen (N) in the soil is the main reason for accumulation of this element in plants, but negative effects of this phenomenon become more pronounced by deficiency in the soil of other nutritive compounds ( $P_2O_5$  and  $K_2O$ ). Plants' reaction to excessive concentrations of nitrogen in their tissues may adopt various forms. One of the early symptoms is discolouration of leaves which turn brown and then wither. Pine trees growing in the areas affected by excess on nitrogen produce extremely long needles, sometimes as long as 25 cm while their normal length is about 7-9 cm. Such gigantic needles usually wither in midsummer making the death of the whole tree imminent. Birch trees perish a year later.

The damages inflicted upon forests by industrial pollution can be categorised as acute, caused by harmful gaseous pollutant occurring in high concentrations, such as  $SO_2$  acting almost immediately ("acid rain"), and chronic, being a result of prolonged exposure to chemical compounds of lower concentrations. The effects of such damages are clearly visible as disolouration of leaves and needles with their consequent fall, or even as death of the whole tree.

Sensitivity of different tree species to air pollution varies significantly. The research conducted so far indicates that among the most vulnerable species are fir, common pine and varieties of spruce. Deciduous trees seem to be more immune to destructive action of pollutants, but also come conifers are quite resistant. The latter group comprises the following species: larch (Larix), black pine (Pinus niger), weymouth pine (white American pine, Pinus strobus). Among the most resistant deciduous trees are red oak, robinia, birch, grey alder, aspen and many varieties of poplar. Apart from direct poisonous action, pollutants destroy the tree's natural immunity system making it susceptible to infestation and diseases.

The most severe damage to forests is usually done in highly industrialised areas where concentration of air pollutants can reach the highest values, particularly when the means aimed at emission control are insufficient.

Vegetation plays a very important role in control of the chemical composition of air, mostly due to absorption of carbon dioxide and production of oxygen by plants. This process liquidates some of the pollutants originating in industrial processes involving combustion of coal. If, however, concentrations of these pollutants exceed certain values, the trees die, being incapable of fulfilling their air purification role.

"Where forests die, people die, too" - the saying first created in Germany now gives a warning to the societies of the world emphasising the dangerous effects of air pollution to woodlands.

Air pollution largely contributes to changes of many climate factors thus indirectly affecting vegetation. Among such factors are wind patterns, solar radiation, occurrence of fogs, cloud build-up, atmospheric precipitations and temperature (Table 8).

1. Winds	Average velocity (annually)	20%-30% lower	
	Extremal velocities	10%-20% lower	
	Number of days of still	5%-10% higher	
2. Solar radiation	Total, in horizontal plane	15%-20% less	
	Sunlight in the summer	5% less	
	Sunlight in winter	15% less	
	UV in the summer	5% less	
3. Clouds	Annual average	5%-20% greater	
4. Occurrence of fogs	Winter fogs	100% more	
	Summer fogs	30% more	
5. Air pollution	Dust particles	10 times more	
_	SO <sub>2</sub> concentration	5 times higher	
	CO <sub>2</sub> concentration	10 times higher	
	CO concentration	25 times higher	
6. Rains	Total precipitation, annually	5%-10% greater	
	Number of days with rain below 5 mm	10% higher	
7. Relative humidity	Annual average	6% lower	
of air	Winter average	2% lower	
	Summer average	8% lower	
	Annual average	0.5-1.0°C higher	
8. Air temperature	Minimum (winter)	1.0-1.5°C higher	

 
 Table 8. Changes of some important climate factors caused by European type of urbanisation, as compared to the environment outside the cities

Air pollution causes miscellaneous losses and damages. Apart from harmful influence on living organisms, such losses are of economic nature, e.g. increased costs of illumination of cities due to cutdown of sunlight by atmospheric pollution. Pollutants exert their destructive influence on various inorganic man-made materials, for instance the materials used for construction (old buildings), ceramic and metal structures, clothes etc. They are gradually destroyed by aggressive pollutants, chiefly gaseous compounds of sulfur, nitrogen and fluorine. HF and other compounds of acidic character are among the most dangerous pollutants in this respect.

The performed calculations indicate the figure of total losses in Great Britain amounting to USD 750 million. In USA the losses amount to several, sometimes even more than ten billion dollars annually. According to some authors, reduction of pollution in urbanized areas of USA

by 50% would result in savings of about USD 2 billion a year, only on costs of medical care and absence from work.

Similar estimates made in Germany show that reducing emission of pollutants by 37% would cost approx. DM 1 billion, but at the same time would result in savings of DM 600 million on reduced metal corrosion. Considerably greater benefits would then be achieved by decrease of pollution of forests and agricultural areas.

# 9. FLY ASH

Table 9 shows the sources of fly ash being an effect of human activity.

Table 9. Antropogenic sources of aerosol particles in the atmosphere (195	Antropogenic sources of aerosol particles in	the atmosphere (1996)
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Source	Flux, Mt/y
<b>Primary</b> Industrial dust, etc. Soot (elemental carbon) from fossil fuels	100 8
Soot from biomass compussion Secondary Sulfates from SO <sub>2</sub> as (NH4)2SO4	5 140
Biomass burning Nitrates from NO <sub>x</sub>	80 36
Total	370

Coal used in power station furnaces is first pulverised and then fed into the furnace. The coal typically contains 5 to 40% of mineral constituents which do not undergo the combustion process and are emitted in the form of solid particles at the end of this process. Fig. 9 illustrates the manner in which the particles of fly ash are formed in the coal combustion process. Large particles, of about 1-20 µm size, are formed by agglomeration of mineral inclusions on the surface of burnt particles of coal. Due to comminution, each particle of coal generates 3-5 particles of fly ash whose diameter falls in the range of 10-20 µm and a large number of smaller particles, with the diameter of 1-3 µm. Very small particles, of diameters below 0.1 µm are formed by evaporation and then condensation and sublimation of small portions of the mineral matter on the surface of burning coal grains. In the conditions prevailing in boilers fired with pulverized fuel (flame temperature 1400-1600°C) approx. 1% of mineral components of coal evaporate forming volatile inorganic vapors, such as Na, As, Sb, Fe, Mg and SiO. The vapors, after oxidation of metals, form condensation nuclei for alkaline vapors causing formation of large amounts of small agglomerates with the grain size of 0.1-1  $\mu$ m. The size range of fly ash particles emitted after combustion comprises the diameters between 0.01 and 100 µm while 90% of the particles have spherical structure.



Fig. 9. Possible ash transformation processes during pulverized coal combustion.

In developed countries, most pulverized coal-fired power stations are fitted with particulate control systems that are more than 99% efficient. The emission standards for new large combustion plants in various countries generally require particulate emissions of less than 50 mg/m<sup>3</sup>. This typically requires more than 99.5% of the particulates to be retained. Eleven elements commonly found in coal are among the substances identified as "hazardous pollutants": As, Be, Cd, Co, Cr, Hg, Ni, Mn, Pb, Sb, Se. Their concentration is normally enhanced in fly ash, as demonstrated in Table 10.

	In hard coal mg/kg	In particulate matter
As	$4.0 \pm 2.0$	868
Be	$2.0 \pm 3.1$	29
Cd	$0.0 \pm 0.07$	7
Со	$16.4 \pm 4.7$	234
Cr	$0.9 \pm 0.44$	8
Hg	$0.1 \pm 0.1$	2
Ni	$10 \pm 4.3$	291
Mn	$38.8 \pm 23$	588
Pb	$6.5 \pm 3.1$	274
Sb	$0.6 \pm 0.26$	29
Se	$2.6 \pm 1$	3140

Table 10. Trace elements concentration in particles downstream of a wet FGD(according to Dutch data)

Quite big amounts of mercury are emitted during fossil fuel combustion which are later deposited in soil and water. About 35% of anthropogenic mercury emission orginates from coal combustion. Concentration of Hg in coal is one order of magnitude higher in comparison with oil. One coal fired 1000 MW block emitts 0.41-4.1 tons of mercury annualy. It is estimated that annual emission increase in global scale is 5% per annum due to above fact. Efficiency of trace elements capture at ESP and BF is given in Table 11. FGD systems also reduce particulate emissions and change their particle size distribution (Fig. 10, Japan). This reduction efficiency may reach 95% after the high removal efficiency already achieved by ESP.

Element	Removal efficiency [%]		
	Electrostatic precipitator	Bag filter	
Arsen (As)	98,43	99,94	
Cobalt (Co)	99,79	99,95	
Chromium (Cr)	99,80	99,70	
Mercury (Hg)	60,00	67,14	
Manganium (Mn)	94,23	99,94	
Nickel (Ni)	96,33	99,83	
Selenium (Se)	97,16	98,52	
Uranium (U)	99,50	99,93	
Vanadium (V)	99,91	99,95	
Zinc (Zn)	99,73	99,93	

Table 11. Efficiency of trace elements capture at dust collectors (USA data)

Very dangerous for human health, as it can be noticed from Fig. 6, are particles with diameter less than 10  $\mu$ m or even below 2.5  $\mu$ m. Therefore two terms concerning ambient air pollution were introduced; those equal to or less than 10  $\mu$ m in diameter are referred to as PM<sub>10</sub> and the fine particles of diameter  $\leq 2.5 \mu$ m are called PM<sub>2.5</sub>.

Gaseous emissions, such as  $SO_2$  and  $NO_x$ , undergo oxidation in the atmosphere and form, after chemical reactions, secondary particulate matter, mostly  $PM_{2.5}$ . A group of elements with affinities mainly to sulfate and aluminosilicate cenospheres are enriched by a factor of two to twenty in  $PM_{10}$  compared with their concentrations in the total fly ash: As, B, Be, Bi, Cd, Co, Cr, Cu, Ga, Ge, Hg, Mo, Na, Ni, Pb, S, Sb, Se, Sn, Ti, V, U, W and Zn. Leaching tests (Australia, bag house) show further enrichment in  $PM_{2.5}$ :

	≤ 2.3 μm	≤ 10.9 μm
As	56	8
Cd	20	0
Cu	4	0
Sb	18	18
Se	57	21
Zn	3	0

According to the schemes presented in chapter earlier,  $SO_2$  and NO are oxidised to form acids which react with NH<sub>3</sub> present in atmosphere resulting in nitrate and sulfate aerosols (NH<sub>4</sub>NO<sub>3</sub> and (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>). These aerosols precipitate through wet deposition mechanism.

![](_page_36_Figure_0.jpeg)

Fig. 10. Reduction in particulate concentration and particle size distribution through an ESP, pre-scrubber and FGD.

Fine particulate and acidic pollutants synergetically influence human health as presented in Table 12.

Symptoms	Concentration		Concentration figure	
	SO <sub>2</sub>	Fly ash	expressed as	
	m	ıg/m <sup>3</sup>		
Lowered visibility discomford	0.08	0.08	annual arythmetic mean	
			value	
Occurrence of respiratory	0.10	0.10	annual arythmetic mean	
problems in children			value	
Health condition deterioration	0.25-0.50	0.25	daily arythmetic mean	
in persons suffering from lung			value	
diseases				
Increased number of deaths	0.50	0.50	daily arythmetic mean	
and illnesses requiring			value	
hospitalisation				

Table 12. Combined influence of SO<sub>2</sub> and fly ash in the air

 $PM_{10}$  and  $PM_{2.5}$  have been associated with health effects across several population studies. According to the UK Department of Health the deaths of 8100 individuals may be brought forward annually by  $PM_{10}$ . Up to 10,500 hospital admissions for respiratory problems can be added. According to the review by the CEC, long-term exposure to low concentrations of particulate matter in air is associated with a reduction in life expectancy in the order of one on health effects as well, increase in  $PM_{10}$  to 50  $\mu$ g/m<sup>3</sup> over three days already causes instances of death. The same is observed with  $PM_{2.5}$  rise of 10  $\mu$ g/m<sup>3</sup> over the background concentration.

Children are more susceptible than adults to the effects of particulate matter or its constituents.

A study of babies in Mexico City has shown a "starting" link between  $PM_{2.5}$  and infant mortality. A rise of 10  $\mu$ g/m<sup>3</sup> in  $PM_{2.5}$  concentrations, typically observed several days a month, caused a 5% increase in infant mortality.

#### **10. CARBON MONOXIDE (CO)**

Normal practice to ensure conversion of CO to  $CO_2$  during combustion process is to supply the boiler with a greater than stoichiometric air-to-fuel ratio; around 20% excess air which leaves around 4% of  $O_2$  in the dry flue gas.

Paradoxically, emission control measures can increase CO emissions. The control of  $NO_x$  emissions by primary measures generally involves minimizing excess air and reducing combustion temperatures. Both of these can lead to increased CO emissions. The optimum burner zone stoichiometry for several large brown coal fired boilers was found to be approximately 0.8. This gave  $NO_x$  concentrations of around 100 mg/m<sup>3</sup> but also lead to excessive CO formation. A higher air to fuel ratio (~0.95) gave  $NO_x$  emissions that were still within the legal requirements (<200 mg/m<sup>3</sup>) with CO emissions of the order of 100 mg/m<sup>3</sup>.

CO is a very toxic gas, showing 200 to 300 times greater affinity to haemoglobin than oxygen. It forms carboxyhaemoglobin which obstructs  $O_2$  transport in the blood.

#### 11. SULFUR DIOXIDE (SO<sub>2</sub>)

Intensive research is being conducted worldwide in order to reduce SO<sub>2</sub> emission from power production sources based on coal combustion process. Global power of coal-fired electropower stations amounts to 968 GW. Out of this total, in power plants of 274 GW capacity low sulfur content coal is used, 198 GW plants have been equipped in wet desulfurization installations, 19 GW - in semidry spray scrubbers and 12 GW - in other type desulfurization installations (sorbent injection processes: 4 GW, regenerable systems: 4 GW, combined SO<sub>2</sub>/NO<sub>x</sub> systems: 3 GW, dry scrubbers: 1 GW). Unfortunately, still (1998 data) power plants producing 465 GW electricity have no desulfurization installations. Generally, if no FGD is provided, 90% of sulfur originally present in coal is emitted to the atmosphere as sulfur oxides. If a certain kind of coal contains 1% sulfur and has a calorific value of 29 MJ/kg, uncontrolled emission of SO<sub>2</sub> of around 700 g/MJ would be expected. To meet the standard applicable in much of continental Europe 400 mg/m<sup>3</sup> (~140 mg/MJ), the sulfur content would have to be around 0.2%. In some cases, when combustion temperature is relatively low and coal cointains alkaline compounds (MgO, CaO etc.) SO2 emission is lower than expected. Part of the emitted sulfur is in the form of SO<sub>3</sub>. Typically, the SO<sub>2</sub>/SO<sub>3</sub> ratio in flue gas falls in the range from 20:1 to 30:1.

Until now less than 5% of sulfur contained in known deposits of oil and coal has been released to the atmosphere. Since the lifetime of sulfur dioxide and sulfates in atmosphere spans over several days, these compounds are carried by winds and precipitate in areas distant from the source of emission. E.g. 92% sulfur precipitation in Norway comes from non-Norwegian sources. It should be emphasised, however, that rain acidity and sulfur precipitation in Norway decreased by 35% in the period 1980-1993.

Although in the global scale the mass of sulfur compounds emitted from natural sources (volcanic eruptions,  $H_2S$  produced from decay of biological matter, quickly oxidized to  $SO_2$  in the atmosphere, etc.) is slightly greater than that originating from human activity, in highly industrialised areas of Europe and North America only 10% of sulfur emission can be attributed to natural processes.

Almost one-half of  $SO_2$  mass in the atmosphere is removed by oxidation to sulfates or sulfuric acid, the remaining part precipitates in the form of dry aerosol and with rains. The average annual precipitation of sulfur compounds (expressed in tons of pure sulfur per sq. km per year) reported in different countries was 8.5 in Czech Republic and Slovakia, 7.7 - in Poland, 7.6 - Germany (East), 5.6 - Germany (West), 2.7 - France. Low sulfur precipitation in France is a result of a relatively high proportion of electricity generation in nuclear power plants.

Harmful influence of  $SO_2$  on vegetation manifests either in a direct or indirect manner. In the first case, leaves and needles suffer damages from  $SO_2$  present in the air. Natural wax coating of leaves and their stomata is partly destroyed. Also inner membranes of leaves and needles are destroyed which causes serious disturbances in the plant nutrition system and water balance. On the other hand, indirect damages are inflicted by acidification of rains and soil. Various species of trees, bushes and wood undergrowth show different degree of sensitivity to chemical pollutants of the atmosphere.

Deciduous trees and bushes usually show greater resistance to air pollution than do coniferous species. This is largely due to the fact that in moderate climatic zones deciduous plants shed their leaves annually thus being much less exposed to  $SO_2$  influence. At high concentrations of  $SO_2$  the plant tissue undergoes a process of biological degradation. The leaves' edges and intervascular areas become practically destroyed. Permanent exposure of plants to  $SO_2$  causes chlorosis, i.e. bleaching or yellowing of normally green parts of leaves. As

the air humidity grows, the damage becomes more severe which is also the case during the daytime when the plants' stomata are open facilitating gas exchange with the atmosphere. Continuous exposure throughout 72 hours to  $SO_2$  concentration of 0.15 ppm is known to have caused diminishing of wheat and barley crops by as much as 42 to 44% while a 3-hour exposure to 1.2 ppm  $SO_2$  in the air did not inflict any damages. An interesting fact is that most plants are able to withstand a short exposure to relatively high concentrations of  $SO_2$  much better than prolonged action of  $SO_2$  at low concentration.

Sulfur dioxide in the atmosphere, after its conversion to sulfuric acid in aerosols and rains, causes damage of leaves visible as tiny holes in the leaves burnt through by droplets of the acid. Fig. 11 illustrates destructive influence of  $SO_2$  on vegetation. Even the lowest  $SO_2$  concentrations are sufficient to interfere with the stoma-closing mechanism. The effect is an excessive loss of water.

![](_page_39_Figure_2.jpeg)

Fig.11, Effects of SO<sub>2</sub> action on vegetation.

Presence of sulfur dioxide in the air exerts a negative influence on human respiratory system. Staying in the polluted atmosphere for a prolonged period of time causes difficulties in breathing. People suffering from asthma are most vulnerable under such conditions. Laboratory tests carried out on animals did not indicate any undesired effects at  $SO_2$  concentration of 5 ppm.  $SO_2$  concentrations at the level of approx. 500 ppm are lethal for humans. Harmful effects of  $SO_2$  action on human health are shown in Fig. 12.

![](_page_40_Figure_1.jpeg)

Fig. 12. Effects of SO<sub>2</sub> action on human health.

# **12. NITROGEN OXIDES (NO<sub>X</sub>)**

Nitrogen oxides are among the major environmental pollutants that have a significant detrimental effect on the atmosphere. The nitrogen oxides present in the atmosphere are nitrogen oxide (NO), nitrogen dioxide (NO<sub>2</sub>), collectively known as NO<sub>x</sub>, along with smaller amounts of nitrous oxide (N<sub>2</sub>O). NO<sub>x</sub> contributes to photochemical smog formation, to the formation of acid rain precursors and to the greenhouse effect through the formation of ozone.

Reactions involving NO and  $O_3$  in the stratosphere and those in the troposphere are quite distinct. In the stratosphere the reactions commonly lead to the depletion of  $O_3$  whereas in the troposphere there is a tendency towards  $O_3$  production.

On a global scale, fossil fuel combustion is by far the largest source of NO<sub>x</sub>, accounting for over half of all emissions (including those from natural sources). N<sub>2</sub>O, whose residence time in atmosphere is about 130 years, was responsible for around 6 % of the enhanced greenhouse effect during the 1980s. Concentration of N<sub>2</sub>O in the atmosphere increased from 280-290 ppbv in 1980 to around 310 ppbv in 1988 and is still increasing at a rate of 0.2-0,3% per year - corresponding to 3-4.5 megatons of nitrogen equivalent per year (Mt(N)/y). 0.24-0.09 Mt(N)/y equivalent orginates from conventional coal combustion where N<sub>2</sub>O is formed only from fuel-contained nitrogen. New environmentaly friendly fluidized bed combustion process unfortunately emits relatively high concentrations of N<sub>2</sub>O (0.2-5 ppmv). It is due to the fact that FBC boilers are operated at temperatures between 800° and 900°C that NO<sub>x</sub> and SO<sub>2</sub> emissions are reduced.

Primary reduction technologies can be applied to control NO<sub>x</sub> emission at pulverised coal boilers: low NO<sub>x</sub> burners, furnace air staging, fuel staging (reburning). Eventually selective catalytic reduction (ammonia on catalyst at 300-360°C) or selective non-catalytic reduction (ammonia or urea at 900-1100°C) are applied for flue gas treatment and NO<sub>x</sub> removal.

 $NO_x$  emission has not been limited to the same extent as has the emission of  $SO_2$ . Of the figure 968 GW of fossil fuel burning electricity generation plants mentioned in one of the previous chapters, 313 GW corresponds to the plants where primary measures for  $NO_x$  emission control have been applied, flue gas treatment - 14 GW and both means in 60 GW. Without any  $NO_x$  control 581 GW plants are still operated.

The estimates are that 60% of lake acidification in Norway is attributable to emission of nitrogen compounds. Nitrogen is associated with chronic as well as episodic acidification of acid - sensitive Adirondack lakes in the USA. In Europe (1994) NO<sub>x</sub> emissions were responsible for 32% of the acidification, SO<sub>2</sub> was resposible for 44% and NH<sub>3</sub> for 24%. Combustion processes were responsible for 34% of the acidification equivalent units (of SO<sub>2</sub>, NO<sub>x</sub> and NH<sub>3</sub> in weight percentage of H<sup>+</sup>ions). The second source (23%) was agriculture and forestry.

HNO<sub>3</sub> alone and the mixture of NO<sub>2</sub> and SO<sub>2</sub> (SO<sub>2</sub> + NO<sub>2</sub> + H<sub>2</sub>O  $\rightarrow$  SO<sub>4</sub><sup>2-</sup> + 2H<sup>+</sup> + NO) are very corrosive. This action is amplified in warm regions. O<sub>3</sub> formed in reactions involving NO<sub>x</sub> is corrosive to rubber, plastics, textiles, paints and other surface coatings. Estimates for the US say that reduction in O<sub>3</sub> concentration by 10 ppb below the average levels results in savings of 5.4 bilion USD annualy. Estimates of SO<sub>2</sub> and NO<sub>x</sub> corrosive effects for Europe give the figure of losses in the range of 2.9-5.3 billion ECU/year.

Nitrogen dioxide is removed from the atmosphere in the form of nitric salts or organic compounds in areas where photochemical smog occurs, or as nitric acid. Droplets and vapors of the latter precipitate with rains or in dry aerosols.

Similarly to carbon monoxide and nitrites, nitrogen oxide is bound by haemoglobin blocking the access of oxygen. However more toxic and biochemically active is nitrogen dioxide.

Every year, 60 million people have their lung functions impaired by 2-5% due to average concentration of NO<sub>x</sub> exceeding 60  $\mu$ g/m<sup>3</sup>. Since NO<sub>x</sub> emissions can lead to increase of O<sub>3</sub> concentration, health effects from the secondary product must also be taken into account. Health effects from O<sub>3</sub> exposure include impairment of lung functions, coughs, pulmonary inflammation, increased susceptibility to respiratory infections and lung structure damage.

Vegetation exposed to  $NO_x$  action suffers severe damage. Most of the destructive effects are probably a result of a secondary reaction of  $NO_x$  leading to formation of peroxyacetyl nitrate (PAN) during occurrence of photochemical smog.  $NO_2$  concentrations at the level of several ppm cause shedding of leaves and decay of plants' tissue as well as weakening of photosynthesis processes.

Since the toxicity of NO<sub>2</sub> is considered to be relatively low, the critical level is set for a combination of NO<sub>2</sub>, SO<sub>2</sub> and O<sub>3</sub>. The level for NO<sub>2</sub> has been set at 30  $\mu$ g/m<sup>3</sup> as a yearly average with 95  $\mu$ g/m<sup>3</sup> as a peak value. The limit for SO<sub>2</sub> is 10-20  $\mu$ g/m<sup>3</sup> and for O<sub>3</sub> is 40 ppb (80  $\mu$ g/m<sup>3</sup>).

It has been estimated that forest soil can accept 3-20 kg of nitrogen per hectare per year, depending on the degree of productivity, before nitrogen begins to leak out of the system. The average deposition in Europe is 30-40 kg/y.

## 13. HALOGENS

Typically the range of halogens contents in coal is 50-2000 ppm for chlorine, 20-500 ppm for fluorine, 0.5-90 ppm for bromine and 0.5-15 ppm for iodine.

During combustion, it has been estimated that 94% of the chlorine is emitted, mostly as HCl. Coal can be the major source of atmospheric chlorine (as HCl) in countries that rely on coal for a large percentage of their electricity generation. The flue gases contain around 80 ppmv for each 0.1% of chlorine in the coal. An uncontrolled (no FGD), 500 MWe, power station using 0.12% chroride coal would emit about 1300 t/y of HCl. The fluorine in coal is found in mineral matter and the type of mineral may affect the emission rate of HF from the combustion zone. When fluorine is present mainly in fluorite, emission of up to 90% of the fluorine as HF can occur. Preliminary work indicates that emissions may be reduced by a factor of ten or more when fluorine is present as fluorapatite.

Hydrogen chloride exerts similar to  $SO_2$  influence on the natural environment becoming one of components of acid rains. Plants relocate fluorides absorbed by the roots into the edge and tip zones of needles and leaves. Therefore, after slight HF exposures over long periods of time, the highest fluoride concentrations are found in older needles. Deciduous trees are less sensitive to fluorine.

#### 14. PAH INFLUENCE ON HUMAN HEALTH

Polycyclic aromatic hydrocarbons including benzo(a)pyrene are among the compounds showing the highest mutagenic, teratogenic and carcinogenic activity. On the list of the most severe environmental poisons PAH occupy the third place behind  $SO_2$  and fly ash (Polish Academy of Sciences, Environment Toxicology Committee). US Environment Protection Agency lists 17 PAH compounds as a group creating high mutagenic hazard. They are: naphtalene, acenaphtalene, fluorene, phenanthrene, anthracene, benzo(a)anthracene, chrysene, pyrene, fluoranthene, benzo(b)fluoranthene, benzo(e)pyrene, benzo(a)pyrene, indeno(1,2,3-c,d)pyrene, dibenzo(a,h)anthracene, benzo(g,h,i)perylene. Benzo(a)pyrene is a powerful carcinogen, and often the occurrence of PAHs are reported in term of this substance. The members of PAH group share common properties, such as relatively low solubility in water, with the most important members being lipophylic.

Increasing consumption of fossil fuels enhances the exposure of humans to PAHs. A major PAH source can be household furnaces burning coal, wood or oil. Diesel engines significantly contribute to PAH concentration in the air.

Some PAH compounds, such as benzo(a)pyrene, show little acute toxicity but their longterm action causes chronic poisoning. This means that a single large dose may not give immediate effects, but continuous exposure to even small concentrations will probably cause cancer. For non-smokers, the main source of PAH (over 95%, average daily intake approx. 3  $\mu$ g) is the food. PAH concentrations in different food products vary significantly, e.g. in unwashed leaf vegetables - 20-40  $\mu$ g/kg, in unrefined cereal - 10  $\mu$ g/kg, meat and fish smoked over charcoal fire - 10-20  $\mu$ g/kg. PAH intake through lungs, as it is the case in polluted air or as a result of cigarette smoking, leads to greater absorption of these compounds by the organism than from impure food.

# 15. SOIL DEGRADATION INDUCED BY ATMOSPHERIC PRECIPITATION OF POLLUTANTS

The term "soil" refers to the surface layer of the "crust of the earth", or lithosphere, made from the matrix rock as a result of soil formation processes. These processes comprise action of a number of factors, such as microorganisms, vegetation, animals, climate, water and human activity.

One of important features of soil is its fertility, a quality connected with the content of humus and nutritive mineral components easily assimilated by plants. The widest-known processes of soil degradation attributable to air pollution are excessive acidification, alkalisation and accumulation of phytotoxic substances (poisonous for vegetation). These processes cause deficiency of nutritive constituents. Sandy soils are susceptible to chemical degradation in the first place, since by their nature they are characterised by shortage of nutritive substances and are slightly acidic.

Acidity of soil is determined by the content of hydrogen ions (H<sup>+</sup>). This is the reason why even small concentrations of acidic pollutants impair biological activity of soil in the areas where the soil is acidic by its nature.

A major factor increasing soil's resistance to the action of pollutants is the content of clayey substances, humus in the first place. The main constituents of clay are cations of calcium, sodium. potassium and magnesium. Therefore it is possible to say that it is the content of alkaline metals in the soil that contributes most to its immunity to harmful influences. Unfortunately, such cations can easily be leached out of the soil when treated with sulfuric acid. Direct influence of toxic constituents of air pollutants manifests itself when their penetration of the soil is sufficiently intense and when there are biochemically and physicochemically active compounds among them. Depending on the type of soil, such direct action can cause negative or positive effects in the soil. In some cases the effects can be periodically positive or temporarily positive with transition to negative.

Indirect impact of pollutants is associated with their ability to interfere with one or more factors of the soil formation process. Such interference consists mainly in chronic damage of the plants' assimilation system by gaseous components. These indirect negative effects may take a long time before affecting the soil.

Elemental sulfur after getting into soil undergoes oxidation to  $SO_3$  which, reacting with water, gives sulfuric acid. The environment acidified in such manner impedes growth of soil microorganisms and creates highly unfavourable conditions for assimilation of nutritive substances by plants. Sulfuric acid facilitates dissolving of some sparingly soluble mineral substances thus leading to the release of such substances as sulphides and the excess of manganese, aluminium and iron.

The intensity of changes caused in the soil by pollution depends on the soil type and the type of its matrix rock. A significant role in the process play also water relations in the soil. The soil acidification process runs at a higher rate if the soil character changes along its geological profile. The same applies to the situation where plants are more ground water and not precipitation water - dependent.

Ground water coming from a reception area of low pH causes increase of general acidity of the soil. Among many effects of ground water acidification the most significant is leaching from the soil of the basic cations:  $Ca^{2+}$ ,  $Mg^{2+}$ ,  $K^+$ ,  $Na^+$ . The process largely depends on pH of the soil and consequently on the volume of acid rains in the area, amounts of fertilizers added, soil type and the amount of water percolating through the soil.

Nitrogen oxides are converted to nitric acid and precipitate in acid rains where they behave in a manner similar to acidogenic sulfur dioxide. It is difficult to differentiate between the effects of NO<sub>x</sub> and SO<sub>2</sub> for the water - soil environment since these pollutants usually occur jointly in the atmosphere and both are constituents of acid rains containing nitric and sulfuric acid. Therefore the effects caused by NO<sub>x</sub> are also attributable to sulfur oxides.

Table 13 shows various degrees of hazard to which different crops are exposed as a result of permanent contact with  $SO_2$  and for comparison, with HF and HCl.

Crops	Type of plants	SO <sub>2</sub>	HF	HCl
	Cereal, incl. maize	++	++	+++
	Beans, clover, alfalfa	+++	+++	+++
General	Sunflower	+	+	++
	Potatoes	+	+	++
	Beetroot, cabbage	+	+++	+
	Grass and grass-like plants	++	++++	+++
Fodder	Fodder beans, clover-like fodder plants	+++	+++++	+++
	Fodder cabbage	+	+++++	+
Field crop	Papilionaceous	+++	+++	+++
vegetables	Whorl-like	+	+	+
	Pumpkins and similar	+	+	+
Meadows and	Prevailing grass	++	++++	+++
pastures	Large percentage of clover-like plants	+++	+++++	+++
	Drupe fruit	++	****	+++
	Berries, walnuts	++++	++++	++++
Fruit	Hazelnuts	+++	++++	****
	Grapes	+++	++++	+++++
	Strawberries	+	++++	<b>+++</b> +++
	Fir, spruce, weymouth pine	+++++	++++	+++++
Forests	Australian pine, juniper, thuja, yew, cypress	+++	+++	+++
	Deciduous trees	+++	+++	+++
Decorative	Lilies	+	++++	++
plants and	Roses	++	++	++
flowers	Papilionaceous plants	+++	+++	+++
	Aralias	+	+	
	Carnations	++	<b>+</b> ++	
	Heather-like	+	+	+
Effect intensity: + very weak, ++ weak, +++ average, ++++ strong, +++++ very strong				ong

# Table 13. Susceptibility of various crops to harmful effects of SO2, HF and HCl at permanent exposure to these pollutants

# **16. CONCLUSIONS**

Environmental pollution resulted from fossil fuel combustion and forseen shortage of these type energy resources are the challenges for the present civilization.

New technologies concerning combustion modification and air pollution control have to be introduced.

Moreover scientists, engineers and politicians have to prepare honest program concerning energy generation sources for the next century.

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