

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



MINISTARSTVO ZAŠTITE Okoliša i energetike







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Energy Research and Environmental Protection Institute



PARTICULATE MATTERS

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Opatija, 07.11.2017.

TWO-COMPONENT SYSTEMS

Continuous phase

Hydrosol Foam **AEROSOL**

Liquid Solid or liquid Gas/mixture of gases **Dispersed phase**

Liquid and/or solid Gas/mixture of gases Liquid and/or solid

Environmental air we observe as a complex aerosol
Continuous phase
Dispersed phase

mixture of gases

solid and/or liquid particles





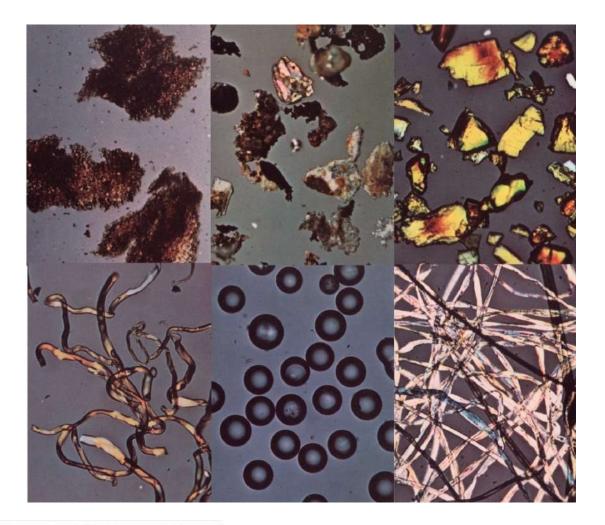
TYPES OF PARTICULATE MATTERS

- The individual particles: small amounts of the substance, of regular shape with a density close to inrtinsic density of the substance from which are made up
- **Aggregates:** groups of particles that stick together with a powerful atomic and/or molecular forces. In the air behave like individual particles.
- **Agglomerates:** groups of particles that stick together with a weaker forces adhesion or cohesion.
- **Floccules:** groups of particles are related to each other even weaker forces, that are easy to break down by vibrations, air flow, etc. In the air behave completely differently than individual particles.
- **Fibres:** natural (biological or mineral origin) or artificially manufactured fiber **Condition:** $L > 5 \mu m$; L/D > 3





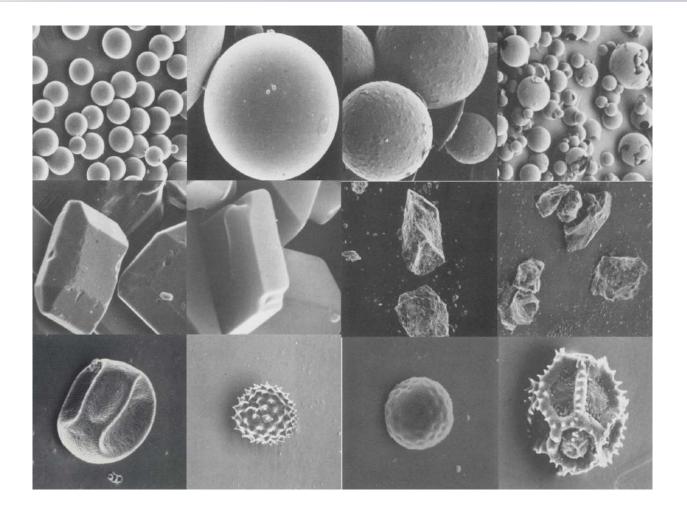
EXAMPLES OF PARTICULATES







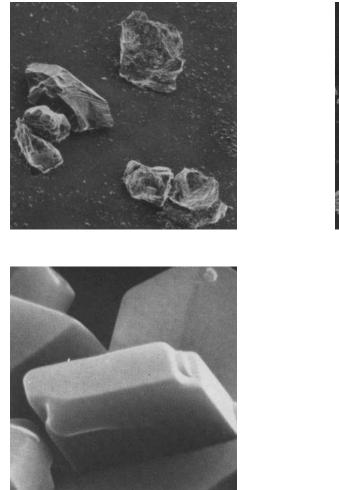
EXAMPLES OF PARTICULATES

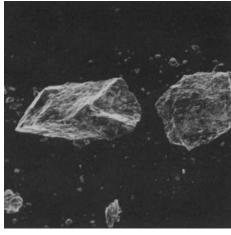


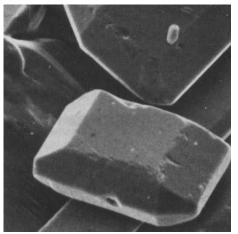




EXAMPLES OF INDIVIDUAL PARTICULATE MATTERS





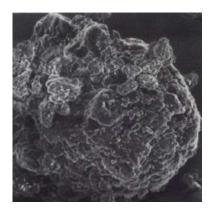


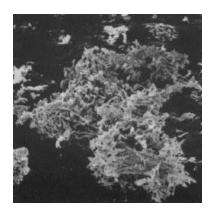




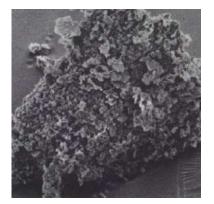
EXAMPLES OF AGGREGATES





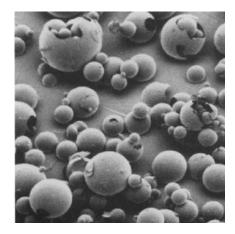


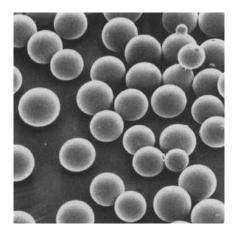


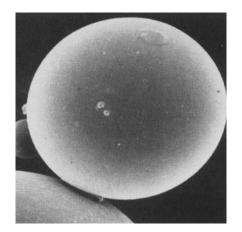




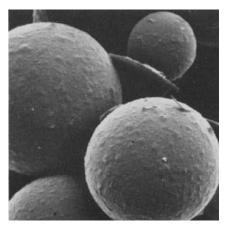
EXAMPLES OF SPHERICAL PARTICLES







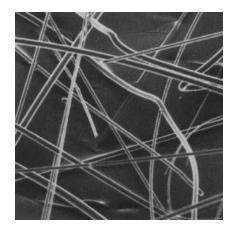


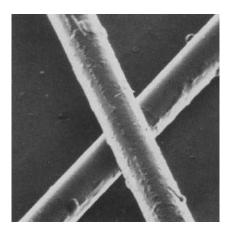






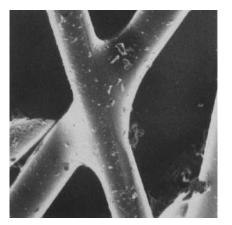
EXAMPLES OF FIBERS





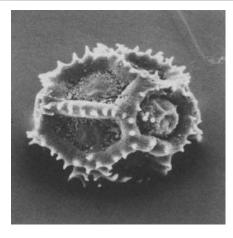


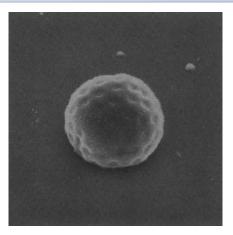
EKONERG

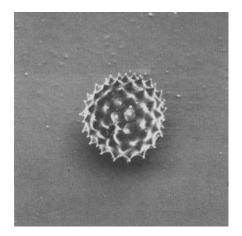




EXAMPLES OF POLLEN













WHAT AND HOW TO DO NEXT?

- •The different particle size
- Different forms of particulate matter
- The different composition of the particles
- Different densities of the particles
- •Different concentrations of particles •etc.
- All of these properties determine the behavior of particles in the air.

How to describe them?







PARTICULATE MATTER

The volume factor (ϕ) – the volume of particles in relation to the volume of the gas.

In order to ignore the interaction between particles that ratio needs to be $\phi < 10-3$ (mass concentration of ~ 1 g m-3).

In the environmental air of this condition is always satisfied.

The size of the particles – a characteristic linear dimension of a threedimensional object.





PARTICULATE MATTER

Monodisperse aerosol:

all particles are of an identical shape and size.

The deal in practice: Dp= Dpavg (1±0.1)

Otherwise-polydisperse aerosol

Particulate matter in the air are always polydisperse aerosol.







DIAMETERS OF THE PARTICLES IN THE PLANE

The definition of the size and shape of the particles are spherical in shape. In reality the particles are always in different sizes and shapes!

Definitions of diameter

Martin's diameter(D_m): We divide each particle (always in the same direction) into two parts of equal area.

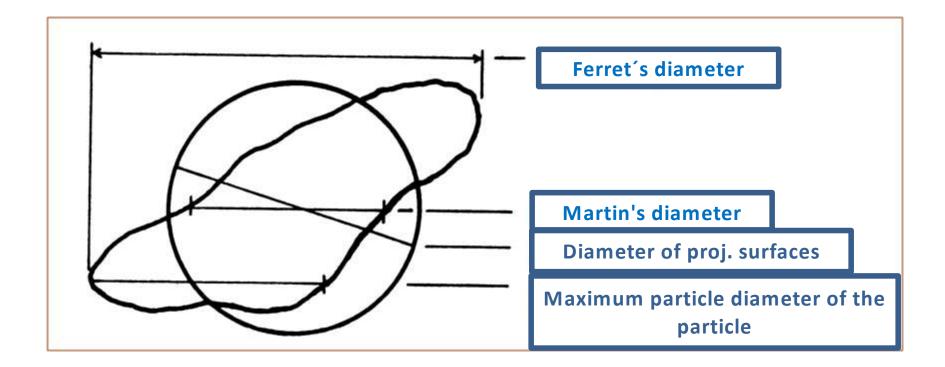
Ferret's diameter (Df): we measure the longest dimension of the particles (always in the same direction)

At calculation of average value of Dm and Df always we have to take into account a large number of particles, so we can ignore the error due to the different Rotational position of a particle in a plane.





DIAMETERS OF THE PARTICLES IN THE PLANE







EQUIVALENT DIAMETERS

The diameter of the equivalent sphere we can base it on the basis of: **Projected surface area** – the diameter of the sphere equal to the projected surface like particles investigated (optical detectors – light scattering)

The surface of the sphere - the sphere diameter equal to the surface like particles investigated (total area of the aerosols, adsorption of gases)

The volume of the sphere - the diameter of a sphere of equal volume, such as the examined particles

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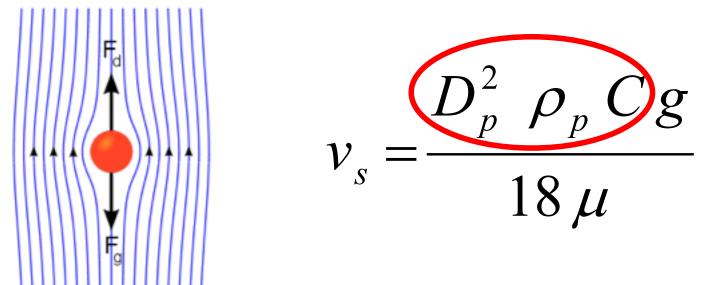
The masses of the sphere- the diameter of a sphere of mass equal to the mass of the test particles





SPEED OF DEPOSITION

Terminal velocity dive particles in the air due to gravity, called yet and at the speed of deposition of, is achieved at the annul gravity with installed and force of friction.

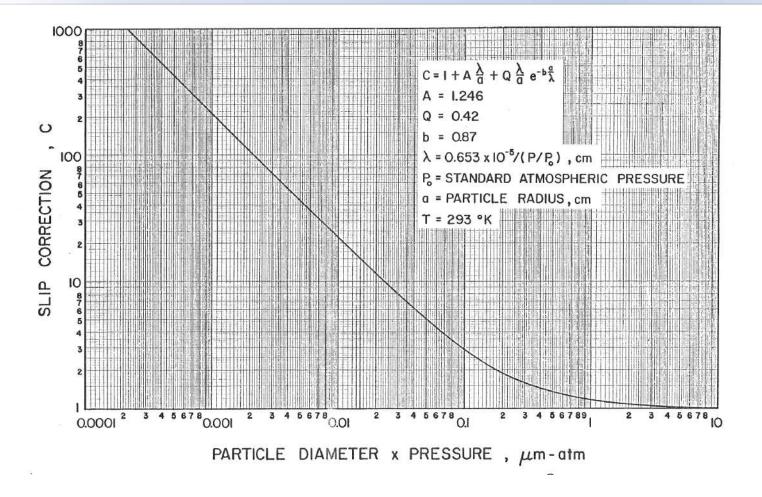








SPEED OF DEPOSITION





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EQUIVALENT DIAMETERS

Diameters based on speed of deposition :

Stokes diameter— the diameter of the sphere that has the same speed of precipitation as well as the observed particles.

Aerodynamic diameter- the diameter of a sphere of unit density that has the same speed of precipitation as well as the observed particles.





ADDITIONAL TYPES OF PARTICLE DIAMETER

For special purposes are used more and diameters are based on:

•Electrical mobility

- •The scattering of light
- Rather than diffusion THERMODYNAMIC DIAMETERetc.

The use of different types of diameter gives different results, therefore, it is necessary to always indicate which species is the diameter used.

In gathering, the analysis and interpretation of results of monitoring airborne particulate matter, which is the primary purpose of the budget of the health effects, always use the aerodynamically particle diameter, because he best describes the behavior of particles.







THE RANGE OF THE SIZE OF THE PARTICULATE MATTER

Range of diameter $0.002 - 100 \,\mu\text{m}$ The ratio of the diameter $1:10^5$ The ratio of the surface $1:10^{10}$ The ratio of the volume (mass) $1:10^{15}$





THE CONCENTRATION OF PARTICULATE MATTER

The number concentration— the number of particles in a unit volume of air. It is used most when studying the health benefits of insoluble particles (number of particles deposited within the respiratory system)

Mass concentration– the mass of the particles in a unit volume of air. It is used most when investigating the health effects of toxic soluble particles (mass of particles deposited in the respiratory system)







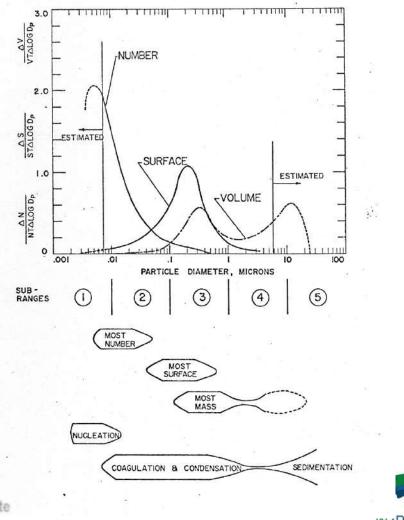
PARTICULATE MATTER IN ENVIRONMENTAL AIR

Small ratio~ 10-5

Typical for the number, surface and volume of the distribution by size of particles

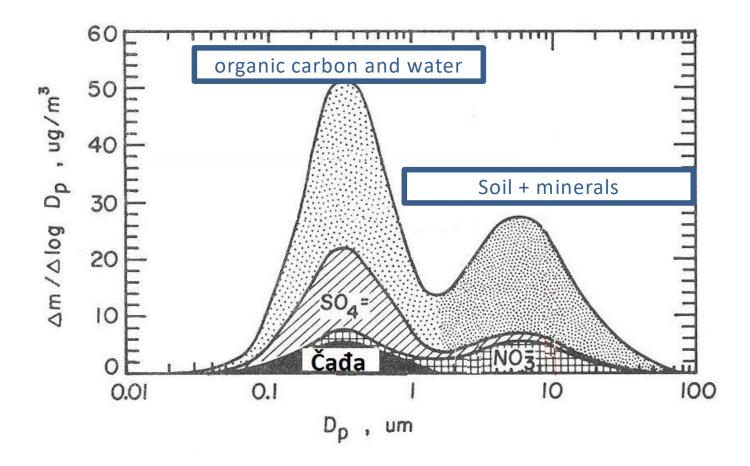
A rough dvision into three categories

nucleation mode : $\sim 0,01 - 0,04 \ \mu m$ Accumulation mode: $\sim 0,1 - 1 \ \mu m$ Large particles: $\sim 5 - 50 \ \mu m$





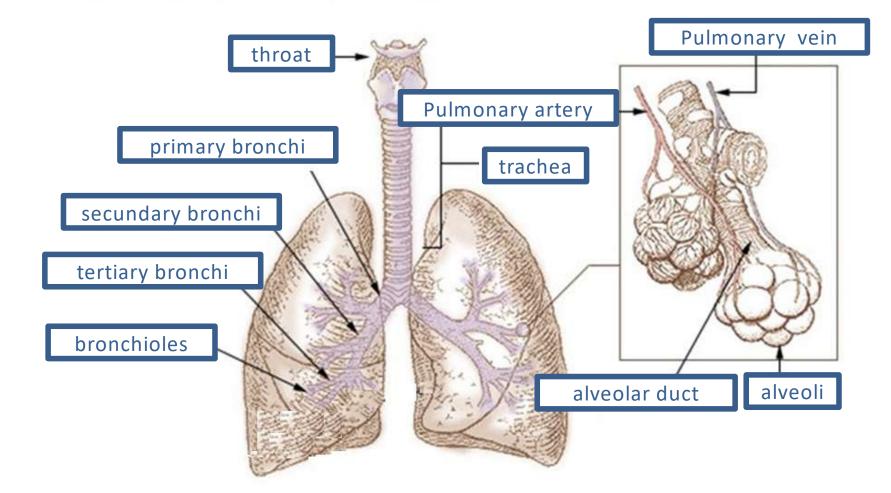
TYPICAL COMPOSITION OF PARTICULATE MATTER





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SCHEMATIC VIEW OF THE RESPIRATORY SYSTEM







DEFINITIONS OF THE FRACTION OF THE PARTICULATE MATTER

For many years, they collected samples (TSP-total Suspended Matter). The results of mass concentration and their compositions are significantly different with respect to the design of an entrance area collector who was not standardized. In this way of comparing the level of pollution particulates from different locations were difficult, or the disabled. Linkage with health effects has also been harder to observable.

HRN ISO 7708:1998 The definitions of the faction of the particles by size for sampling works on health impact assessments(ISO 7708:1995)

Inhalation faction: mass fraction of total suspended particles that we inhale on the nose or mouth (depends on the direction and speed of the air flow, frequency of inhalation, etc.) Inhalation convention: target specification of inhaled factions.

Extrathoracic fraction : mass concentration of inhaled particles that do not penetrate deeper than the throat.

Extrathoracic convention: target specification sampler extrathoracic factions.





DEFINITIONS OF THE FACTION OF THE PARTICULATE MATTER

Thoracal fraction: mass fraction of suspended particles that reach below the throat.

Toracal convention: the target specimen of the inhaler fractional sampler (given the existence of large differences between individuals, this convention represents an average value). It is described by a cumulative lognormal distribution with a median of 11.64 μ m and a geometric standard deviation of 1.5.





DEFINITIONS OF THE FACTION OF THE PARTICULATE MATTER

Tracheobronchial fraction: mass fraction of particulate matter penetrating lower than the throat, but not penetrating the areas without a ciliaar epithelium.

Tracheobronchial convention: the target specification of tracheobronchial fraction samplers (given the existence of large differences between individuals, this convention represents an average value).







THE DEFINITIONS OF THE FRACTION OF THE PARTICULATE MATTER

Respirable fraction: mass fraction of airborne particles that penetrate into the area without the ciliary epithelium.

Respirable convention: the target specimen of the respirable fractionator (given the existence of large differences between individuals, this convention represents an average value). It is described by a cumulative lognormal distribution with a 2.5μ m median geometric standard deviation of 1.5.



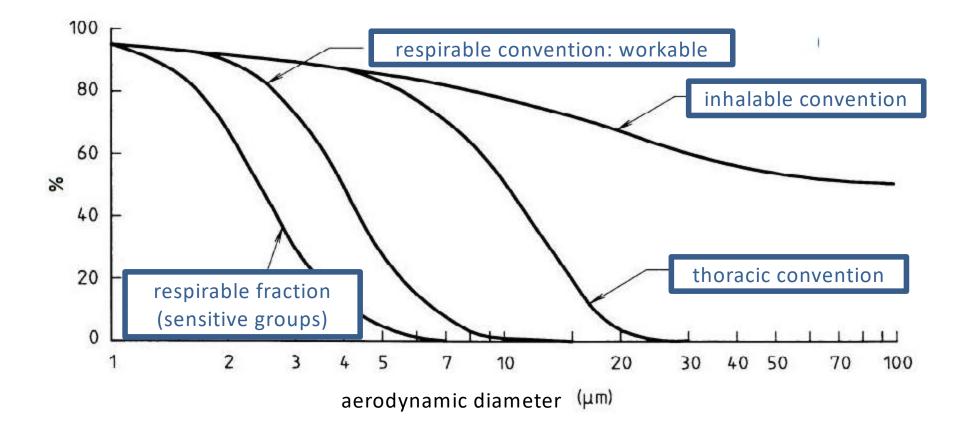
THE DEFINITIONS OF THE FRACTION OF THE PARTICULATE MATTER

Each of the above convention, approximating the faction suspended particles that penetrate in a particular region of the respiratory system, not a faction that is deposited in that region.

In this sense, the above-mentioned convention to overestimate their health effects, because we assume that them can cause only deposited particles.

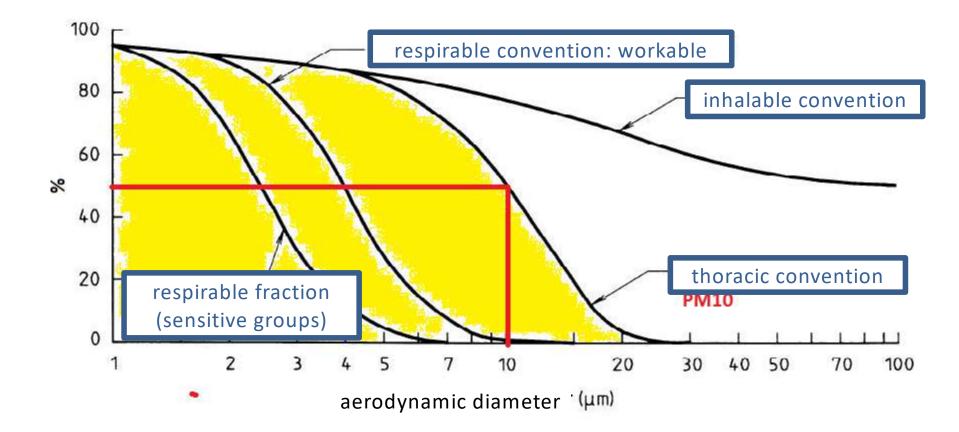






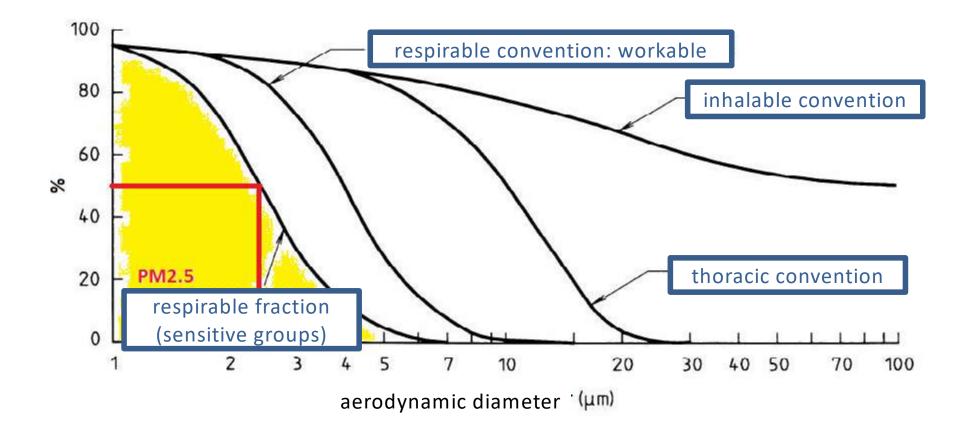


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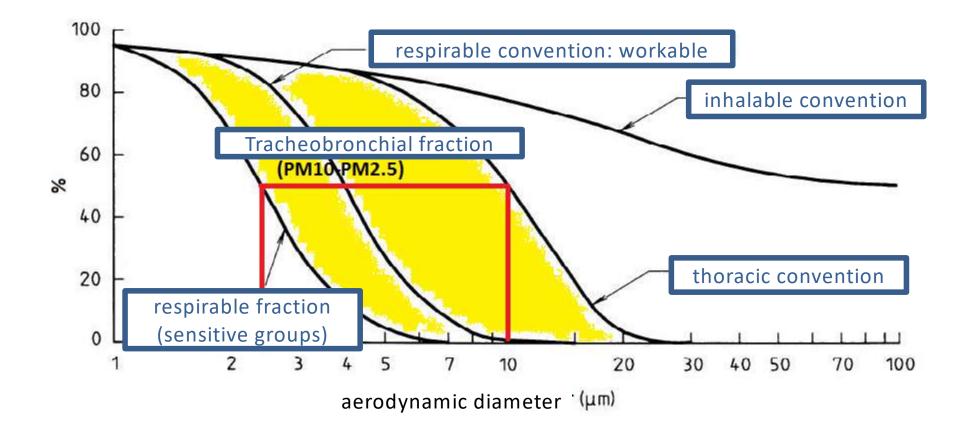








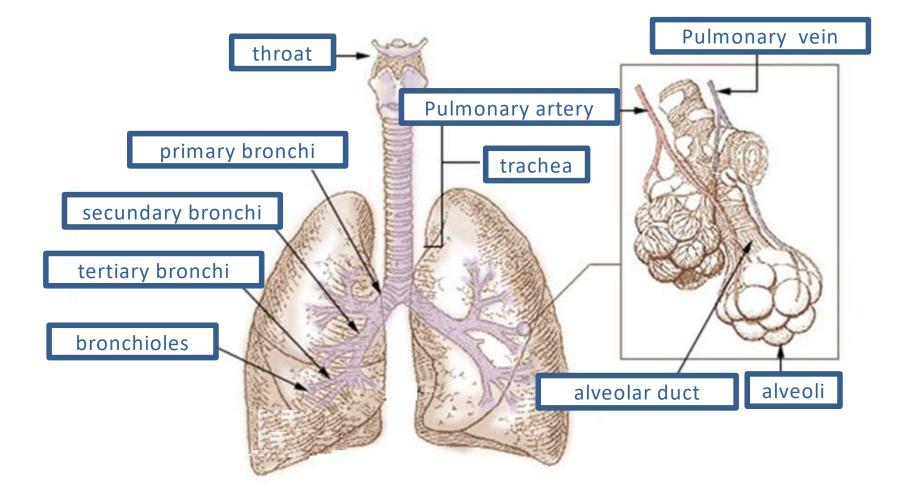
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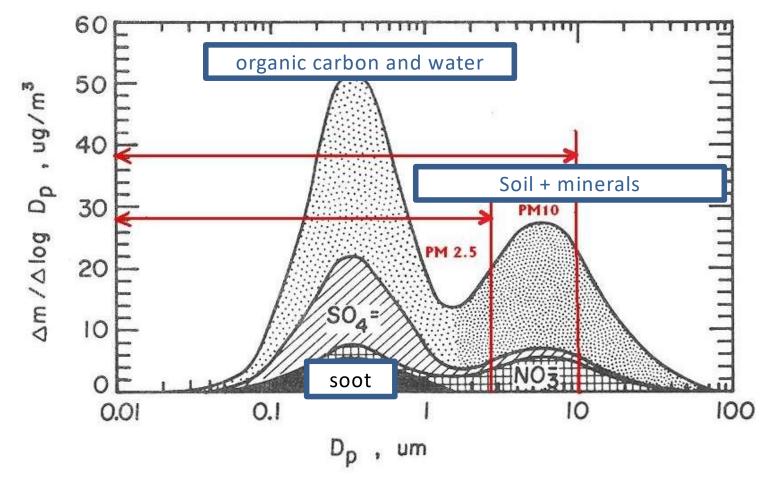
THE CONVENTION – ANATOMICAL VIEW







TYPICAL COMPOSITION of PM10, PM 2.5 and PM10-2.5 FRACTION PM

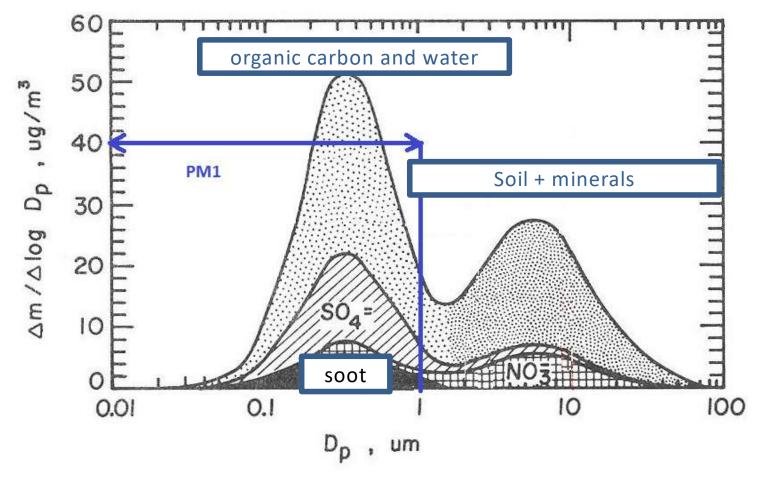




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TYPICAL COMPOSITION OF THE PARTICULATE FRACTIONS OF PM1





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EXAMPLES OF MONITORING PARTICULATE MATTER

Measurement of automatic Analyzers (in situ analysis)

Advantages:

- •Getting the results in real time (validation required)
- •The abundance of data allows for a good statistical processing of the results
- •Allows you to track short term variations

Disadvantages:

- Complex and expensive
- •The necessary frequent calibration
- •Very limited or impossible chemical analysis of samples





EXAMPLES OF MONITORING PARTICULATE MATTER

SAMPLING AND SUBSEQUENT ANALYSIS Advantages:

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Time-integrated pattern that gives the average value Much of the material for analysis Simpler instruments, of easily adaptable Suitable for a wide range of chemical analysis

Disadvantages:

The particles can be agglomerate The possibility of chemical reactions between particles, or between particles and base Possible errors when sampling and transport of samples















"Homemade production" PM10 i PM2.5 Inlet separators(1998.)

The volume of the sample: ~ 100 m³ /dan

The diameter of the nozzle: 11 mm i 2.5 mm

The number of nozzles: 3 i 12

Reynolds number: ~ 3 000







AirMetrics collectors

Suitable for ad hoc and interim surveys in the vicinity of the industry and roads. *Power supply:* 220 V AC ; 12 V DC

Fractions of particles: PM10 i PM2.5 *Programmable:* time, day, day of week, etc. It is easily mounted on pillars, trees, walls, fences etc. A strong pump, air flow rate 5 L/min The possibility of collecting gases in bags of Tedlara of up to 8 h







LVS3

Reference collectors Fractions: PM10,PM2.5, PM1

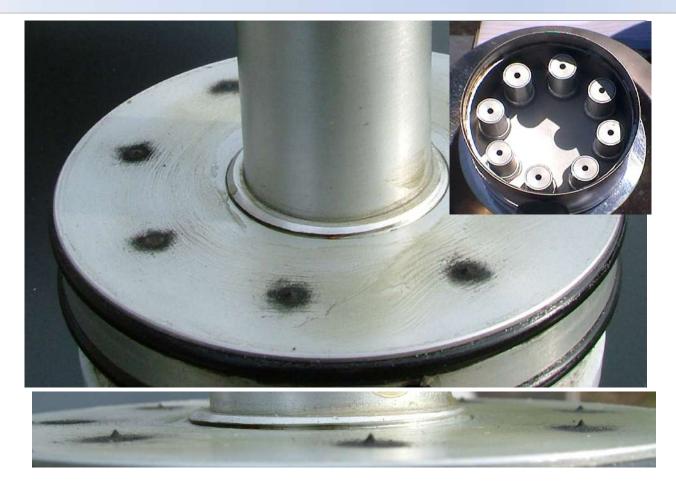
The number of nozzles: 8 The flow of air: 2.3 m³h⁻¹

Filter types: Quartz, teflon, glass fibers









Nozzles and Impact base (PM2.5)





























Digitel HVS Automat DHA-80 15 filter diameter150 mm The factions: PM₁₀ ili PM_{2.5} The flow of air: Total PM : 700 L/min (1008 m³ dan⁻¹) PM10, PM2.5: 500 L/min (720 m³ dan⁻¹)

INZRAK7

EXAMPLES OF AUTOMATIC ANALYZERS



TEOM



β - gauge

TEOM - Tapered element oscillating microbalance

Measures the change in the frequencies of the vibration caused by the increase in the mass of collected particles.

Beta Gauge Particulate Monitor

Measures the β -air attenuation at passing through the sample collected particle.





Teflon PTFE filters are:



- Strong and resistant to acids, alkalis and solventsHydrophobic
- •Very clean, suitable for chemical analysis
- •Suitable for gravimetric analysis
- •Resistant up to 260 ° C
- •Ideal for collecting airborne particulate matter, especially in a damp environment.
- •When weighing the need to the electrostatic break out
- •The high price







Quartz fibers filters

Suitable for research on air pollution.

Made of pure (SiO2) Microfiber (QMA), no binders or additives. Very low contents of alkaline metals.

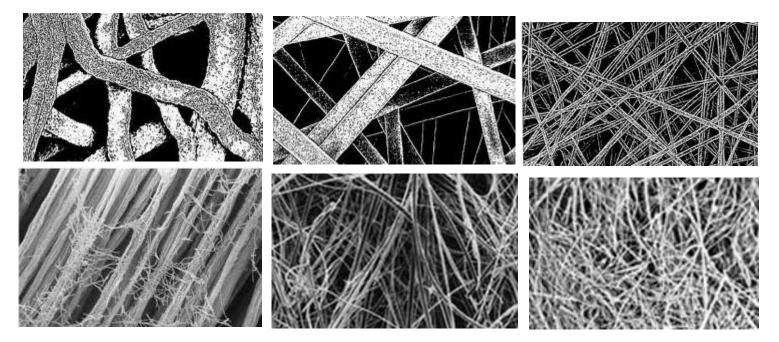
The separation of particles: efficient separation of small particles. **Permeability:** very high. Allows large flow rates of air.

Kemijska stabilnost: very stable in the presence of acidic gases (HCl, SO₂, SO₃, H_2SO_4 , NO and NO₃).

Resistance to the chemical reagent: resistant to acids (except HF) and bases. **Temperature stability**: more resistant than filters, consisting of glass fibre. Resistant up to 950 ° C; above these temperatures are starting to lose their good properties.







Quartz fibers filters







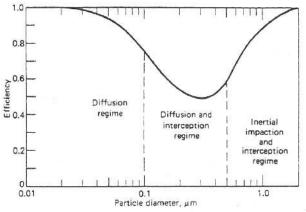


Figure 1. Schematic filter efficiency vs. particle size mustrating the different

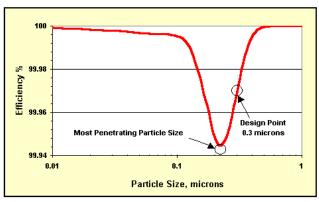


Figure 1: Typical Performance of a HEPA 99.97% Filter.

There are three basic mechanism of separation of particles from air currents in fibrous filters: •Diffusion

- Interception
- Impaction

The total efficiency of the filter is the sum of the efficiency of these mechanisms, the separation of the particles.

Minimum efficiency (the biggest passage of particles) is for particles with diameter of $0.2 - 0.3 \mu m$ and the efficiency of the filters are always measured in the area size.





Air Protection Act

Narodne novine <u>130/11</u>, <u>47/14</u>, <u>61/17</u>

The regulation on the levels of pollutants in the air Narodne novine <u>117/12</u>

Regulation on air quality monitoring Narodne novine 79/17

Regulation on the determination of the zones and agglomerations according to the levels considerable pollution of the air in the territory of the Republic of Croatia Narodne novine 1/14

The program of pollution level measurement of the air in the State network for permanent monitoring of air quality

Narodne novine 73/16





HRN EN 12341:2006

Withdrawn

Air quality--determination of the PM10 fractions by size of the suspended particles--the reference method and field testing for the purpose of proving equivalence measurement methods (EN 12341:1998)

HRN EN 14907:2006

Withdrawn The quality of the outside air--a standard gravimetric method for the determination of the PM2, 5 mass fraction of airborne particles (EN 14907:2005)

These norms are withdrawn 2014. year and merged into an improved standard:

HRN EN 12341:2014

Outdoor air--determination of the mass concentration of suspended particulate matter PM10 ,PM2, 5 with standard gravimetric method (EN 12341:2014)





Finally, what kind of sample we have in the end?

The sample is collected in accordance with the expected health effects to the selected convention.

We're collecting the integrated sample through the defined period of collecting.

Particles are accumulated closely so the possible chemical reactions between particles, as well as between the particles and the surface.

Due to the norm EN 12341:2014 prescribed conditioning samples terms of air temperature, air pressure and relative humidity are altered in relation to the environmental conditions so permit the evaporation and condensation of water and volatile substances.

During the conditioning the samples were exposed to the settlement: and the absorption of substances from the air chambers for conditioning and weighing room (eg. burned conditioning filters for collecting organic and carbon-elementary).





Collected sample is significantly different from "the cloud particles" from which it was taken, so it raises the question of what we accomplished with the default procedures?

•Uniformity procedure which allows the comparison of the results obtained by the "around the world".

- •A good base for further statistical analysis.
- •The possibility of conducting uniform epidemiologic studies and meta studies.
- •Planning and implementation of uniform and simultaneous measures to reduce pollution levels.
- •The unique legislative
- Unique control levels of air pollution.





Testing equivalence of results (PM 2.5) – example 1

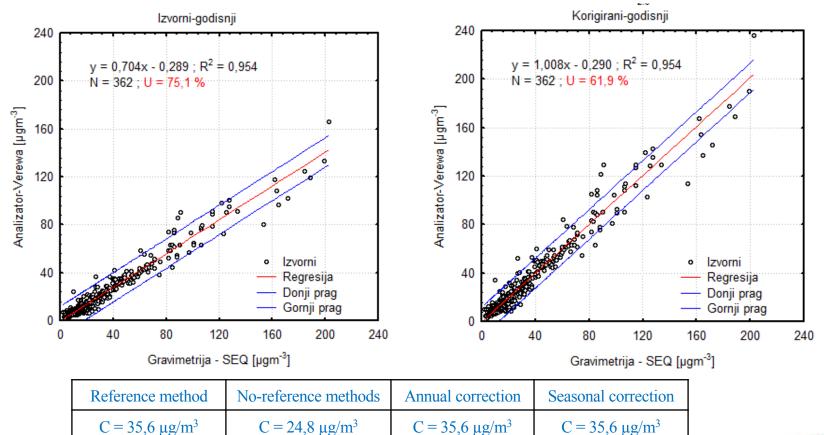
A comparison of the original and the seasonally corrected data of certain reference SEQ47/50 by collector and automatic analyzer for the PM 2.5 fraction during 2014. and 2015.

Original data	Corrective data	Corrective function				
Winter ; $N = 90$; $R^2 = 0,935$						
y = 0,699x + 1,880 U = 76,2 %	y = 1,012x - 0,705 U = 89,2 %	$y_1 = 1,430y - 2,688$				
Spring; $N = 91$; $R^2 = 0,804$						
y = 0,591x + 0,747 U = 77,5 %	y = 1,058x - 0,840 U = 30,4 %	$y_1 = 1,692y - 1,264$				
Summer ; $N = 92$; $R^2 = 0.627$						
y = 0,512x + 1,826 U = 85,7 %	y = 1,173x - 2,663 U = 48,3 %	$y_1 = 1,954y - 3,569$				
Autumn ; $N = 89$; $R^2 = 0.945$						
y = 0,670x + 1,173 U = 74,5 %	y = 1,011x - 0,596 U = 73,5 %	$y_1 = 1,492y - 1,750$				
Year period; $N = 362$; $R^2 = 0,954$						
y = 0,704x - 0,289 U = 75,1 %	y = 1,008x - 0,290 U = 61,9 %	$y_1 = 1,420y + 0,411$				





Testing equivalence of results (PM 2.5) – example 1





Testing equivalence of results (PM 2.5) – example 2

A comparison of the original and the seasonally corrected data of certain reference SEQ47/50 collector and automatic analyzer for the PM10 fraction

Original data Corrective data		Corrective function				
Summer; $N = 27$; $R^2 = 0.929$						
y = 1,018x + 1,113 U = 10,2 %	y = 0,999x + 0,009 U = 12,9 %	$y_1 = 0,983y - 1,094$				
Autumn ; $N = 28$; $R^2 = 0.956$						
y = 0.998x + 0.820 U = 6.9 %	y = 1,000 - 0,001 U = 10,9 %	$y_1 = 1,002y - 0,821$				
Winter; $N = 45$; $R^2 = 0.926$						
y = 0.843x + 2.821 U = 22.4 %	y = 1,007x - 0,138 U = 13,9 %	$y_1 = 1,187y - 3,348$				
Spring; $N = 30$; $R^2 = 0.950$						
y = 0.947x + 0.792 U = 11.1 %	y = 1,001x - 0,029 U = 12,5 %	$y_1 = 1,055y - 0,836$				





Testing equivalence of results (PM 2.5) – example 3

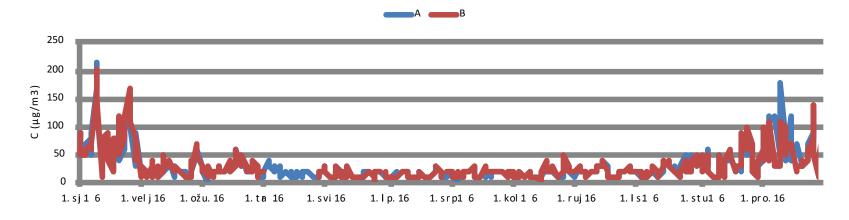
A comparison of the original and corrected data of certain reference SEQ47/50 collector and collector Digitel HVS Machine the DHA-80 for the PM10 fraction After correction of the number of daily overdrafts increased by ~ 50% (35 allowed)

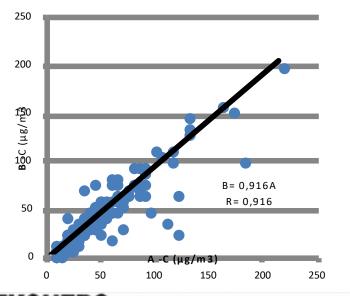
Reference LVS vs. HVS ; $N = 125$; $R^2 = 0.968$				
Original data	Corrective data	Corrective function		
y = 0,892x - 3,133 U = 37,2 %	y = 1,002x + 0,357 U = 16,9 %	$y_1 = 1,122y + 3,514$		

Parameter	Reference LVS	HVS	Annually corrected HVS	Seasonally corrected HVS
Cavg [µg m ⁻³]	38,3	31,1	38,3	38,3
> 50 [µg m ⁻³]	83	56	80	83









Display uniformity clouds PM10

Comparison of daily concentrations measured during 2016, with the same collectors at two city metering stations located in different parts of the city are distant from each other 4.7 km airline.





Monitoring the PM2, 5, on particulate fractions of urban background measurement station Measuring period 2000.0-2015.

Measurements carried out in accordance with the prescribed standards

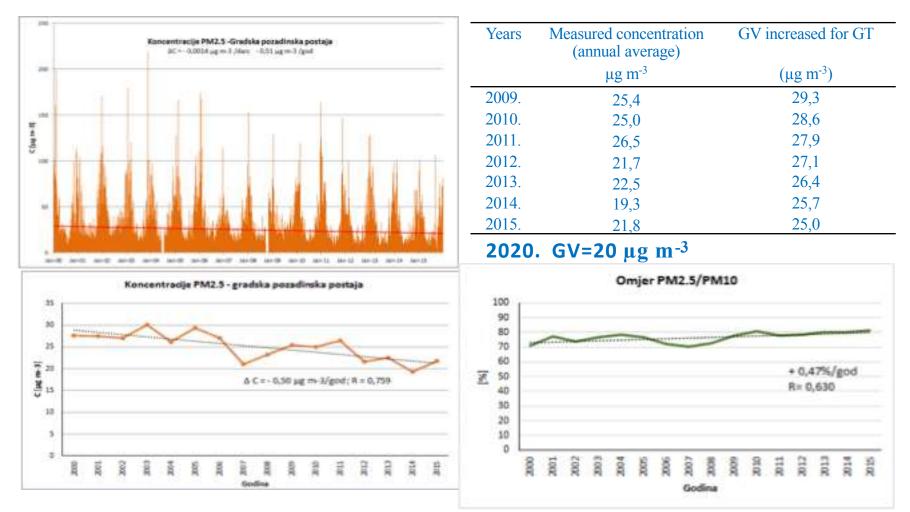
The coverage of data > 98%

Daily patterns (from noon to noon)

Used reference devices: LVS3, SEQ 47/50



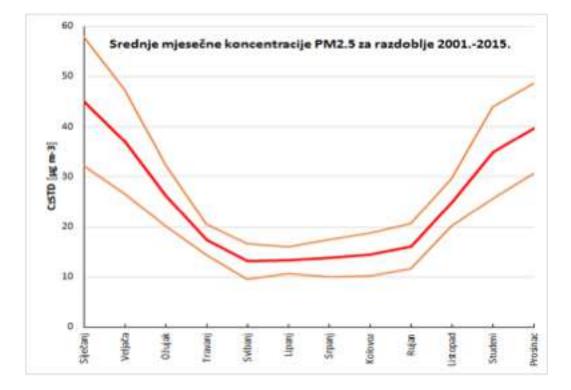






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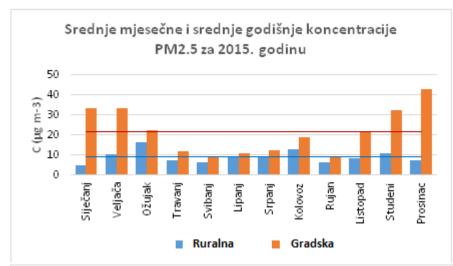
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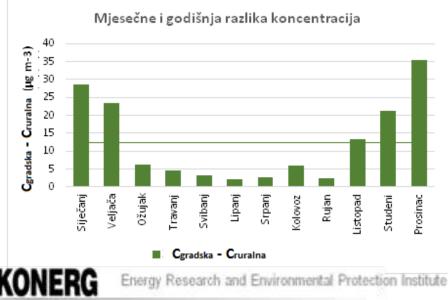


A prominent seasonal dependence

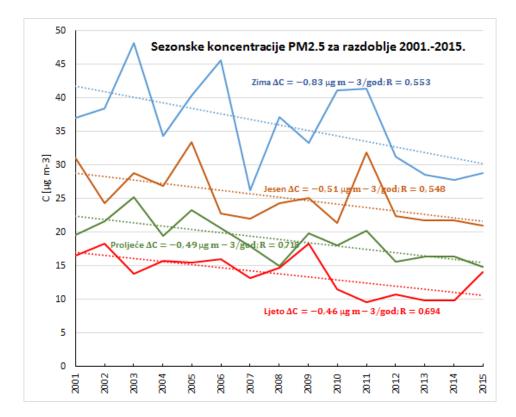








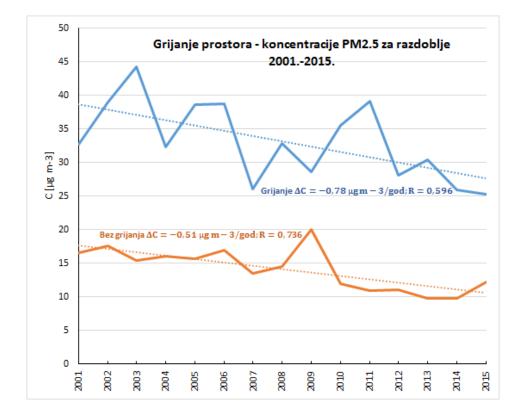




Trends of seasonal concentration through the measuring period

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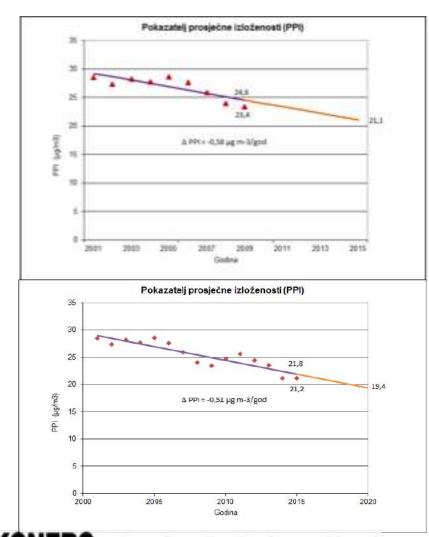




Trends of concentrations for the periods without (May-September) and with heating (November-March)







An indicator of average exposure (PPI) a three-year average of the annual mean concentrations of backwards: PPIX = (CX + CX-1 and CX-2)/3

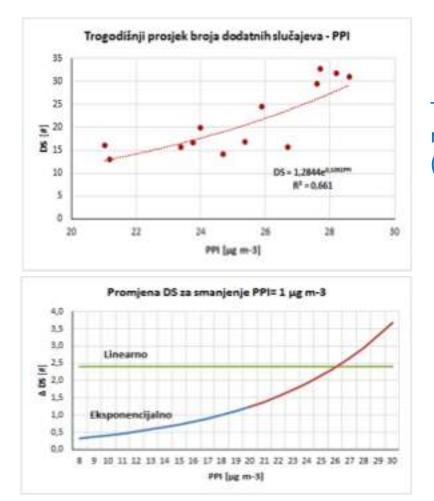
The value of the PPI for 2015. of 21.2 μ g m-3 is higher than the required level of exposure from 20.0 μ g m-3 for 2015.

The model was given an excellent prediction value of PPI for 2015.

Prediction for 2020. year is 19.4 μ g m-3. If the prediction comes true, it would mean that the exposure reduction target at the national level of 20% will not be reached.



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The average three-year dependance the number of additional cases of total mortality (ΔDS) with regard to the change in PPI.

The budget shows that during the period of 2001. up to 2015. ΔDS is reduced from 3,2 #100 000 for 2001. to 1,4 #/100 000 Residents for 2015. evaluation ΔDS for 2020. is 1,2 #/100 000 inhabitants.



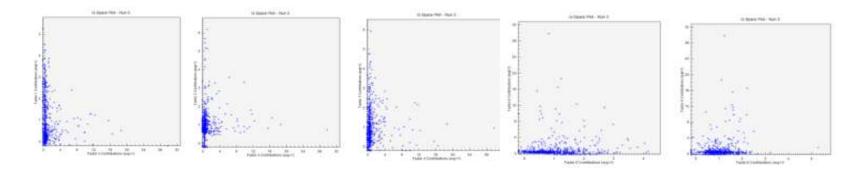
Observation of colored precipitation when sediment analysis indicates the presence of a Sahara dust is rare inland Croatia. Most of these events pass unnoticed, and it is only possible to prove a complex analysis of elemental composition of particulate and modeling the existence and strength of the individual sources of pollution.

Type of pollution: 24-hour samples PM2.5 The number of samples: 619 The filter base: PTFE Measurement methods: HRN EN 14907:2005; HRN EN 12341:2014 Measurement period: 20. January 2014. – 30. September 2015. Sampler: SvenLeckel SEQ47/50 Elemental analysis: ED XRF The Analyzer: EPSILON5, PanAnalytical Analysis of results: EPA PMF5; NOAA HYSPLIT





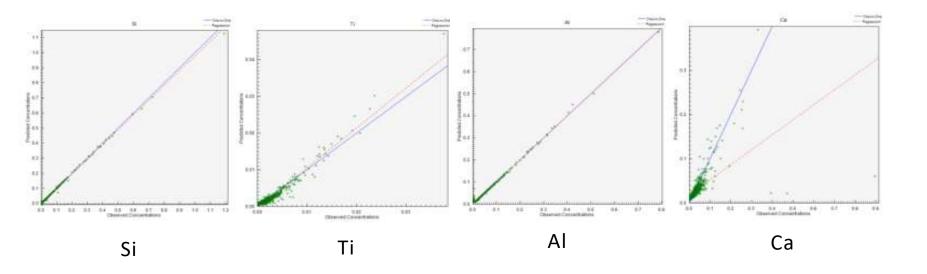
The analysis has highlighted the six important factors (sources of pollution PM 2.5 fraction of airborne particles). Factor 4 which we can call a Saharan dust is completely independent and does not show dependence on other factors (the rotation of the factors shows no effect)



Orthogonal Factor 4 on other factors



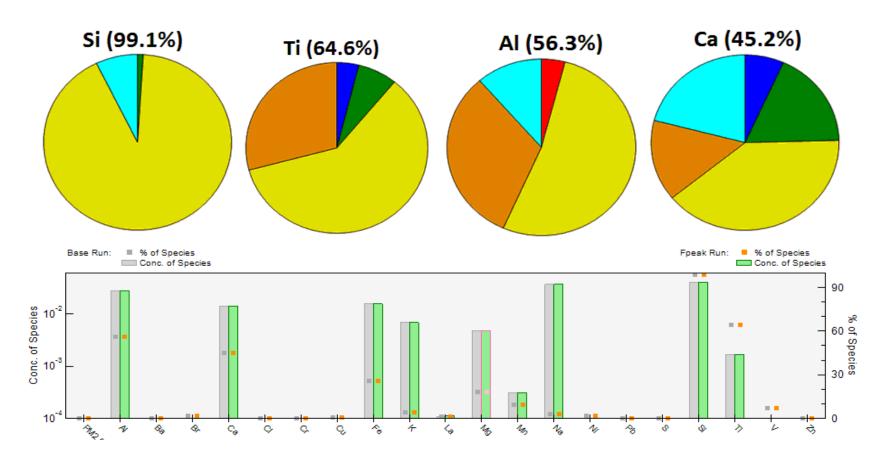




Arrenged modelled with measured values for Si, Ti, Al and Ca







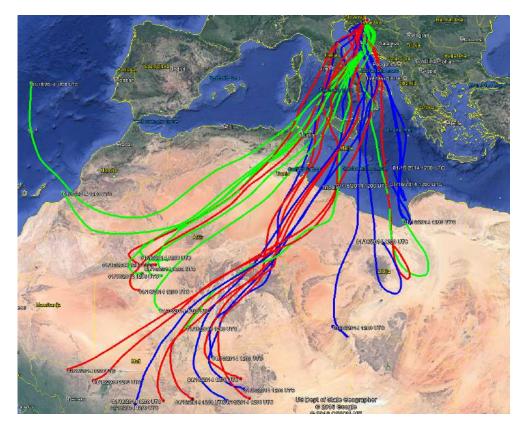
The percentage of single element included in the Factor 4

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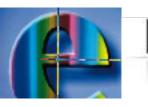
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The results show that in Zagreb every occurrence of the trajectory of the air originating from the North of Africa (30-40 per year) has been registered as a contribution to the content of the PM 2.5 fraction of airborne particles, representing the transport of pollution from the Sahara desert in Central Europe.

The survey was conducted as part of the project IAEA RER1/013 TC project "Supporting Air Quality Management (Phase II)





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THANK YOU FOR YOUR ATTENTION !

Disclaimer: The contents of this publication are the sole responsibility of EKONERG – Energy Research and Environmental Protection Institute, Ltd. and can in no way be taken to reflect the views of the European Union



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