

# GASEOUS POLLUTANTS TRANSPORT IN URBAN ATMOSPHERE

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# 1. TRANSPORT OF GASEOUS POLLUTANTS IN ATMOSPHERE GENERAL REMARKS

As it was presented in the previous sections, the understanding of the pollution concept is approached in integrated manner, considering the pollution source, the pollutant released, its transport and effects on human health, natural and built environment.

The aim of this unit is to present the pollutant transport in environment, based on physical and chemical processes in which the atmospheric pollutants are involved. Directly linked to the transport, we are faced with the question "where the pollutants arrive?" This is translated by the analysis of the pollutants' effects on human health and on the natural and/or built environment.



The *atmospheric pollutants* can be directly emitted in atmosphere, or they are formed as result of reactions among atmospheric components.

The primary pollutants are directly emitted in atmosphere, such as primary particulate matter, sulfur dioxide, ammonia, carbon monoxide, methane.

The secondary pollutants are those formed by chemical reactions among precursor substances which can be pollutants. Among secondary pollutants we mention: secondary particulate matter, tropospheric ozone, nitrogen dioxide, acid aerosols, and the smog.

In European Union documents the key atmospheric pollutants are those producing the most harmful effects on human health, and they are: particulate matter, nitrogen dioxide, tropospheric ozone. In the following sections of the unit these pollutants, together with the sulfur dioxide as major atmospheric pollutant, will be described.





The gaseous *pollutants transport* at atmospheric level is by dispersion, caused by air masses movements. The atmospheric processes are distinguished in physical and chemical processes, and both types may be operating simultaneously in complicated and interdependent ways. The physical processes of transport by atmospheric winds and the formation of clouds and precipitation strongly influence the patterns and rates of acidic deposition, while chemical recations govern the forms of the compounds formed.

Considering the stability of the chemical species, these can be transported on various distances from the source, generating local/regional or global pollution. The transfer of substance in air to surfaces, including soil, vegetation, surface water, or indoor surfaces, done by dry or wet processes, is called *atmospheric deposition*. The dry deposition involves nonaqueous chemicals, usually with non-polar molecules. The wet deposition is the process encompassing the transfer of pollutants to the Earth's surface by rain, snow or fog, by aqueous solution. If the atmosphere is contaminated with acidic pollutants (sulfur oxides, sulfates, nitrogen oxides, nitrates, ammonium compounds), the deposition is called acidic deposition, and it can be either wet (pollutant specied dissolved in atmospheric water and the acid precipitation occurs) or dry (the acid pollutants are adsorbed to particles and deposited in nonaqueos form).

In atmosphere, a huge number of chemical reactions occurs. Several examples are:

- *photochemical processes*, which are chemical reactions brought about by the light energy of the sun; as example, the reaction of nitrogen oxides with hydrocarbons in the presence of sunlight to form ozone; tropospheric ozone, fotochemical smog are relevant examples of secondary pollutants formed by this type of reactions;





- *acid-base reactions* which occurs in the presence of water, between acidic species (as CO<sub>2</sub>, SO<sub>2</sub>, NO<sub>x</sub>, etc.) and basic species (mostly NH<sub>3</sub>); acidic precipitation, sulfate aerosols are relevant pr of this type of processes;
- redox reactions occurs between species having opposite character. Species like O<sub>2</sub>, hydrogen peroxide, hydroxyl radical, ozone act as oxidants, sulfur dioxide, nitrogen monoxide, carbon monoxide are/can be oxidized in atmosphere generating secondary pollutants.

Under the sun light radiation in atmosphere are generated aggressive species, with high reactivity, with very short life-time, in the range of seconds to several hours. These species cause pollution at micro-environment level, being involved in reactions generating secondary pollutants. For example, the hydroxyl radical being involved in numerous chemical and photo-chemical processes with organic or inorganic compounds, is called "the atmosphere detergent".

Species moderately long lived, in the range of days, are primary or secondary pollutants, cause pollution at local level, urban or rural.

The most stable species (with very low reactivity), those with long lifetime in the range of years can be transported over long distances at troposphere level, or at high altitude, producing pollution at global level. Example includes nitrous oxide and crabon dioxide which are greenhouse gases with significant contribution to climate change.



The *effects of air pollution* can reach different targets/receptors. Generally speaking, at human health level, air pollution causes a major risk for respiratory, cardiovascular disease, and also can





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affect the central nervous system functions. Human exposure is defined as the event when a person comes into contact with a pollutant of a certain concentration during a certain period of time. The exposure occurs where people spend their time in the polluted environment. It depends on the level of pollution of the air in the environment where people spend the time, on the amount of time spend in the polluted environment, and also on the personal activity.

The World Health Organization mentions the following effects as result of specific symptoms:

- after short-time exposure (over a few years hours or days) linked to accute heatth effects (like wheezing, coughing, phlegm production, respiratory infections, physiological changes in lung functions): daily mortality, respiratory and cardiovascular hospital admissions, respiratory and cardiovascular emergency department visits, respiratory and cardiovascular primary care visits, use of respiratory and cardiovascular medications, days of restricted activity, work absenteeism, school absenteeism;
- after long-time exposure (over months or years) linked to chronic disease: mortality due to cardiovascular and respiratory disease, chronic respiratory disease, chronic respiratory disease incidence and prelevance, like asthma, chronic changes in physiologic functions, lung cancer, chronic cardiovascular disease, intrauterine restriction.

The global evaluation of the impact of the poor air quality on human health is quantified by indicators, like mortality, morbidity, premature deaths, years of life lost.

*Mortality* reflects the reduction in life expentancy owing to premature deaths as result of air pollution exposure. *Morbidity* relates to the occurrence of illness and years lived with a disease and disability, ranging from subclinical effects and symptoms such as coughing to chronic conditions that my require hospitalisation. The *life expectancy* is the number of years that a person can expect to live on average, based on estimation of data on death rates of the population.

The *premature deaths* are deaths that occur before a person reaches an expected age. This expected age is typically the age of standard life expectancy for a country or gender. Premature deaths are considered preventable if their cause can be eliminated.

*Years of life lost* (YLL) are defined as the number of years of potential life lost owing to premature detah. It is an estimate of the average number of years that a person would have lived if he/she had not died prematurely.



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At the level of European Union member countries, it was estimated the impact of the key air pollutants  $PM_{2.5}$ ,  $NO_2$ ,  $O_3$  using specific health metrics – premature deaths and years of life lost. For pollutant, it was estimated the percent of urban population exposed in the period 2013-2015 to pollutants in concentration above the limits imposed by European Union and by World Health Organization. In table below it is presented the estimation of values for the years of life lost for 100 000 persons in EU-28 countries in the period 2013 – 2015, as result of exposure to a pollutant. The data are taken form "Air quality in Europe- 2017 Report". The report concluded evidence of the direct correlation between the indicator and the air pollutant concentration in air.





The impact of air pollution on ecosystems manifests by degradation on environmental factors quality, like soil, freshwater or lake acidification, damages of crops, forests, or eutrophication. The components of the polluted atmosphere have impact on climatic changes, influencing the increase of the mean global temperature.

The atmospheric pollution also affects the built environment, the cultural heritage by damages of the construction materials, metallic materials corrosion, surfaces soiling, weathering and/or fading.

# 2. SULFUR DIOXIDE

The sulfur dioxide is a primary pollutant of the atmosphere, being directly emitted by pollution sources. In atmosphere, it can be transported by the air masses, or can participate to physical, chemical, or photo-oxidation processes, generating secondary pollutants with high adverse effects on human health and natural and built environment.





#### 2.1. Sources for SO<sub>2</sub> emissions

The sulfur dioxide can be emitted by natural or anthropic sources.

By volcanic eruption, as localized natural pollution source, in atmosphere huge quantities of sulfur dioxide are released. As example, during the eruption of the Pinatubo volcano in Philippines, in June 1991, in atmosphere were released 20 mega-tons of sulfur dioxide. Another natural source for sulfur dioxide emission is the biological decomposition of sulfur-containing organic matter from proteins. The product of decomposition is the hydrogen sulfide, which is oxidized to sulfur dioxide.

From the anthropic sources, the most important is the fossil fuels combustion. Both coal and crude oil contains sulfur, which by combustion generates sulfur dioxide together with other primary and/or secondary pollutants. By refining processes the sulfur content in gasoline is reduced, thus SO<sub>2</sub> emissions due to road transportation are not very high. Emissions from non-road transportation sector have slightly higher contribution, since for shipping crude oil (with higher content of sulfur) is burned favoring SO<sub>2</sub> release. The highest contribution of emissions as result of fossil fuel combustion belongs to coal burning, since this energy carrier has high sulfur content. It has to be noticed that over the past decades the SO<sub>2</sub> emission decreases, mainly due to technological developments in sulfur removal from fuel and/or from exhaust gases.

An important source of sulfur dioxide is the nonferrous smelting industry. In this case, the process of roasting the sulfide ores generates the sulfur dioxide.







# 2.2. SO<sub>2</sub> properties

The sulfur dioxide is a gaseous, colorless with specific odor compound. It has a non-polar molecule, allowing the dry deposition. It is also soluble in water, allowing also the wet deposition, by precipitation. It reacts with water, the result is the sulfurous acid, a weak acid generating two types of anions – bisulfite and sulfite.



Colorless, sharp, acrid odor

 $SO_2$  non polar molecule  $\rightarrow$  dry deposition

Highly water soluble  $\rightarrow$  wet deposition

 $SO_2 + H_2O \rightarrow H_2SO_{3 (aq)}$  Sulfurous acid, weak acid

 $H_2SO_3 \leftrightarrow H^+ + HSO_3^-$  Bisulfite ion

 $HSO_3^- \leftrightarrow H^+ + SO_3^{2-}$  Sulfite ion

#### 2.3. SO<sub>2</sub> atmospheric concentration limits

In unpolluted atmosphere the sulfur dioxide should have a concentration of one part per million in volumes. Due to anthropic emissions its concentration are increased. The limits imposed by





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Air Quality Directive and those recommended by the World Health Organization are established to protect the human health.

European Commission air quality standard (EU-AQD): 350  $\mu$ g/m<sup>3</sup> for 1 hour mean 125  $\mu$ g/m<sup>3</sup> for 24 hours mean

WHO Air Quality Guideline (WHO-AGQ):
20 μg/m<sup>3</sup> for 24 hours mean
500 μg/m<sup>3</sup> for 10 minutes mean

According to EU – Air Quality Report, in 2015, 30% of all SO<sub>2</sub> stations registered concentrations above the daily WHO guidelines consequently, 38% of EU-28 urban population was exposed to SO<sub>2</sub> levels exceeding the limit for health protection. It has to be mentioned that it was registered a significant decrease, since in 2000, 80% of total EU population was exposed to exceeding levels of SO<sub>2</sub>.

# 2.4. SO<sub>2</sub> atmospheric transport

Form the atmosphere, the sulfur dioxide can be transported by dry deposition, being adhered on particulate matter. In the presence of atmospheric water and oxidative species, like hydrogen peroxide, hydroxyl radical, ozone, the tetra-valent sulfur from sulfur dioxide or sulfite anions, is oxidized to hexa-valent sulfur, to sulfate anions. The oxidation process occurs over a period of hours or days. In the oxidative processes, the hydrogen ion is also formed, thus the reaction product is the sulfuric acid dissolved in atmospheric water. Thus, acid aerosols are generated and they are deposited by acidic precipitations as rain, snow, mist, etc. It is called acid precipitation the one with the pH value lower than 5. Naturally, in un-polluted atmosphere, the rain has the pH value of 5.6.

The acid can undergo acid-base reaction with ammonia, resulting ammonium sulfate salt. Initially generated in aqueous droplets, the evaporation of water can occur, and solid particles of ammonium sulfate are formed. Aerosols dominated by oxidized sulfur compounds are often called sulfate aerosols.

Dry deposition:  $SO_{2(g)} + PM_{(s)} \rightarrow PM_{(s)}$ Wet deposition:  $\{0\}_{aq} + S(IV)_{aq} \rightarrow 2H_{aq}^{+} + SO_{4(aq)}^{2-}$ 





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The urban atmosphere can be polluted with sulfur dioxide and also with particulate matter, as ash or soot. These pollutants are emitted especially as result of activities where the coal is used as energy source. This type of pollution is called industrial smog.

The word smog is formed by combining two English words – smoke and fog. The industrial smog is produced in industrialized centers, where the energy is produced by coal burning, usually in winter time, on wet and cold weather.

### Industrial smog

A mixture of fly ash, soot, SO<sub>2</sub> and some VOCs

SMOG = SMOKE + FOG

Produced in industrial centers, typically in winter, under wet and cold weather

# 2.5. SO<sub>2</sub> effects on human health

Population exposure to sulfur dioxide is only by inhalation. The most vulnerable groups at sulfur dioxide action are the children, elderly people, and those who already have pulmonary affections. Among the adverse effects of sulfur dioxide on human health we exemplify the eye irritations, respiratory problems, increased risk of heart attack.

During the first half or the XX<sup>th</sup> Century, acute pollution episodes caused by industrial smog are reported (such as 1930 in Meuse Valley, 1939 Saint Louis, 1948 Donora, etc.). It is well-known the case of industrial smog in London (London smog), in December 1952, when 4000 of deaths were registered due to respiratory and cardio-vascular disease as result of exposure to smog mainly containing sulfur dioxide and particulate matter.





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London smog

#### 2.6. SO<sub>2</sub> effects on ecosystems

Once in contact with soil or water surface (lakes and rivers), sulfur dioxide produces their acidification. It is harmful for trees and plants, by damaging the foliage and influencing their growth. Also, it favors the biodiversity loss.



#### 2.7. SO<sub>2</sub> effects on built environment

The sulfur dioxide brings a negative impact on built environment, by degradation of historical monuments, because of calcium and magnesium carbonate reactions with acidic aerosols. Acidic aerosols damage the building materials as limestone, dolomite, marble from ordinary buildings, but also from cultural and historical sites.





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# 3. Nitrogen oxides - NO<sub>x</sub>

A significant number of nitrogen compounds are present in the atmosphere. We mention the oxides like:

- nitrous oxide, known as "laughing gas" (due to its euphoric effects upon inhalation,, used as safe medicine, and as oxidizer in rocket propellants, in motor Racing, etc.), a primary pollutant of the atmosphere;
- nitrogen oxide and nitrogen dioxide, major pollutants of the atmosphere, collectively designated as NO<sub>x</sub>.

Practically, the nitrogen oxide once released in atmosphere is rapidly oxidized to nitrogen dioxide. Thus, nitrogen oxide is a primary pollutant and nitrogen dioxide is a secondary one. Very low quantities of nitrogen dioxide are directly released in atmosphere.

Nitrogen oxides participate in chemical and photochemical processes, generating secondary pollutants like: nitric acid, nitrate radicals, peroxyacetyl nitrate, and tropospheric ozone.

Primary or secondary nitrogen-containing pollutants are known as generating adverse effects on human health, natural or built environment.





# 3.1. Sources for NO<sub>x</sub> emissions

The natural sources of the nitrogen oxides emission have a major contribution to their presence in troposphere. As result of the natural processes, the background concentration of nitrogen dioxide is 0.02 ppmv. The biochemical decomposition of organic matter is one the natural sources for nitrogen oxides (as  $N_2O$ ,  $NO_x$ ) formation. Volcanic eruption and lightning during storms release nitrogen oxides in troposphere.

Among anthropic sources, the important contribution belongs to energy production by fossil fuels combustion, both in stationary and mobile sources. The industrial processes like nitric acid production, the use of explosives, welding, are also sources for nitrogen oxides emissions. The agriculture sector has to be mentioned, since the use of synthetic nitrogen-based fertilizers, during denitrification, release an important quantity of nitrogen in troposphere.





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The official documents issued by European Union and by World Health Organization impose the limits for atmospheric concentration of nitrogen dioxide at  $40\mu g/m^3$  as annual mean, and  $200\mu g/m^3$  as hourly mean.

# 3.2. NO<sub>2</sub> properties

Among oxides, the most aggressive pollutant is the nitrogen dioxide. At temperature below - 11.2°C it is a colorless solid, formed by dimer molecules. In the temperature range -11.2 °C to 21.2 °C it is a yellowish-brown liquid, and above 21.2 °C is a reddish-brown liquid. Both in liquid and gaseous form it has a radical structure, because on the impair electron at the nitrogen atom. This gives to nitrogen dioxide high reactivity.

The nitrogen dioxide has characteristic, pungent odor, its presence it atmosphere in high concentration can be noticed due to reduced visibility as reddish- brown haze.

With the atmospheric water it forms a mixture of nitric and nitrous acids which can be neutralized by the ammonia, if present.

Nitrogen dioxide has oxidizing properties, it can react with the hydroxyl, forming acidic species. It is a precursor for tropospheric ozone and it plays important role in photochemical smog formation.

temperature (°C)	11.2°C	-11.2°C21.2°C	21.2°C
state	solid	liquid	gas



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form	dinitrogen tetroxide $N_2O_4$ (dimer)	Nitrogen dioxide 'NO <sub>2</sub> (free radical)	Nitrogen dioxide 'NO <sub>2</sub> (free radical)
color	colorless	yellowish-brown	reddish-brown

- Characteristic pungent odor
- $\blacktriangleright$  Absorbs visible solar radiation  $\rightarrow$  contributes to decrease the atmospheric visibility
- ▶ Reacts with water  $\rightarrow$  nitric acid + nitrous acid
- > In the presence of ammonia  $\rightarrow$  ammonium nitrate
- > Regulator of the oxidizing capacity of the troposphere  $\rightarrow$  reacts with hydroxyl radicals
- > Plays a critical role in ozone formation/removal in troposphere  $\rightarrow$  photochemical smog

#### 3.3. NO<sub>2</sub> - key precursor of a range of secondary pollutants

As result of its reactivity, nitrogen dioxide is responsible for at least two major problems of the atmosphere pollution:

- acidic aerosol
- photochemical smog.

The photochemical smog is formed under solar radiation, in regions with intense road traffic and industrial activity. The photochemical smog precursors are nitrogen dioxide, volatile organic compounds, hydrocarbons, which under sunlight undergo a series of photochemical reactions to form secondary pollutants such as tropospheric ozone, peroxyacetyil nitrate, formaldehyde. Thus, the photochemical smog is a complex combination of pollutants in developed as a yellow-brown haze in hot sunny weather cities where automobile traffic is congested (it is also known as Los Angeles smog).







# 3.4. Effects of NO<sub>2</sub>

Nitrogen dioxide exerts a range of adverse effects on human health by reductions in respiratory, pulmonary functions when population is exposed by inhalation.

When deposited from atmosphere, nitrogen dioxide but also nitrous oxide contributes to imbalance in nitrogen nutrient in aquatic ecosystems, leading to eutrophication.

Once deposited on soil, and/or in surface water nitrogen oxides generates acidification.

In contact with built environment components, due to acidity, the nitrogen-based gaseous pollutants lead also to damages.

It is important to mention that the nitrous oxide has no direct adverse effects on human health, but it is a greenhouse gas and has contribution to climate change.



#### $\rm N_2O$ is a green-house gas, contributing to climate change



# 4. GROUND-LEVEL OZONE4.1. Ozone in the atmosphere

In the Earth atmosphere, the ozone is naturally present in *stratosphere*, at about 25 kilometers altitude. It is formed by photo-oxidation of bimolecular oxygen, under the UV-solar radiation. Thus, the stratospheric ozone is beneficial for the Earth, because it absorbs the harmful UV solar radiation.

In *troposphere*, at ground level, the ozone is a gaseous pollutant with adverse effects on human health and natural and built environment. It is known as the most representative and toxic pollutant of the class of ambient oxidants. The tropospheric ozone is a secondary pollutant, is not directly emitted by a source:

- stratosphere
  - ➢ ozone layer
  - ▶ (+) absorbs harmful UV solar radiation
- troposphere
  - ground-level ozone (tropospheric ozone)
  - ➢ (-) dangerous pollutant

Applying the pollution model, one can explain that tropospheric ozone is a secondary pollutant. The ozone precursors, pollutants emitted by their specific sources, under solar radiation, produce the *photochemical smog*. At local level it has adverse effects on human health, on natural and built environment. The photochemical smog is defined as the combination of fog and chemicals resulted from road transportation and industrial sources, which react in the presence of solar radiation.

In photochemical smog, the nitrogen dioxide, in the presence of solar radiation and some hydrocarbons (from volatile organic compounds family), form nitrogen monoxide and atomic oxygen. The atomic oxygen reacts with other pollutants released by automobiles, like carbon monoxide, forming a large variety of products, among which is the ozone. It has also to be mentioned the hydrogen peroxide, organic compounds like peroxyacetyl nitrates, aldehydes, like formaldehyde.





# 4.2. Ground-level Ozone: sources for precursors

The sources of production the tropospheric ozone precursors can be natural –the plants which emit substances from terpenes category or anthropogenic like urban traffic, but also some specific activities in agriculture sector.

#### Natural sources

- Biogenic emissions of precursors
- ➢ e.g. VOC emissions by vegetation

#### **Anthropogenic sources**

- Photochemical reactions of precursors emitted by own sources
- ➢ e.g.: urban traffic, agriculture

#### 4.3. Ground-level Ozone: properties

The ozone is a triatomic form of oxygen, is an unstable gas, colorless, with pungent odor, highly reactive and a strong oxidizing agent.

The limit concentration for human health protection has been established as 100 micrograms per cubic meter as 8-hours mean.

# 4.4. Ground-level Ozone: effects





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Among effects on human health as result of exposure to atmosphere polluted with ozone, we mention the acute ones, at the level of respiratory and cardiovascular systems. Among the chronic disease there are reported the diminishing of pulmonary functionality, development of asthma, reduction in life expectancy.

The ecosystems are also negatively influenced, by damages on vegetation and reduction of growth rate. Ground-level ozone is considered to be more damaging to vegetation and crops tan exposure to any other pollutant.

The presence of tropospheric ozone leads to degradation of fibers, rubber, construction materials. Also it produces the watering and fading the surfaces and construction materials.

The tropospheric ozone is a greenhouse gas, contributing to climate change.

human health	<ul> <li>Acute response: pulmonary system effects; cardiovascular effects</li> <li>Chronic response: reduced lung function; development of asthma; reduction in life expectancy</li> </ul>	
ecosystems	<ul> <li>Damages forests, vegetation and crops by reducing their growth rates</li> </ul>	
built environment	<ul> <li>Damages fabrics, rubber in tires, construction materials</li> <li>Weathering and fading of colors</li> </ul>	

Ground-level ozone is a green-house gas, contributing to climate change

# 5. PARTICULATE MATTER

The atmosphere, naturally or as result of anthropic activities is characterized by the presence of particulates, from both natural and man-made sources, with dimensions, between 0.5 mm for the dust particulates, sand or mist, and molecular dimensions for ones released from anthropic activities.

# 5.1. Particulate matter symbols

We define the particulate matter (symbol PM) the mixture of solid and/or liquid particles dispersed in air. The particulate matter consist of a mixture of fine solid and liquid particles suspended in the air. In evaluating the impact of particulate matter on environment and human health the most important issue is their dimension.





#### PMaerodynamic diameter

To the PM acronym is associated as subscript the number denoting the size fraction, or aerodynamic diameter. Based on this characteristic, the particulate matter are classified in:

*Total suspended matter* (quite an older name) which denotes all particles having dimension below 100 micrometers; these particles can be seen with naked eye, knowing that the visibility limit is around 50 micrometers;

The fraction *coarse particulates* contains those with the diameter range between 2.5 and 10 micrometers,

The fraction *fine particulates* contains those with diameter up to 2.5 micrometers

The fraction *ultrafine particulates*, or nanometric particulates, are those with diameter below 0.1 micrometers.

All particulates having dimensions below 10 micrometers cannot be seen with naked eye, they are visible with microscopes.

To describe the particulate matter, or simply, particulates, there are used terms like:

Aerosols, defined by the system of solid and liquid dispersed in air;

*Dust, soot* – for solid particles dispersed in air

*Mist, fog* - for the liquid particles dispersed in air.

Fraction	Range of the aerodynamic diameter	Symbol	Notes
Total suspended particles	$\leq 100 \mu m$	TSP	Can be seen with naked eye
Coarse particulates	$d \le 10 \mu m$ $2.5 \mu m \le d$ $\le 10 \mu m$	PM <sub>10</sub> PM <sub>2.5-10</sub>	
Fine particles	d < 2.5µm	PM <sub>2.5</sub> PM <sub>1</sub>	Can only be detected with microscopes
Ultrafine particles	$d < 0.1 \mu m$	UFP	





Considering the particulates' emission, one can distinguish between *primary particulate matter*, those directly emitted and *secondary particulate matter*, those formed in atmosphere as result of physical and chemical processes among gaseous pollutants like sulfur dioxide, nitrogen oxides, which are released by specific sources.

Once entered in atmosphere, the particulates are transported by air masses movements or they deposit. As function of their dimensions, there are variations in particles atmospheric lifetime, and consequently their transport distance. The particulates composition, depending on the emission source, dictates their dimension, transport and also the effect they have on human health, natural and/or built environment.



#### 5.2. Sources for PM emissions

Particulates are emitted by a huge number of sources, both natural and anthropic. Naturally, particulates exists as result of soil erosion, dust transported by air masses. The marine aerosols, well-known as sea-spray are rich in salts and organic matter. Particulate matter have also biologic origin, like pollen, mold. An important quantity of particulates is emitted during volcanic eruption. The most important source for particulate matter emission is the fossil fuel combustion, even if it

is coal, oil, oil products or biomass.





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Among the industrial sources we mention the construction sector, mining, cement, ceramic materials fabrication, smelting industry. An important source of particulates is the road erosion by traffic, and last not at least the activities in agriculture.

The precursors for secondary particulates are gaseous pollutants of the atmosphere like sulfur dioxide, nitrogen oxides, ammonia, which generate substances with low volatility, like sulfuric acid, ammonium sulfate, ammonium nitrate which condense, coagulate generating aerosols. They are transported as inorganic particulates, or deposit as crust on carbonaceous particulates.

The gaseous pollutants can be organic, released by natural sources, like terpenes, or by anthropic sources, like polycyclic aromatic hydrocarbons. They can generate secondary organic aerosols (SOA), by oxidation reactions. Compared to primary particulates, the chemical processes involved in the formation of secondary ones are relatively slow and their persistence in the atmosphere is prolonged.

#### Natural sources

- ➢ Soil and dust carried by wind
- Generation of marine aerosols (sea spray)
- Pollen, mold spores, plant parts
- Volcanic ash

#### Anthropogenic emission of primary PM

- > Combustion of fossil fuels (coal, oil, gasoline, biomass)
- Construction sites,
- > Building, mining, manufacture of cement, ceramic
- Smelting industry
- > Unpaved roads, erosion of pavement by road traffic

#### Secondary PM formation

- ➢ Formed in the air through reactions of gaseous pollutants → substances of low volatility which condense into solid/liquid phase → PM
- Sources of primary gaseous inorganic pollutants (SO<sub>2</sub>, NO<sub>x</sub>) or organic compounds (naturally emitted – monoterpenes, or resulted from anthropic activities – aromatic hydrocarbures)

# 5.3. PM composition

Considering their formation mechanism, the particulate matter have different composition and consequently, different dimensions. The fine particulates usually contains inorganic species,





water, and a core of elemental carbon, polycyclic aromatic hydrocarbons, secondary organic aerosols and also biological organic substances. Usually these particles contain soot or sulfate/nitrate aerosols, and their character is predominantly acidic.

The coarse particulates mainly contains dust, ashes, metallic oxides, sodium chloride from marine aerosols, biological components. Generally speaking, these particles mainly contain soot or inorganic compounds similar to those in soil, consequently they have predominantly alkaline character.

# **PM**<sub>2,5</sub>

- Inorganic species:
  - Anions: sulfates, nitrates, chloride
  - > Cations: ammonium, hydrogen, Sodium, Potassium, Calcium, Magnesium
  - > Transition Metals (Cadmium, Copper, Nickel, Zinc)
- Particle-bound water
- Organic carbon, elemental carbon (EC)
- Polycyclic aromatic hydrocarbons
- Secondary organic aerosols
- Biogenic organics
- Predominantly: soot or sulfate/nitrate aerosols
- Usually acidic (un-neutralized acids)

#### $\mathbf{PM}_{10}$

- Re-suspended dust, soil dust, street dust,
- ➢ Coal and oil fly ash,
- Oxides of Si, Al, Mg, Fe; CaCO3; NaCl
- ➢ Sea salt
- Biologic components: pollen, mold spores
- Predominantly: soot or inorganic soil like
- Usually basic (soil content)

# 5.4. PM transport

The transport of particulate matter by air masses movement depends on particles' dimension. The fine and ultrafine particulates have quite a long atmospheric lifetime, being transported over long distances, hundreds of kilometers, thus their impact is perceived at regional level.







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The coarse particulates have a lower atmospheric lifetime, in the range of minutes to several hours, thus they have a higher sedimentation rate. Their transport by air masses takes place over short distances, below 10 kilometers, thus the impact is manifested at local level.

Fine and ultrafine PM	Coarse PM
Lifetimes: days and weeks	Lifetimes: minutes to hours
100 – 1000 km travel distance	1 - 10 km travel distance
Affect regional and wider area	Affect local scale

# 5.5. PM air concentration for human health protection

The atmospheric concentrations established by Air Quality Directive at European Union level, are 25 micrograms per cubic meter, as annually mean for particulates with aerodynamic diameter up to 2.5 micrometers. For particulate matter with aerodynamic diameter up to 10 micrometers, limits are 40 micrograms per cubic meter annual mean and 50 micrograms per cubic meter, annual mean.

The limits proposed by the World Health Organization are stricter, values are below those recommended by European Union.

	<b>PM</b> <sub>2,5</sub>	PM <sub>10</sub>
EU limit (AQD):	25µg/m <sup>3</sup> -year	40µg/m <sup>3</sup> -year 50µg/m <sup>3</sup> - 24 hours
WHO limit (WGO guidelines):	10µg/m <sup>3</sup> - year	20µg/m <sup>3</sup> -year 20µg/m <sup>3</sup> - 24 hours

# 5.6. PM effects on human health

The effects of particulate matter on human health depends on their dimensions.

Even in Europe, the particulate matter emissions decreased over the period 2000-2015, still exist a significant percent of population exposed to particulates (even PM2.5, even PM10), in concentrations exceeding the limits imposed by EU or recommended by world health organization.





Considering the penetration into the human body, by inhalation, the coarse particulates are considered inhalable or thoracic particles, penetrating in the respiratory system, and filtered by nose and throat.

Fine particulate matter, the respirable particulates, penetrate deep into lung, in alveoli and bronchioles.

In the case of the coarse particulates, having a higher sedimentation rate, the long-time exposure by inhalation is reduced, but the short-time exposure causes respiratory disease.

There is a large number of studies demonstrating the fact that fine particulates are responsible for disease of the respiratory, cardiovascular systems and also at central nervous system level.

#### **PM**<sub>2,5</sub>

# EU-28 population exposure to PM<sub>2.5</sub> levels (2015): above EU limit (25µg/m<sup>3</sup>-year): 7%

#### above WHO limit (10µg/m<sup>3</sup> - year): 82%

- Respirable particles: usually travel to lungs, deep into the gas-exchange portions (alveoli and terminal bronchioles) and can be absorbed by cells surfaces
- Respiratory and cardiovascular morbidity (aggravation of asthma, respiratory symptoms
- Mortality from cardiovascular and respiratory disease, lung cancer
- Consistently implicated in adverse neurological processes, being related to central nervous system diseases

#### **PM**<sub>10</sub>

EU-28 population exposure to PM<sub>10</sub> levels (2015): above EU limit (50µg/m<sup>3</sup>-day): 20%

above WHO limit (20µg/m<sup>3</sup> – year): 62%

- Inhalable particles, thoracic particles: when inhaled, are efficiently filtered by nose and throat,
- penetrate only into the lower respiratory system
- Settle out quickly human long-term exposure via inhalation is reduced
- Short term exposure: effects on respiratory health

# 5.7. PM effects on environment

The adverse effects of the smoke released by the coal burning have been mentioned since the 13<sup>th</sup> Century. Over the centuries, a large number of pollution episodes caused by particulate matter







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were registered. With technological development, the particulate emitted in atmosphere have a more complex composition, thus their effect is manifested in more diverse ways. In atmosphere, the presence of particulates is perceived by reduced visibility. As consequence of their dimension and composition, particulates are dry or wet deposited, thus at the level of soil or water surface changes occur.

Smoke from coal burning known in UK from the 13<sup>th</sup> Century



Strongly reduce visibility



After deposition (wet/dry) - acidification of soil/surface waters Changing nutrient balance in surface waters Depleting nutrients in soil



# 5.8. PM effects on built environment





The presence of particulate matter in atmosphere leads to damages of building materials, degradation of objects and even of historical monuments. Surfaces soiling, watering, corrosion of metallic materials, are only a few examples of damages produced by particulate matter on built environment.

Damages on building materials, including the culturally important objects by degradation and soiling

Damages related to acid rain - weathering, corrosion,



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