



INZRAK

Enhanced environmental protection inspection for efficient control of air quality monitoring and of all entities under obligation within system of greenhouse gas emission allowance trading, in order to achieve better quality of air in Republic of Croatia



REPUBLIKA HRVATSKA

MINISTARSTVO ZAŠTITE  
OKOLIŠA I ENERGETIKE



 **safu** | SREDIŠNJA AGENCIJA ZA  
FINANCIARANJE I UGOVARANJE



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**EKONERG**

Energy Research and Environmental Protection Institute

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## THEME 2: Pollutants

## 2.1 O<sub>3</sub> – CHEMICAL CHARACTERISTICS



**Ground level ozone is the most important photochemical oxidizer in the troposphere. O<sub>3</sub> is the secondary pollutant because it is not emitted directly from sources, but creates by photochemical reactions (the radiation of the Sun) from the nitrogen dioxide (NO<sub>2</sub>) and easily volatile organic compounds (VOC) in the troposphere.**

## 2.2 O<sub>3</sub> – CHEMISTRY OF PRODUCTION AND DEGRADATION



Urban troposphere abounds in these compounds, and with favorable conditions comes to the formation of photochemical smog. The first condition is the creation of hydroxyl radicals (OH), which is formed by the reaction of free radicals and O\* and water molecule (O\* excited form of atomic oxygen):



## 2.2 O<sub>3</sub> – CHEMISTRY OF PRODUCTION AND DEGRADATION



Hydroxyl radical is the most important oxidising agent in the troposphere and it can react with all of the organic compounds in the air. The products of these reactions are molecules of water (H<sub>2</sub>O) and an organic radical:



where R (CH<sub>3</sub> ili CHO ili CH<sub>2</sub>CH<sub>3</sub>), and R\* is an organic radical



## 2.2 O<sub>3</sub> – CHEMISTRY OF PRODUCTION AND DEGRADATION

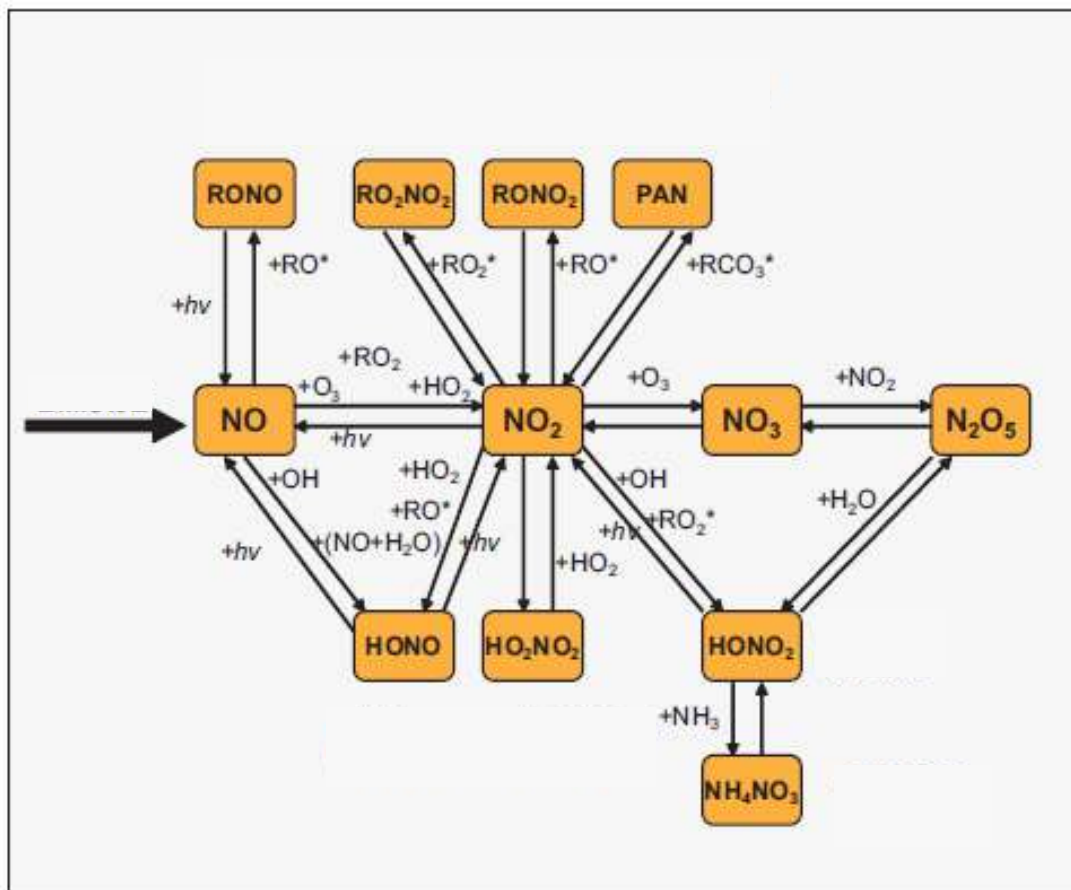
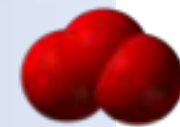


RO<sub>2</sub> \* allows oxidation NO in NO<sub>2</sub> without degradation of a molecule of ozone (O<sub>3</sub>), as shown in the reaction:



In the photochemical reactions in the troposphere by oxidation, NO<sub>x</sub> products are created, such as HNO<sub>3</sub>, HNO<sub>2</sub>, HO<sub>2</sub>NO<sub>2</sub>, peroxyacetyl nitrate, N<sub>2</sub>O<sub>5</sub>, nitrate radicals and organic nitrates, and all together represent the biological irritants.

## 2.2 O<sub>3</sub> – CHEMISTRY OF PRODUCTION AND DEGRADATION



Summary of interconversion ways of the oxidation of nitrogen in creation of photochemical smog.

## 2.2 O<sub>3</sub> – CHEMISTRY OF PRODUCTION AND DEGRADATION



### Summary the creation of photochemical smog

1. Photochemical smog is a mixture of primary and secondary pollutants in the troposphere.
2. Photochemical smog is created by a series reactions in which it transforms nitrogen (N) in the different compounds in the atmosphere.
3. Cars emit NO and small amounts of NO<sub>2</sub>.
4. Nitric oxide (NO) is actually the starting compound that is oxidized to atmospheric nitrogen dioxide (NO<sub>2</sub>), and he is further oxidized to nitric trioxide (NO<sub>3</sub>), which is transformed into nitric pentoxide (N<sub>2</sub>O<sub>5</sub>). Each of these nitrogen oxides then reacts in the photochemical processes with other atmospheric compounds, creating numerous biological irritants.



## 2.2 O<sub>3</sub> – CHEMISTRY OF PRODUCTION AND DEGRADATION



5. In the reactions of the creation of photochemical smog is coming to the concentrating of ground-level ozone (O<sub>3</sub>) in the lower layers of the troposphere.
6. The resulting mixture of photochemical smog consists of more than 100 chemical compounds.

## 2.3 O<sub>3</sub> – SPATIAL AND TEMPORAL DISTRIBUTION



The ambient ozone concentrations depend on several factors: the intensity of insolation, the height of the atmospheric layer of temperature inversion, concentrations of nitrogen oxide and volatile organic compounds and their ratios. The most favourable ratio for the creation of ozone is:

VOC: NO<sub>x</sub> = 4:1 or 10:1

## 2.3 O<sub>3</sub> – SPATIAL AND TEMPORAL DISTRIBUTION



Ozone shows significant spatial variations that depend on the:

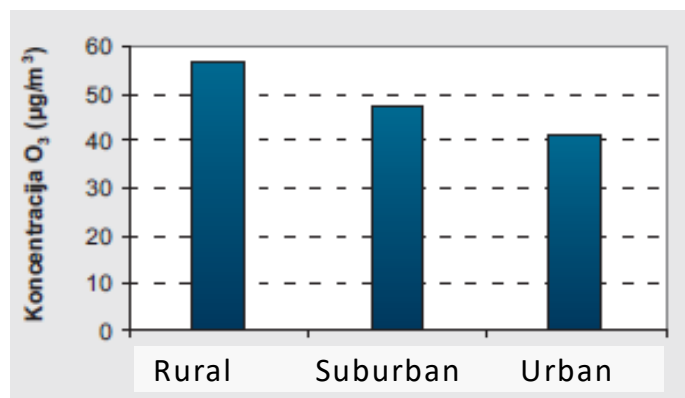
- prevailing wind directions
- tendency of achieving a higher concentration in the suburbs and rural areas,
- higher elevations

In the vicinity of the big source of emission of nitric oxides concentrations of ozone are less because with them get in a chemical reaction. This results in higher concentrations of ozone in the suburbs and the rural areas of such as those along the major roads.

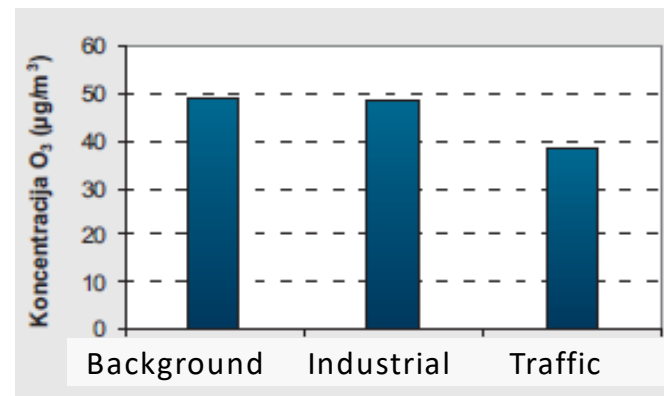
## 2.3 O<sub>3</sub> – SPATIAL AND TEMPORAL DISTRIBUTION



Annual mean values of ozone measured in Europe have shown the highest value on the background stations (49  $\mu\text{g}/\text{m}^3$ ) and stations which are located in rural areas (57.1  $\mu\text{g}/\text{m}^3$ ). The values measured in urban areas and along major roads are lower by about 24%.



The average annual values of concentration of O<sub>3</sub> is categorized according to the location of the measurement. Source: AIRNET.



The average annual values of concentration of O<sub>3</sub> is categorized according to a source of pollution. Source: AIRNET.

## 2.3 O<sub>3</sub> – SPATIAL AND TEMPORAL DISTRIBUTION



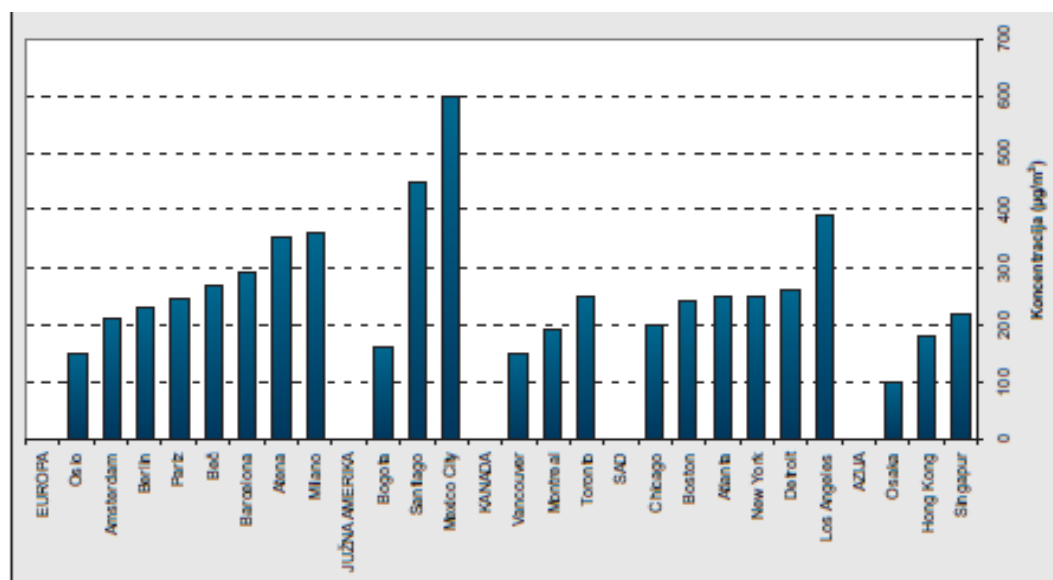
The values of maximum ozone hourly concentration measured in urban environments of different continents range between 100 to 380  $\mu\text{g}/\text{m}^3$ , except in South America where they are much more (200 to 600  $\mu\text{g}/\text{m}^3$ )

Area	$\mu\text{g} / \text{m}^3$
Africa	120 - 300
Asia	100 - 250
Australia/New Zeland	120 - 310
Canada/USA	150 - 380
Europe	150 - 350
South America	200 - 600

## 2.3 O<sub>3</sub> – SPATIAL AND TEMPORAL DISTRIBUTION



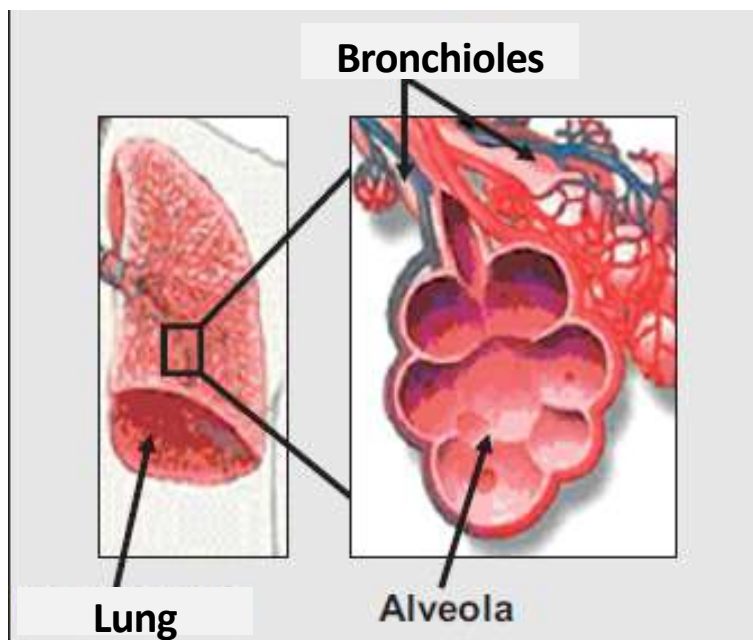
The values of the measurements of the highest average ozone hourly concentration in the big cities of Europe are increasing to the South, and so in Oslo amounts 150  $\mu\text{g}/\text{m}^3$ , in Vienna 280  $\mu\text{g}/\text{m}^3$ , while in Athens and Milan is around 350  $\mu\text{g}/\text{m}^3$ . Santiago and Mexico City are noted for very high values (450  $\mu\text{g}/\text{m}^3$  and 600  $\mu\text{g}/\text{m}^3$ ), while in the United States by the amount of ozone concentration extracts only Los Angeles 390  $\mu\text{g}/\text{m}^3$



## 2.4 O<sub>3</sub> – TOXICOLOGICAL AND PUBLIC HEALTH ASPECTS



Ozone enters into the body inhaling and since it is poorly soluble in water, inhaled is transported deep into the lungs where it damages the bronchioles entering the alveoli.



## 2.4 O<sub>3</sub> – TOXICOLOGICAL AND PUBLIC HEALTH ASPECTS



The short term ozone inhalation causes diffuse inflammation of the entire respiratory system, just as some parts of (nasal and the walls of the alveoli) more sensitive, so it is an inflammation of the stronger expressed.

Ozone on its way into the deeper airways damages the cells of the respiratory tract, causing inflammation of the lungs and reduce respiratory function. Inflammation is detected almost immediately after exposure on the basis of the occurrence of inflammatory mediators in the bronchi, and inflammatory cells usually appear after several hours.

There are indications that acute inflammation induced by ozone is not limited to the respiratory system because they are the markers of systemic inflammation such as complement activation and increased protein synthesis and found in the liver.



## 2.4 O<sub>3</sub> – TOXICOLOGICAL AND PUBLIC HEALTH ASPECTS

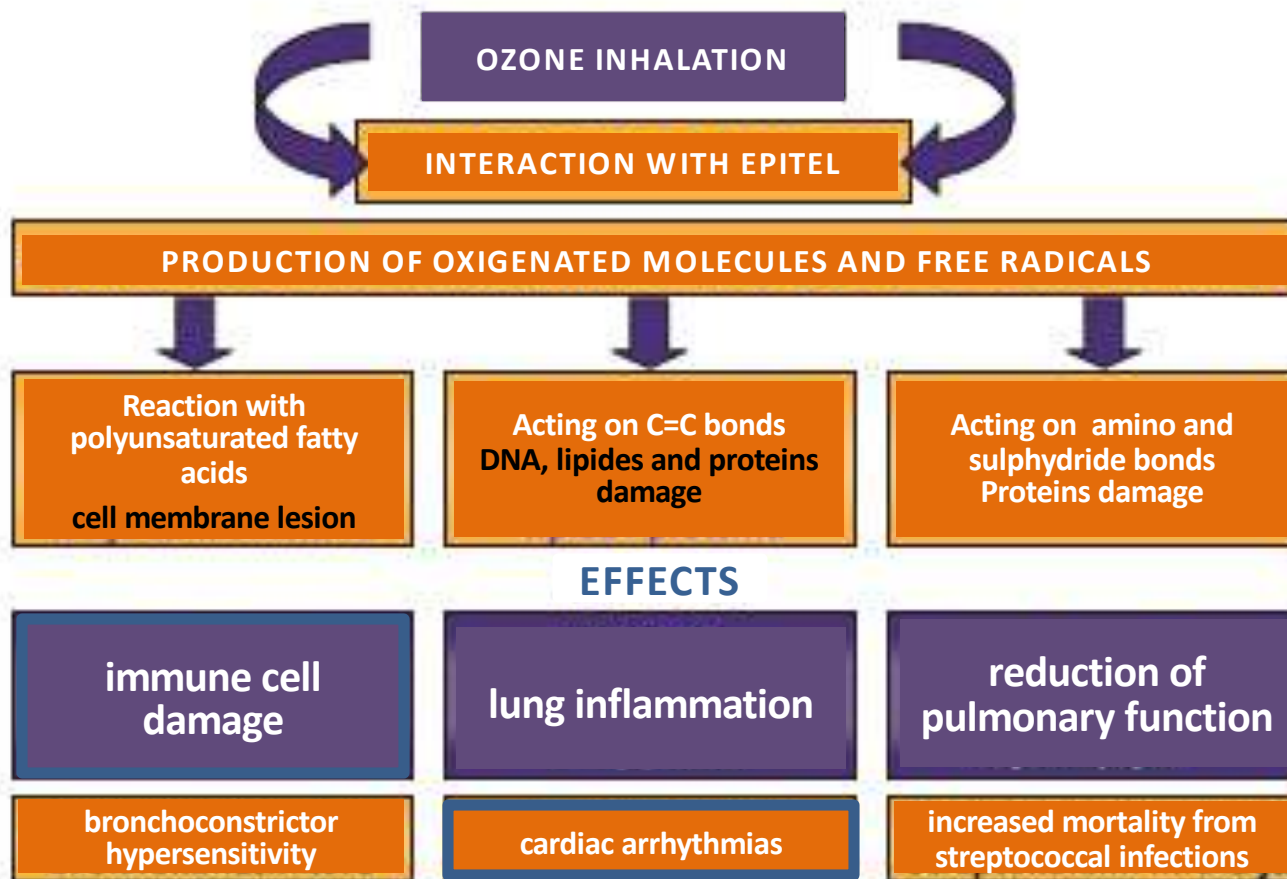


Depending on the concentration of ozone, repeating or long-term exposures and individual sensitivity, comes to the irreversible changes in the respiratory tract, including the damage to the DNA molecule.

This cell damage are a consequence of oxidative stress that cause secondary oxidation products.

Inflammation of the lung tissue, fluid accumulation and mobilization of macrophages in three weeks after exposure to lead to duplication of lung epithelial cells, proliferation of fibrous tissues and thickening of the pulmonary alveoli.

## 2.4 O<sub>3</sub> – TOXICOLOGICAL AND PUBLIC HEALTH ASPECTS



### Systemic effects of ozone oxidative stress mechanism

## 2.4 O<sub>3</sub> – TOXICOLOGICAL AND PUBLIC HEALTH ASPECTS



Ozone is associated with a greater number of serious effects on health that may be associated with acute and chronic exposure.

Acute exposure to ozone causes adverse systemic effects on the lung tissue and cardiovascular system.

Chronic exposure causes a reduction in lung function, the development of atherosclerosis, asthma, and shortening of the expected duration of life.

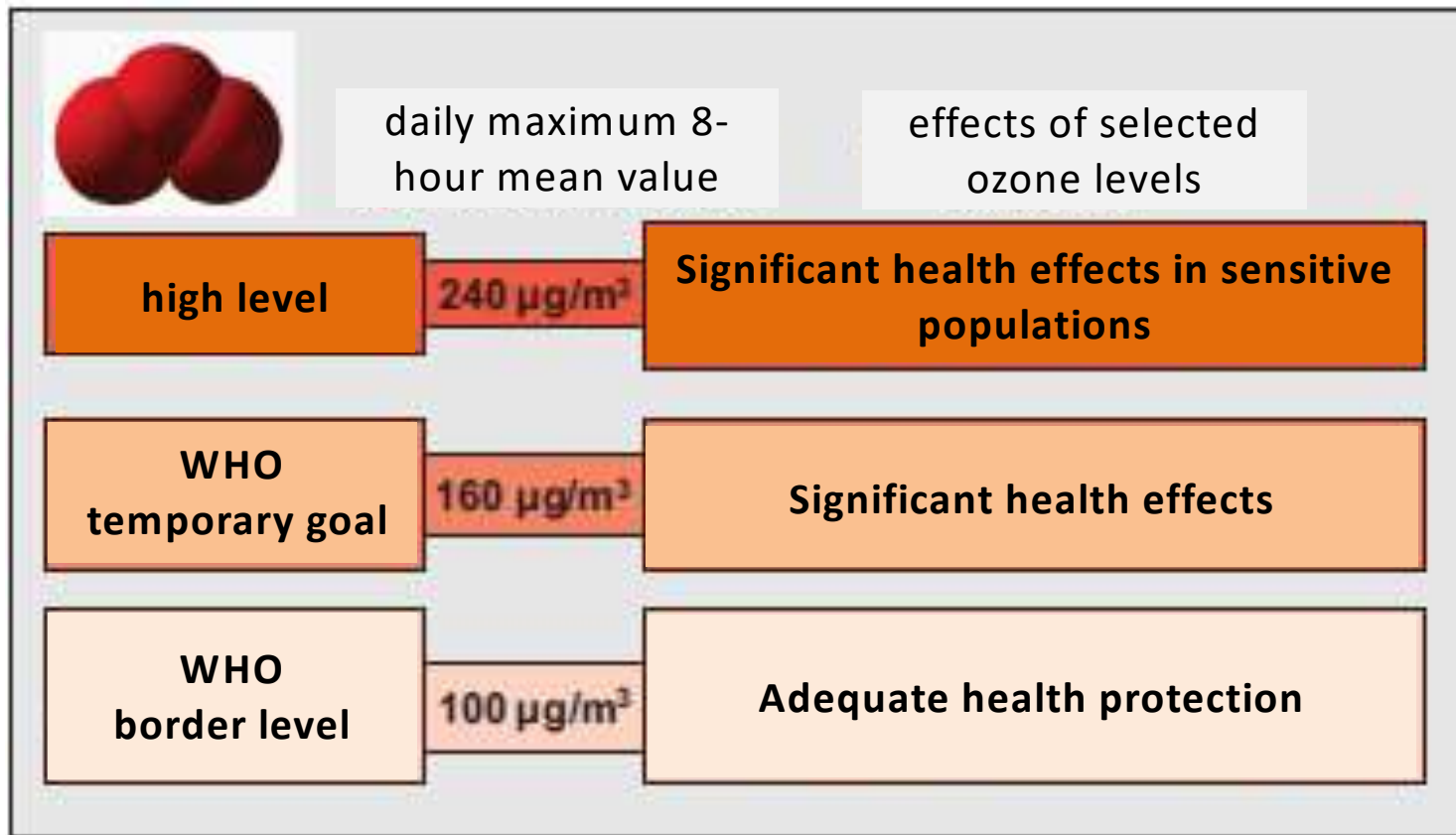
## 2.4 O<sub>3</sub> – TOXICOLOGICAL AND PUBLIC HEALTH ASPECTS



According to the recommendations of the World Health Organization (WHO) is set border concentration of ambient ozone, which refers to the 8-hour daily maximum in which in the majority of persons should not occur the appearance of the disease.

It is possible that at an extremely sensitive person and below those concentrations show up negative health effects. As the ozone concentration greater than the limit values, these are the health effects of all the more serious and more frequent and affect a larger part of the population.

## 2.4 O<sub>3</sub> – TOXICOLOGICAL AND PUBLIC HEALTH ASPECTS




The risk of adverse health effects in a healthy population at selected 8-hour daily maximum ozone concentrations. Source: Air Quality Guidelines-The WHO.

## 2.4 O<sub>3</sub> – TOXICOLOGICAL AND PUBLIC HEALTH ASPECTS



Recommended values ( $\mu\text{g}/\text{m}^3$ ), the concentration of O<sub>3</sub> in the air-the WHO

 World Health Organization (WHO Air Quality Guidelines)			
Pollutant	Time of averaging	Temporary goal	Recommended value
Ozon (O <sub>3</sub> )	8 sati	160	100

## 2.5 O<sub>3</sub> – MEASUREMENT METHODS



The reference method for the measurement of ozone

Ultraviolet (UV) photometry  
(HRN EN 14625)

Prescribed by regulations of the Republic of Croatia and the European Union. In the European Union and Croatia, was adopted by 2012. year

## 2.5 O<sub>3</sub> – MEASUREMENT METHODS



The method is based on a property of ozone that absorbs the UV-radiation.

Sampled air at the entrance of the instrument are filtered out by a constant and known flow, leads to a reaction of the cell in which the conditions are constant pressure and temperature. In such conditions the air exposes the constant radiation exposure low pressure lamps with peak values of 253.7 nm.



## 2.5 O<sub>3</sub> – MEASUREMENT METHODS



Sensitive photodiode or photomultiplier detectors measure the intensity of the radiation that is passed through the reaction cell. Ozone in the air absorbs a certain amount of radiation that is in constant terms proportional to the concentration of ozone in the sample.

There are two basic ways of quantifying and absorption:

- one is to get through the same reaction cell passes alternating pattern of air and air without ozone
- another is that there are two identical cells and through one continuous passes air sample, and through other air without ozone

## 2.5 O<sub>3</sub> – MEASUREMENT METHODS



In both modes the air without ozone is obtained by conducting air through the catalytic convector for ozone. The difference in intensity of radiation that is measured in the air with ozone and no ozone represents the absorption of radiation.

Sampling of air containing a known concentration of ozone instrument is calibrated and is possible with the help of absorption from the calibration directions to calculate the concentration of ozone.

## 2.5 O<sub>3</sub> – MEASUREMENT METHODS

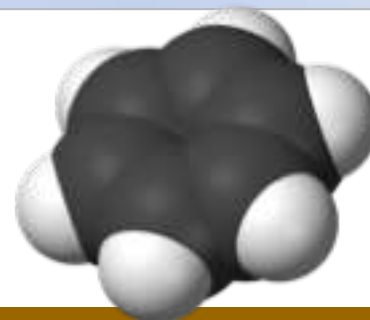


If the instrument is calibrated in volume/volume units, concentrations of O<sub>3</sub> are measured directly in volume/volume units (ppb) whereas the absorption in the UV spectrum is proportional to the concentration of O<sub>3</sub> in the volume/volume units.

After that, the obtained concentrations in ppb are converted to  $\mu\text{g}/\text{m}^3$  using standard conversion factors for a temperature of 20°C and an atmospheric pressure of 1013 hPa.

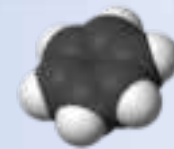
$$1 \text{ ppb (nmol/mol) O}_3 = 2.00 \mu\text{g}/\text{m}^3 \text{ O}_3$$

## 2.1 C<sub>6</sub>H<sub>6</sub> – CHEMICAL CHARACTERISTICS

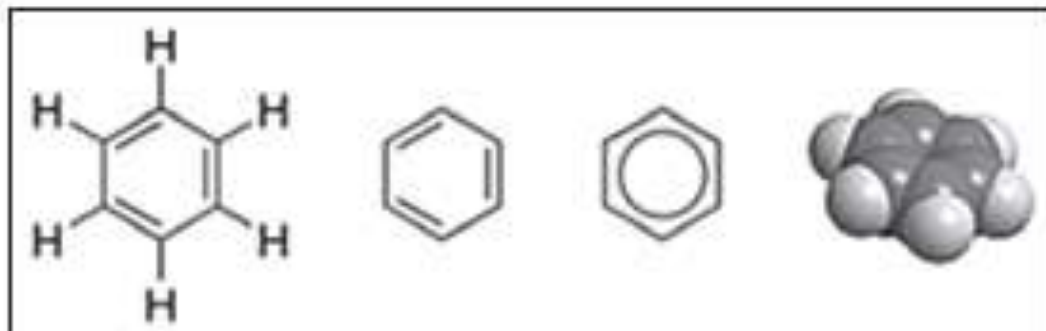


**Benzene (C<sub>6</sub>H<sub>6</sub>) is a colourless liquid, easily volatil at room temperature. In the air is located mostly in the gas stage, with a time of retention varies between a few hours to a few days. The retention time in the air depends on the environment, the climate and the concentration of other pollutants. From the air is removed by rain, and decomposes in the reaction with hydroxyl radicals.**

## 2.1 C<sub>6</sub>H<sub>6</sub> – CHEMICAL CHARACTERISTICS



**Benzene is a cyclic hydrocarbon with alternation single and double bonds in the ring**



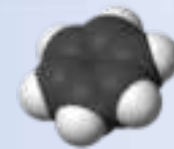
**Different ways of displaying the chemical formula of benzene**

## 2.1 C<sub>6</sub>H<sub>6</sub> – CHEMICAL CHARACTERISTICS



By using X-ray, it was found that all of the C-C bond in benzene are the same length (140 pm). However, this is greater than the length of the double C = C bond (135 pm), but smaller than the single C-C bond (147 pm). This indicates the relocation of electrons, which means that all of the electrons in these connections arranged equally between all six carbons by making a resonance structure. Such delocalization of electrons is known as aromatic and gives benzene in particular a strong stability, which is a fundamental property of aromatic molecules that sets them apart from the non-aromatic constituents.

## 2.3 C<sub>6</sub>H<sub>6</sub> – SPATIAL AND TEMPORAL DISTRIBUTION



### Natural and anthropogenic sources

Benzene is a natural component of crude oil and gasoline with a share of 1 to 5 volume percentage. In EU countries, 5% is the maximum allowed proportion of benzene in oil and gasoline.

Up to 1990. year total benzene emissions from cars engines was 60%, but today, the use of catalysts and fuel with a lower proportion of benzene total emissions decreased at 20%.

## 2.3 C<sub>6</sub>H<sub>6</sub> – SPATIAL AND TEMPORAL DISTRIBUTION



**Benzene is emitted into the air and evaporation in the handling, transport and storage of gas chemical industry also represents an essential source of benzene.**

**Various processes fossil fuel combustion (coal with the already mentioned oil and petrol), and we find it and in the smoke of cigarettes. Natural sources of benzene are deposits of oil and natural gas.**



## 2.3 C<sub>6</sub>H<sub>6</sub> – SPATIAL AND TEMPORAL DISTRIBUTION



### Concentration in the air

Average daily ambient concentrations of benzene in rural areas amount to about 1 µg/m<sup>3</sup> in urban areas range from 5 to 20 µg/m<sup>3</sup>. In the vicinity of sources of emissions of benzene concentrations are more important.

Average daily concentration measured in the major cities (Montreal, Toronto, Houston, New York, Pittsburg, Oslo, London) vary in the range of 2.8 to 40 µg/m<sup>3</sup>.

## 2.3 C<sub>6</sub>H<sub>6</sub> – SPATIAL AND TEMPORAL DISTRIBUTION



At gas stations at the time of refueling the concentration of benzene in the air are very high and amount to 3.2 mg/m<sup>3</sup>.

In the homes of smokers amounts 11 µg/m<sup>3</sup>, while they are in the homes of non-smokers is lower (6.5 µg/m<sup>3</sup>).

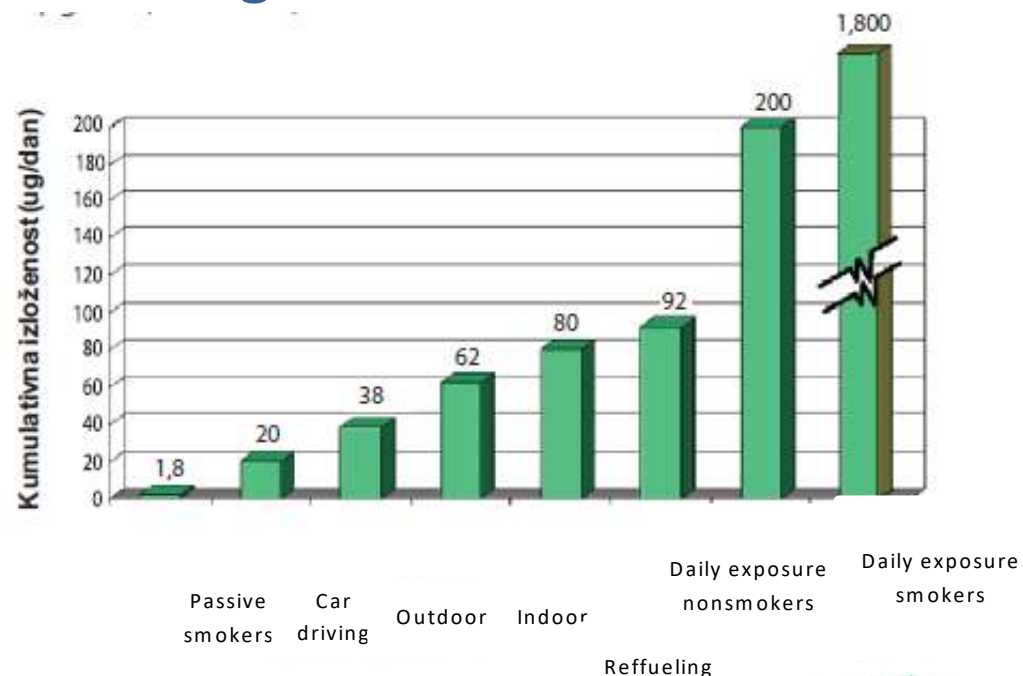
In the interior of the vehicle while driving the concentration of benzene showed values in the range from 10 to 120 µg/m<sup>3</sup> in Germany, 37 to 57 µg/m<sup>3</sup> in Sweden, 30 to 115 µg/m<sup>3</sup> in the Netherlands and 12 to 50 µg/m<sup>3</sup> in the United States.



## 2.4 C<sub>6</sub>H<sub>6</sub> – TOXICOLOGICAL AND PUBLIC HEALTH ISSUES

Inhaling in the organism enters more than 99% of benzene, as they entered a minimum of food and water. The average daily exposure to benzene at non-smokers is about 200 µg/day, while in smokers who smoke 30 cigarettes a day, nine times higher and amounts to about 1800 µg/day.

Daily exposure to benzene non-smokers and smokers who smoke 30 cigarettes a day. Source: Wallace, 1996.; Egeghy, et al., 2000.



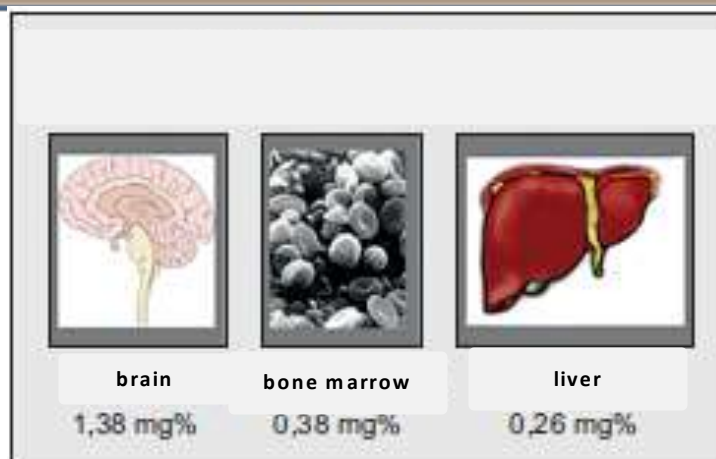


## 2.4 C<sub>6</sub>H<sub>6</sub> – TOXICOLOGICAL AND PUBLIC HEALTH ISSUES

Entered into the body, benzene is, since there is soluble in fats, accumulates in the tissues with a large lipid content, and they are: brains, bone marrow and liver.

Levels in workers who died from exposure to high concentrations amounted to 1.38 mg% in the brain, 0.38 mg% in bone marrow and 0.26 mg% in the liver

(units mg% = mg of some substances in 100 g of tissue in which that substance has accumulated).





## 2.4 C<sub>6</sub>H<sub>6</sub> – TOXICOLOGICAL AND PUBLIC HEALTH ISSUES

In autopsy findings of young addicts who have died because of the deliberate inhalation solution that contained benzene, the value and distribution of benzene in the tissues was the following: 2 mg% in the blood, 3.9 mg% in the brain, 1.6 mg% in the liver, 1.9 mg% in the kidneys and 2.2 mg% in the belly fat the tissue.

Oxidative metabolism of benzene in the body occurs in the liver through a system of cytochrome P-450 2E1. The average time to half-lives of benzene in the organism is 28 hours.



## 2.4 C<sub>6</sub>H<sub>6</sub> – TOXICOLOGICAL AND PUBLIC HEALTH ISSUES

Acute toxicity of benzene is low. Acute effects of benzene inhalation poisoning depend on inhaled concentrations. After inhaling a very high concentration is death, and the inhalation of lower concentrations may affect poisoning symptoms such as dizziness, nausea, rapid heartbeat, tremors, confusion.





## 2.4 C<sub>6</sub>H<sub>6</sub> – TOXICOLOGICAL AND PUBLIC HEALTH ISSUES

**Long-term exposure to increased concentrations of benzene causes harmful effects to your health: haematotoxicity, genotoxicity carcinogenicity.**

**Haematotoxicity manifested in reduced production of blood cells, red blood cells and platelets in the bone marrow. In patients who have been professionally exposed to benzene concentrations of 120 mg/m<sup>3</sup> was found a reduction in the number of erythrocytes and leukocytes in the blood.**



## 2.4 C<sub>6</sub>H<sub>6</sub> – TOXICOLOGICAL AND PUBLIC HEALTH ISSUES

**Genotoxicity of benzene is manifested induction of mutations of genes, structural and numeric chromosomal aberation. Carcinogenicity is reflected in the appearance of leukemia and lymphoma and other malignancies.**


**Benzene is carcinogen, so there is no safe level of the exposure that can be recommended.**





## 2.4 C<sub>6</sub>H<sub>6</sub> – TOXICOLOGICAL AND PUBLIC HEALTH ISSUES

Because of the carcinogenic properties of benzene, the World Health Organization gives recommended values for benzene, have already calculated the risks of contracting the disease of leukemia during the whole lifetime exposure to benzene.

 (WHO Air Quality Guidelines)	
lifetime exposure to concentration ( $\mu\text{g}/\text{m}^3$ )	Risk of leukemia
17	1 / 10 000
1,7	1 / 100 000
0,17	1 / 1 000 000



## 2.5 C<sub>6</sub>H<sub>6</sub> – MEASUREMENT METHODS

The reference method for the measurement of benzene includes

**Sampling suctioning with thermal desorption and analysis of gas chromatography (norm EN 14662-1)**

**Prescribed by regulations of the Republic of Croatia and the European Union. In the European Union is adopted in 2005. years, and in Croatia in 2006.**



## 2.5 C<sub>6</sub>H<sub>6</sub> – MEASUREMENT METHODS

The method is based on the classic gas chromatography and detection with the help of fire (FID) or photoionizing (PID) detectors. It is also allowed to use any other suitable detector.

Measure the air volume by pumping into the pre-column with an adsorbent that binds the benzene from the sample, and the air without benzene exits the instrument.

After that, benzene vapor is released from the adsorbent and by inert gas (most often high nitrogen purity) transferred to a chromatographic column where benzene separates from other easily volatile hydrocarbons (xylene, toluene).



## 2.5 C<sub>6</sub>H<sub>6</sub> – MEASUREMENT METHODS

Benzene will be carried by the inert gas after passing through a column in exactly the specified time called retention time (for the same chemical compound, the same system and the same conditions, the retention time is always the same) to enter the detector that will register the passage of benzene signal proportionate mass of benzene.

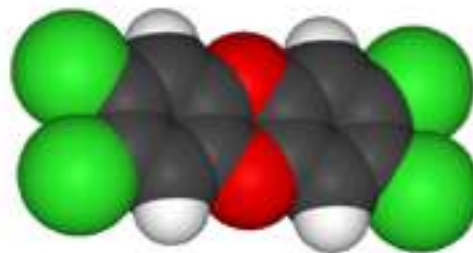
By comparing the signal with the signal of a zero air (air without benzene) and the signal obtained by passing the air with known concentration of benzene obtained during the procedure of calibration of the instrument can calculate the concentration of benzene in the sample sample.



## 2.5 C<sub>6</sub>H<sub>6</sub> – MEASUREMENT METHODS

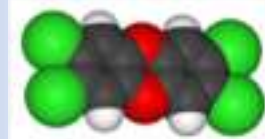
After that, the concentration is calculate in  $\mu\text{g}/\text{m}^3$  using standard conversion factors for a temperature of 20°C and an atmospheric pressure of 1013 hPa.

## 2.1 DIOXINS — CHEMICAL CHARACTERISTICS

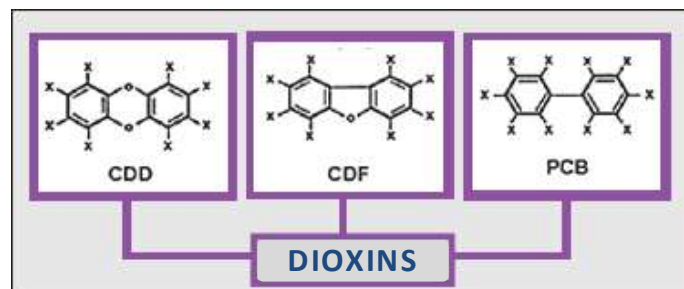


**Dioxins are a group of highly toxic organic chemical compounds. Once they get into the environment (air, soil, water), due to its stability remain a long time in it and is implanted into the food chains with the ability biomagnification (increase of the concentration of in the direction of the upper levels of the food chain). In the body they accumulate in adipose tissue where their half-life is 7 to 11 years.**

## 2.1 DIOXINS — CHEMICAL CHARACTERISTICS

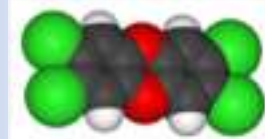


The term dioxins is a general term that refers to chemical compounds that have similar chemical structure and biological characteristics. There are several hundred of such compounds that can be included in three very close subgroups: chlorinated dibenzo-p-dioxins (CDDs), chlorinated dibenzofurans (CDFs) and polychlorinated biphenyls (PCBs).



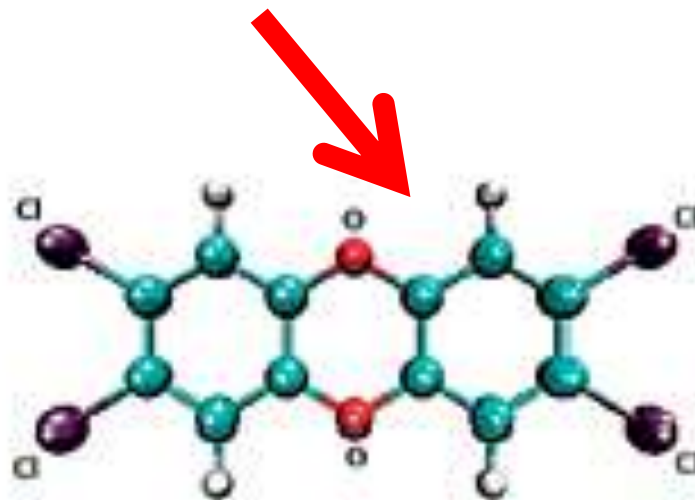
Note: X in formulas can be atom of chlorine (Cl) or hydrogen (H) depending on the type of chemical compounds

## 2.1 DIOXINS — CHEMICAL CHARACTERISTICS



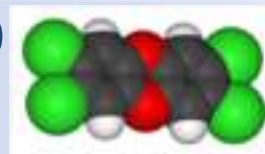
It consists of two benzene rings that are attached to the CDDs by two oxygen atoms in CDF with one oxygen atom and to PCBs directly without oxygen atoms. The chlorine atoms (Cl) are attached to the benzene rings.

The most toxic dioxin is 2, 3, 7, 8-tetrachlorodibenzo-p-dioxin

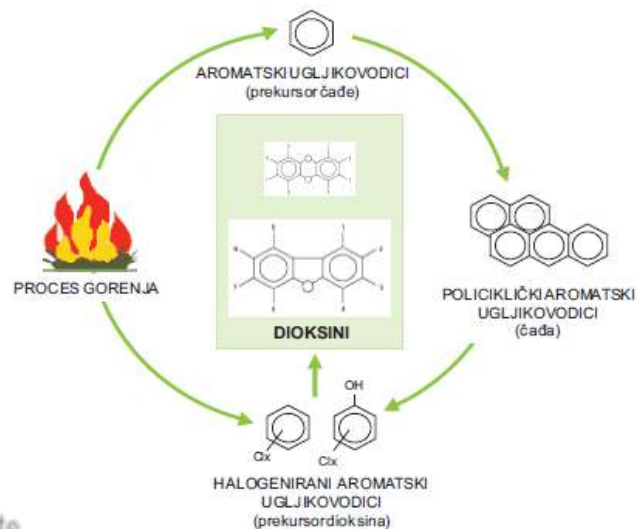




## 2.2 DIOXINS – CHEMISTRY OF PRODUCTION AND DEGRADATION



One of the ways of formation of dioxin are processes of incomplete combustion (e.g. burning of plastics-polyvinyl chloride-PVC) in which it comes to the creation of aromatic hydrocarbons that are fused together in a polycyclic aromatic hydrocarbons, then halogenate, and halogenated aromatic hydrocarbons become precursors for the formation of dioxin.





## 2.3 DIOXINS – SPATIAL AND TEMPORAL DISTRIBUTION

### Anthropogenic sources

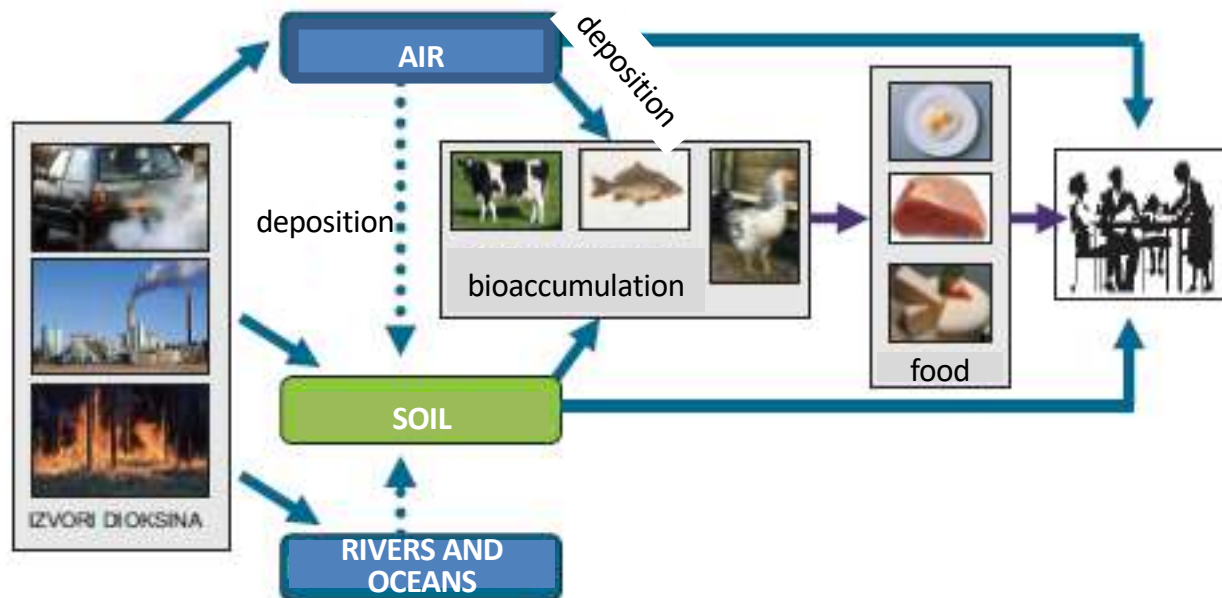
Dioxins and furans are mostly unwanted products formed in industrial processes, power stations, paper factories, herbicides and pesticides, the burning of waste, etc., while PCB products are used as insulators in transformers and other electrical devices. One part of the dioxin pollutes the environment unsuitable long-term storing of industrial oils and oil containing PCBs.



## 2.3 DIOXINS – SPATIAL AND TEMPORAL DISTRIBUTION

### Natural sources

Natural sources of dioxins are mostly volcanic eruptions and forest fires. Although dioxins are created locally, the distribution in the environment is a global, because they are found in all media throughout the world. High levels of dioxin were found in soil, sediment, and feed, particularly in meat, fish and shellfish.

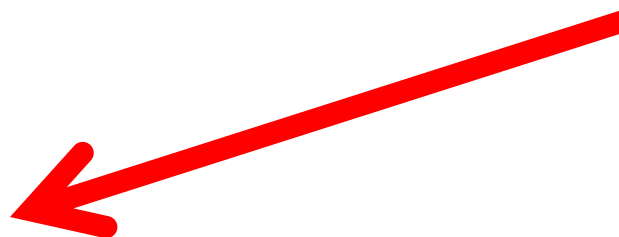




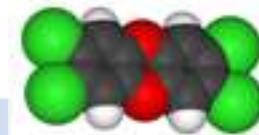
## 2.3 DIOXINS – SPATIAL AND TEMPORAL DISTRIBUTION

The concentration of dioxin in the air vary with the seasons. In the summer is much lower than in the winter and amounts to 0.1- 0.5 pg-TEQ (toxicity equivalent)/m<sup>3</sup>.

Winter ambient concentrations range from 6 to 8 pg-TEQ/m<sup>3</sup>.



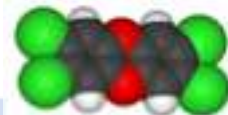
TEQ is equivalent toxicity that was introduced because the received dose of dioxin in the body not only consists of one compound, but mostly of more of them, each of which has its own TEF (toxicity equivalence factor) which is determined by the most toxic dioxin 2, 3, 7,8- TCDD and that has a TEF = 1.



## 2.3 DIOXINS – SPATIAL AND TEMPORAL DISTRIBUTION

TEF values for each individual compound that belongs to the dioxins. Source: WHO.

Compound	TEF
Dibenzo-p-dioksini	
2,3,7,8- TCDD	1
1,2,3,4,7,8 - HxCDD	0,1
1,2,3,4,6,7,8 - HpCDD	0,01
OCDD	0,0001
Dibenzofurani	
2,3,4,7,8 - PnCDF	0,5
2,3,7,8 - TCDF	0,1
1,2,3,4,7,8,9 - HpCDF	0,01
OCDF	0,0001
PCB	
PCB 126	0,1
PCB 169	0,01
PCB 156	0,0005
PCB 167	0,00001

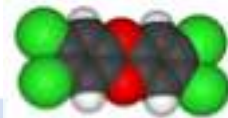


## 2.4 DIOXINS – TOXICOLOGICAL AND PUBLIC HEALTH ASPECTS

95% of dioxins in the organism entered by contaminated food, and a small percentage by the air. When dioxins gets into the organism, tied in to the cellular Ah dioxin receptor. At the time of binding comes to the activation of this receptor and the launch of two fixed event:

- the first is the increase in the transcription of the entire series of genes that encode the synthesis of enzymes such as cytochrome P4501A1, 1A2, 1B1, glutathione S-transferase and UDP-glucurono-siltransferase
- the second is the activation of the enzyme tyrosine kinase. These events result in endocrine changes and changes in the growth and differentiation of cells

**That's exactly the basis of toxicity of dioxin.**

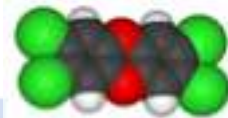


## 2.4 DIOXINS – TOXICOLOGICAL AND PUBLIC HEALTH ASPECTS

Toxicokinetics determinants of dioxin are dependent on its three basic properties:

- **lipophilicity**
- **metabolism**
- **ability of binding to a CYP1A2 protein in the liver**

Since the dioxin slowly metabolized, comes to the bioaccumulation, and the induction of CYP1A2 proteins there is an increase in the concentration of dioxin in the liver, and the reduction in the concentration of dioxin in other organs and tissues.



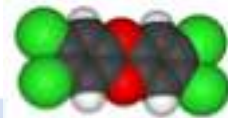
## 2.4 DIOXINS – TOXICOLOGICAL AND PUBLIC HEALTH ASPECTS

The average daily dose of dioxin, which enters the organism is 1.5 to 2 pg per kg of body weight/day.

It is necessary to point out that the amount of dioxin in the organism enters by food, not through the air. Whereas the levels of dioxin in the air is low, inhaling enters in the organism 0.03 pg/kg body weight/day.

According to the WHO limit of daily intake tolerance is 10 pg/kg of body weight.





## 2.4 DIOXINS – TOXICOLOGICAL AND PUBLIC HEALTH ASPECTS

Exposure to dioxins at high doses, it can cause a number of adverse health effects. Health effects associated with the entering of dioxin in the body are dependent on several factors including:

- the level
- the length of the exposure
- frequency location



The most common health effects in people who were exposed to high doses of dioxin (accidents) are the chlorine acne that appear mainly on the face and upper body. Long-term exposure to elevated concentrations of dioxins increases the risk of all types of malignant diseases.

## 2.1 CHEMICAL CHARACTERISTICS OF H<sub>2</sub>S

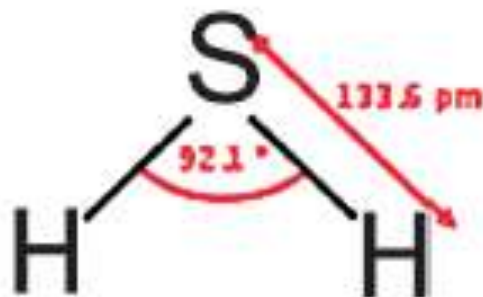


Hydrogen sulphide H<sub>2</sub>S is a colorless, toxic and flammable gas with a characteristic smell of rotten eggs. It is soluble in water and alcohol.

## 2.1 CHEMICAL CHARACTERISTICS OF H<sub>2</sub>S



It consists of two molecules of hydrogen covalently linked to one molecule of sulfur.



## 2.2 H<sub>2</sub>S – CHEMISTRY OF PRODUCTION AND DEGRADATION



Occurs in anaerobic conditions (without the presence of oxygen) at bacterially degradability of sulfates in organic substance, and in industrial processes where sulphur compounds come into contact with organic substances at elevated temperatures.

## 2.3 H<sub>2</sub>S – SPATIAL AND TEMPORAL DISTRIBUTION



### Natural sources

It is most commonly found in:

- the surroundings of geothermal wells
- wetlands
- mixture of gases by volcanic eruptions.

It is an integral part of the crude oil and natural gas, and in some dumps of natural gas the concentrations are up to 42%.

Since it is heavier than air, transports along the Earth's surface.

## 2.3 H<sub>2</sub>S – SPATIAL AND TEMPORAL DISTRIBUTION



The most common anthropogenic sources are:

- paper industry
- wastewater treatment
- refining of crude oil
- production of coke

The usual concentration of hydrogen sulfide in the air is below 0.3 µg/m<sup>3</sup>, except in areas where it is naturally released into the air. So for example in the vicinity of the town of Rotorua in New Zealand (extremely active geothermal area) measured concentrations are more than 80 µg/m<sup>3</sup> in more than 55% of the days in the winter months. In Croatia are elevated concentrations of this gas (more than 50 µg/m<sup>3</sup>) measured near an oil refinery in Sisak and Rijeka.



## 2.4 H<sub>2</sub>S – TOXICOLOGICAL AND PUBLIC HEALTH ASPECTS

At physiological pH (pH 7.4) hydrogen sulphide dissociate as the sulphide anion and is absorbed through the lungs, is spreading quickly in the body, and metabolised in three ways:

- **oxidation**
- **metilation**
- **reaction with cytochrom c and metalo-proteins or disulphide proteins**

The main metabolic pathway is rapid oxidation in liver to sulfate (final product). Sulphate metabolites are excreted by feces and urine as urinary thiosulfates. Since thiosulfates in the urine are held up to 15 hours after acute exposure, they are used as a biomarker for acute exposure to hydrogen sulphide.



## 2.4 H<sub>2</sub>S – TOXICOLOGICAL AND PUBLIC HEALTH ASPECTS

**The toxicity of hydrogen sulfide at concentrations of what we find in the outside air is negligible.**

Acute toxicity of hydrogen sulphide is mainly reflected on the central nervous and the respiratory system. When H<sub>2</sub>S enters the body, it creates a complex with iron from the enzyme cytochrome oxidase and in the mitochondria is blocking the binding of oxygen which stops the cellular respiration.





## 2.4 H<sub>2</sub>S – TOXICOLOGICAL AND PUBLIC HEALTH ASPECTS

The human sense of smell is extremely sensitive to this chemical compound and hydrogen sulphide can smell but also at concentrations of 10 to 12 µg/m<sup>3</sup>. Harmfulness to health hydrogen sulfide at these concentrations, it does not exist.

The World Health Organization (WHO) has given 15 mg/m<sup>3</sup> (15 000 µg/m<sup>3</sup>) as the lowest concentration that causes negative effects on health (LOAEL). The usual method of divide these values with the safety factor (in this case, he's tall -100). WHO issued a recommended value of 24-hour concentrations of hydrogen sulphide of the 150 µg/m<sup>3</sup>.



## 2.4 H<sub>2</sub>S – TOXICOLOGICAL AND PUBLIC HEALTH ASPECTS

**So, only after concentrations of specified pollutants grow for a thousand times of concentration where can smell it, you can expect an acute negative effects on people's health.**

However, as with its unpleasant smell, such compounds can considerably reduce the quality of life in the area which are spread, the WHO recommends that the 30-minutes hydrogen sulphide concentrations should not exceed 7 µg/m<sup>3</sup>.



## 2.4 H<sub>2</sub>S – TOXICOLOGICAL AND PUBLIC HEALTH ASPECTS

At concentrations higher than 15 mg/m<sup>3</sup> comes to the irritation of the conjunctiva.

At higher concentrations (225 mg/m<sup>3</sup>) comes to paralysis of the olfactory nerve and the smell can no longer feel it.

At higher concentration (> 400 mg/m<sup>3</sup>) first comes to the pulmonary edema, and then to the strong stimulation of CNS (central nervous system) with symptoms such as rapid breathing, interruption of breathing, convulsion and death.



## 2.4 H<sub>2</sub>S – TOXICOLOGICAL AND PUBLIC HEALTH ASPECTS

If people are exposed to extremely high concentrations of 1400 mg/m<sup>3</sup> and higher, is coming to a rapid development of brain edema and necrosis of brain tissue.



## 2.5 H<sub>2</sub>S – MEASUREMENT METHODS

For hydrogen sulphide there is no special standard method of measurement, but is measured at the same measuring principle as well as SO<sub>2</sub>:

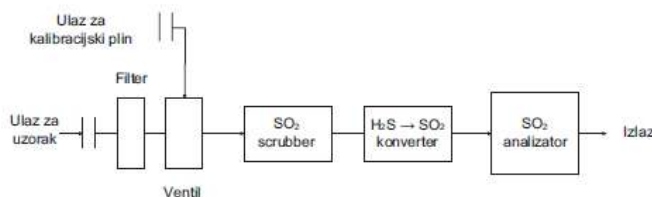
**ultraviolet light (UV) fluorescence**

This method could be applied, but it is necessary before the measurements from the sample of air to remove all the SO<sub>2</sub>.



## 2.5 H<sub>2</sub>S – MEASUREMENT METHODS

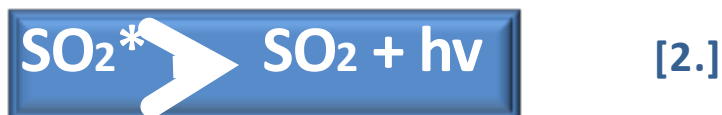
This is achieved with the help of the so-called SOX scrubber which is located at the entrance of a sample of the air in the instrument. It's about powder adsorbent with high affinity binding of the sulfur oxides. The adsorbent is placed in the casing of scrubber which is heated to increase the speed of adsorption. Since these adsorbents have a specific capacity, must be changed regularly, which is included in the regular maintenance of the device. After the removal of SO<sub>2</sub>, a sample of air heat is processed in the so-called converter where the oxidation of total H<sub>2</sub>S-s in SO<sub>2</sub> happend. Further measurement is identical to the one described in the methods for sulphur dioxide. At the end of the obtained concentrations of SO<sub>2</sub> are converted and expressed as H<sub>2</sub>S.





## 2.5 H<sub>2</sub>S – MEASUREMENT METHODS

The method is based on fluorescent radiation molecules if the SO<sub>2</sub> molecule is exposed to ultraviolet light (UV) radiation. Due to exposure to UV-radiation, molecules passes in the spectrophotometer from SO<sub>2</sub> normal to excited condition and after that again returns to normal with the airing of the fluorescent radiation.



where is SO<sub>2</sub>\* excited molecule condition.



## 2.5 H<sub>2</sub>S – MEASUREMENT METHODS

The intensity of the emitted radiation is proportional to the concentration of the SO<sub>2</sub> molecule in the air. Relationship between the concentration of the SO<sub>2</sub> molecule and the intensity of the radiation describes the following equation:

$$F = k \times C_{SO_2} \quad [3.]$$

where:

F = intensity of radiation; k = coefficient of proportionality; C<sub>SO<sub>2</sub></sub> = concentration of SO<sub>2</sub>.





## 2.5 H<sub>2</sub>S – MEASUREMENT METHODS

Before entering in the reaction fluorescent chamber, the air is filtered and passed through a scrubber of hydrocarbons that would otherwise cause interference. In a reaction fluorescent chamber the sample in air is in standardized conditions exposed to UV radiation in the wavelength range of 200 to 220 nm what causes excitation of SO<sub>2</sub> molecules in the sample. Upon return from the excited to the normal state of the SO<sub>2</sub> molecule, they are fluoresced by emitting rays of wavelengths between 240 and 420 nm. This emission passes through selective optical filters and then translates it with the help of photodiode into an electric signal whose intensity is measured. The intensity of the electrical signal is proportional to the concentration of SO<sub>2</sub> which has entered the reaction [1.].



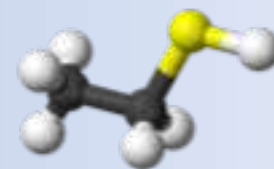
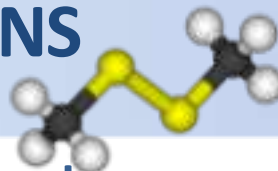
## 2.5 H<sub>2</sub>S – MEASUREMENT METHODS

Concentrations of SO<sub>2</sub> are measured directly in volume/volume units (ppb) whereas the absorption in the UV spectrum is proportional to the concentration of SO<sub>2</sub> in the volume/volume units. After obtaining the concentration at ppb units, the result is converted to µg/m<sup>3</sup> using standard conversion factors for a temperature of 20°C and an atmospheric pressure of 1013 hPa.

$$1 \text{ ppb (nmol/mol) H}_2\text{S} = 1.12 \text{ µg/m}^3 \text{ of H}_2\text{S}$$



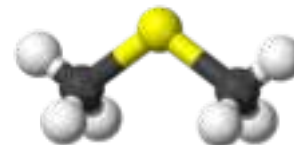
# A COMPLETE AND TOTAL REDUCED SULPHUR COMPOUNDS/MERCAPTANS

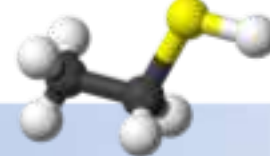


Total reduced sulphur is a mixture of several compounds containing reduced sulfur compounds. Apart from H<sub>2</sub>S in that group include mercaptans, dimethyl sulfide and dimethyl disulfide. This compounds characterized by a very unpleasant smell. How in our regulations to this group of compounds represent the mercaptans on this occasion will be described in more detail.



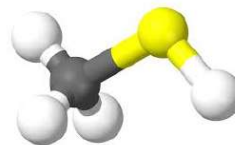
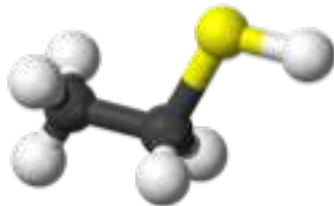
Mercaptans or thiols are a group of organic compounds with the -SH group and are known as unpleasant odors with the lowest threshold of olfactor sensitivity (below 5 µg / m<sup>3</sup>). They are naturally developed by the breakdown of organic matter but can be found in animals and plants. They are one of the causes of unpleasant failures in people with a diseased liver.

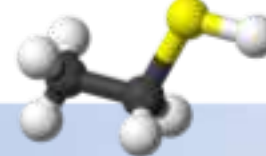




# A COMPLETE AND TOTAL REDUCED SULPHUR COMPOUNDS/MERCAPTANS

This group of compounds is considerably less represented in the present toxicological and medical literature. Not one from a group of these compounds is not represented in the WHO Air quality guidelines, and WHO does not give the recommended values for these compounds. Most often they are represented in the present literature in the area of the protection at work and so the maximum permissible concentration (MPC) for the 8-hour working time after toxicological research is to  $1000 \mu\text{g}/\text{m}^3$  for methyl-and ethyl-mercaptane in most countries.

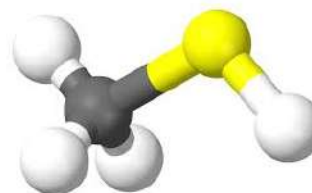
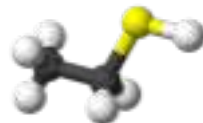




# A COMPLETE AND TOTAL REDUCED SULPHUR COMPOUNDS/MERCAPTANS

The US ATSDR (Agency for Toxic Substances and Registry Disease) gives the concentration of  $5000 \mu\text{g}/\text{m}^3$  at which do not appear on health effects (NOAEL). As far as the maximum acceptable concentration (due to unpleasant smells) data are available from the same agency for some States in the USA, so that New York has a border on  $3.30 \mu\text{g}/\text{m}^3$  for an annual value, and Virginia  $16.0 \mu\text{g}/\text{m}^3$  for 24-hour value for methyl mercaptane. And here is our stricter regulations so the GV (border value) for 24 hour  $3 \mu\text{g}/\text{m}^3$ .

$$1 \text{ ppb (nmol/mol) H}_2\text{S} = 1.12 \mu\text{g}/\text{m}^3 \text{ of H}_2\text{S}$$





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Energy Research and Environmental Protection Institute



**THANK YOU FOR YOUR ATTENTION !**

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