

AIR POLLUTION IN ZLATIBOR DISTRICT AND IMPROVED SOLUTION

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Abstract: The aim of investigation is to reduce air pollution, as accelerated factor of cardiovascular and pulmonary diseases by improved material for filtration of particles lower than 5 microns, designed to prevent or reduce harmful effects. Užice and Kosjerić are third category in accordance to air pollution. Instrumental techniques used for air pollutant analysis were: ICP, GC-MS, UPLC MS-MS. The filters materials were analyzed by SEM, universal camera microscopy and permeability test. PM 10 particles were over maximum permissible value (MPV) for 95, 86, 72 days, while soot was over MPV for 73, 60, 52 days, respectively during 2017, 2018, 2019, 2020 year. The cardiovascular diseases have the largest contribution to mortality in Zlatibor district, 57.8% during 2019. with decreasing tendency in last 2 years. Improvement in air filtration should give impact to the global World Heart Federation target to reduce cardiovascular mortality, by 25%, till 2025. Improved material filters should be used for industrial and heating plants and vehicles pollution.

Keywords: air pollution, PM particles, soot, environmental cardiology, multistage filters, fuel oil

1. INTRODUCTION

Air pollution and climate change were recognized as the top environmental global threats to human health in 2019. by the World Health Organization [1]. There are approximately 9 million annual deaths from global air pollution [2], [3. C Carlsten]. Mortality is a hard endpoint, hospital admissions and emergency room visits for heart failure (HF) exacerbation are more sensitive indicators of air pollutants impact. [4 Modern Tox]. According to the data from the World Health Organization, every year in Serbia about 6,600 people died from the consequences of air pollution, climate change. Serbia is among the top 5 countries in the world with the highest mortality due to air pollution and top 3 cardipulmonary mortality .Two towns in Zlatibor district, Užice and Kosjerić are classified as the 3rd category on the basis of air quality [5]Offic Gazett. The 3rd category means heavily polluted and exceeded the limit value for one or more pollutants. Typical exceedances the limit values of air pollutants for Užice are registered for soot, PM 10 particles with heavy metals, nitrogen oxides, sulphur dioxide and carbon monoxide. Užice is classified as urban zone, with dominant pollution from traffic impact in Omladininska street. The number of vehicles is high, some cars average age is 12 years, some are with saturated DPH filters and catalizators. Some vehicles and civil machine are on diesel fuel. Ultrafine particles, like diesel exhaust emission particles and gaseous are major source of air pollution in urban zone. These particles induce the most detrimental health effects on the cardiovascular and pulmonary systems acute as well as chronically. [6 M. R. Miller, D.E Newby , European Society of Cardiology 2019]. Also heating on fuel oil and charcoal has great impact to quality of air in Užice, and industry, also. Second measuring places in the center of Užice, named "Library", exactly has shown overrange of soot, NO_x, SO₂, CO, PM particles that comes from, heating on fuel oil, that is still here present in 5 vital object in the city center.

Kosjerić is classified as background, suburban zone. Typical air pollutants that are over limit values are suspended particles PM₁₀ and PM_{2.5} particles from cement and other industry, combined with diesel vehicles and civil machines, no gasification still and emission of gasses NO_x and SO₂, CO. In this town dominant impact to air pollution give industry, heating, agriculture pesticide treatment. In addition meteorological condition, T inversion summarized to air pollution and give negative impact to human health.

The cement production in Kosjerić generated PM₁₀, PM_{2.5} and ultrafine particles and gaseous such as nitrogen oxides (NO_x) and sulfur oxides (SO₂). Cement contains a variety of minerals that have hazardous risk to health especially to manufacturing workers. Elkok metal production also give negative impact to air pollution. The minerals, from cement dust might cause respiratory and cardiovascular problems. Toxic dust comes from As, Cr (VI), Si minerals in cement dust at a level higher than the permissible limit in cement plant all over the world.]. The dust can cause cancer and many non-cancer diseases even implementation of prevention and control systems.[7 Kamaludin , Aerosol]. Both PM with heavy metals, soot and gaseous pollutants have been affect to the respiratory organs, and it is chosen that it is more connected with cardiovascular diseases.

The cardiovascular effects of inhaled particles of particle matter (PM) are responsible for a substantial morbidity and mortality attributed to air pollution [6 M.R, Miller, D. E . Newby Cardiovac. research, pp 1-16, European Soc of Cardiology , 2019]

The aim of this paper is to determine in which concentrations air pollutants: PM 10, PM 2,5 and ultrafine particles, with heavy metals (As, Cd, Pb, Ni), soot and gasses NO_x and SO₂, CO and other pollutants adversely affect to human health and for what period. The following activities are define for this purpose

- analysis of aeropolution variation for 5 years in Užice and Kosjerić
- variations during the year and month and day
- to make correlation of excessive pollutants in the air with medical assistance or hospitalization due to deteriorating health status of the population with registered cardiopulmonary problems or in population who have not been previously with these diseases
- to identify, evaluate number of inhabitants that are in health risk caused by the inhalation of PM₁₀, PM 2,5 and ultrafine, particles and their constituents
- to take some action such as improved filtration (materials and products) in heating plants, and dedusting systems in industry and area of traffic.

PM 2.5 and human health issues have investigated by Kovačević et al for inhabitants in Zlatibor district during 2012-2014 period [8 Kovacevic]. Authors applied time-stratified case-crossover design to Emergency department 424 visits for asthma exacerbation occurred in this period. Data were collected in the Užice Health Centre. Air pollutants, odds ratios and their 95% confidence intervals were estimated by conditional logistic regression adjusted for potential confounding influence of weather variables (temperature, humidity and pressure). The study confirms the association between exposure to PM₁₀, PM 2,5 black carbon, NO₂, and SO₂ pollutants and emergency department visits for allergic asthma patients in Užice. Kovčević et al aslo go in for black carbon, parameter typical for Užice that caused pulmonary diseases, (allergies rhinitis, astma) in children age and cardiovascular diseases in adults. Environmental contaminants that mainly originate from: vehicle exhaust emissions, heating processes , industrial processes induce toxicological effects, such as: carcinogenesis, atherogenesis, and teratogenesis. The cardiovascular effects of inhaled particles of particle matter (PM) are responsible for a substantial morbidity and mortality attributed to air pollution, atherosclerosis and heart failure [9 T T. Zhang Beijing], M. N. Todorović et al [10 Todorovic I. Journ. Env. Sci.] give evaluation of cardiovascular, respiratory and total non-accidental mortalities attributed to exposure to PM₁₀, O₃, NO₂ and SO₂ in the three largest cities in Serbia: Belgrade, Novi Sad and Niš. The analysis was performed using AirQ+ modelling, by linking annual baseline mortality rates and daily pollutant exposure during 2011–2015 period, based on cause-specific concentration–response functions. The obtained premature deaths estimated within 95% confidence interval and attributed to PM₁₀, O₃, NO₂ and SO₂ exposure were 2013 (1344–2677), 1411 (685–2086), 831 (555–1107) and 443 (333–530), respectively. Total mortalities due to O₃ and NO₂ exposure were in the range of findings for other regions, while mortalities attributed to PM₁₀ were higher. The cardiovascular mortality caused by these four pollutants was higher than respiratory mortality.

2. EXPERIMENTAL PART

Continous air sampling, (suspend particles PM with heavy metals and rainfall) is done by automatic Tecora Echo High Volume Sampler, with flow and measurement regulated in relation to actual condition. The sampling module for TSP is with filter holder for total particulate (TSP) on membrane of 150 mm diameter. Working flow is 500 l/min The PUF sampling module with filter holder of 102 mm and adsorbing cartridge for PUF of 58 x 125 mm allows simultaneous sampling of particulate (PM₁₀, PM_{2,5} and ultrafine) and gas fractions with flow rate between 180 and 220 l/min. Automated SEPA stations in the Center of Užice and in Kosjerić, are continously sampling and measured hourly PM 10 particles in Užice and PM 10 and 2.5 in Kosjerić ..

2.1.Sampling The analysed dataset includes PM₁₀ mass concentrations, obtained by means of reference Sven Leckel samplers, and daily concentrations of trace metals (As, Cd, Cr, Ni and Pb) and BaP determined by the use of reference methods: gas chromatography mass spectrometry (Agilent GC 6890 MSD 5975) and inductively coupled plasma mass spectrometry (THERMO Scientific iCAP 6000 with software iTEVA) according to standards EN 12341 and EN 14902, respectively. Values below the method detection limits werereplaced by 1/2DL.

2.2.Instruments techniques and methods used for air pollutant analysis

Soot has been determined by gravimetric method .Particle mater PM 10, PM 2,5, fine and ultrafine particles have been determined by gravimetric method Gasseous:concentration of SO₂ by turbidimetry

on 2100N IS, Hach instrument, USA concentration of NO₂ on spectrophotometr, UV 1800, Shimadzu, Japan, Black carbon index using reflectometer, Proekos RM01. Total sediment particles (TSP) with PM 10, PM 2.5 particles are determined and its components within Tools and machine for compacting, sintering improved physical characteristics filters Universal Camera Microscope Me F2, Reichert, Austria used for improved sintered materials investigation. Aparature for measuring permeability of improved filters

3.RESULTS AND DISCUSSION

The data of air pollutants examination in Užice and Kosjerić, two cities in Zlatibor district, where the health of the inhabitants is the most endangered by air quality, climate change and metrological impact in specific geographical configuration that have these towns are presented. Some improved filtration as possible solution also. The measuring places in these two towns were selected in accordance with Serbian Laws and Sampling Standards, adopted from European Union. The results of measuring pollutants from Užice city center local network (Green Market, Library), and state network, SEPA measuring places in Omladinska street, industrial zone (Krčagovo), local measuring places near hospital, Health center of Užice, suburban/industrial area (Sevojno) local network Kindergarten and Ambulance in Sevojno. In discussion are also comment target emitters from industrial surrounding.

Kosjerić have background and suburban zone with 7 measuring places in local network (Dunjići, Crepana, Galovići graveyard, Primary school, Elkok-cross section, Water Supply and Lugovi) and SEPA automatic station and target emitters on Titan cement company.

The air pollution parameters and meteorological conditions are correlated with health inhabitants status for these towns. Analysed period is whole year. The focus is on air pollutant during heating season, period with foggy, T inversion and other climate impact to health status of inhabitants, except air pollutant. The impact of parameters higher than permissible values on cardiovascular and pulmonary diseases has been carefully studied. The global target is to reduce cardiovascular mortality, the biggest cause of mortality by 25%, including diabetes and pulmonary embolism till 2025. by the World Heart Federation. [11 Cardio diseases, "How to overcome the leading cause of death in Serbia", , [www.worldheartfederation.org/what we do /advocacy 25 by 25](http://www.worldheartfederation.org/what-we-do/advocacy)]

The costs of treatment of cardiovascular diseases are uniformly high and show a tendency to increase not only in the Zlatibor district, Serbia, Europe but in Australia, Canada, USA, Asia. This indicates the importance of prevention, the availability of modern drugs and treatment methods that reduce mortality, continual patient education. Socio-economic status (diet, life habit) has joint impact with air pollution to cardiopulmonary diseases. Total cost of noncancer diseases treatment in Serbia was in the range between 237.3 till 260. millions € for period from 2011.–2015.year. [12 Jovovic]. The studios analysis of PM 10, and PM 2,5 partilcels are done for 5 year period. The content of dominat componet within PM particles have also done. Here is only segment of data for PM 10 particles in Užice for months when meteorological conditions are unpleasant for cardivacular and pulmonary diseaeses and it is emphasized humidity, temperature inversion, low T that caused vasonstriction and other health problems.

The table 1 has shown segment of PM 10 particles data in the center of Užice, that are sum of some pollutants, with highest values trend during winter period.

Table 1: PM 10 particles measured in the center of Užice

Month	Data	PM10	Data	PM10	Data	PM10	Data	PM10
		2017/2018		2018/2019		2019/2020		2020/2021
Decembar	12/1/2017	34.5	12/1/2018	188.1	12/1/2019	78.7	12/1/2020	99.56
	12/2/2017	45.5	12/2/2018	245.8	12/2/2019	117.2	12/2/2020	113.71
	12/3/2017	29.9	12/3/2018	242.5	12/3/2019	32.3	12/3/2020	280.74
	12/4/2017	62.8	12/4/2018	179.4	12/4/2019	52	12/4/2020	235.55
	12/5/2017	54.8	12/5/2018	62.9	12/5/2019	82	12/5/2020	159.78
	12/6/2017	59.5	12/6/2018	91.8	12/6/2019	160.5	12/6/2020	97.21
	12/7/2017	140.9	12/7/2018	169.2	12/7/2019	197	12/7/2020	52.6
	12/8/2017	151.5	12/8/2018	168.8	12/8/2019	132.8	12/8/2020	39.18
	12/9/2017	53.3	12/9/2018	47.3	12/9/2019	133.1	12/9/2020	60.75
	12/10/2017	61.8	12/10/2018	52.8	12/10/2019	114.4	12/10/2020	129.51
	12/11/2017	35.6	12/11/2018	78.9	12/11/2019	33.9	12/11/2020	62.04
	12/12/2017	27.9	12/12/2018	74.6	12/12/2019	58.9	12/12/2020	66.57
	12/13/2017	52.1	12/13/2018	78.5	12/13/2019	106.5	12/13/2020	38.63
	12/14/2017	50.2	12/14/2018	61.3	12/14/2019	104.5	12/14/2020	41.89
	12/15/2017	102.8	12/15/2018	32.3	12/15/2019	149.8	12/15/2020	57.5
	12/16/2017	21.2	12/16/2018	46.1	12/16/2019	269.2	12/16/2020	97.95
	12/17/2017	33	12/17/2018	116.1	12/17/2019	236.9	12/17/2020	163.95
	12/18/2017	38.5	12/18/2018	58.8	12/18/2019	260.4	12/18/2020	156.69
	12/19/2017	47.7	12/19/2018	70.9	12/19/2019	277	12/19/2020	58.4
	12/20/2017	60.4	12/20/2018	157.4	12/20/2019	318.5	12/20/2020	74.72
	12/21/2017	63.7	12/21/2018	358.7	12/21/2019	67.3	12/21/2020	101.4
	12/22/2017	49.5	12/22/2018	185.6	12/22/2019	42.6	12/22/2020	186.29
	12/23/2017	59.1	12/23/2018	99.6	12/23/2019	16.1	12/23/2020	195.87
	12/24/2017	44.1	12/24/2018	52.8	12/24/2019	63.3	12/24/2020	114.62
	12/25/2017	127	12/25/2018	24.8	12/25/2019	55	12/25/2020	48.6
	12/26/2017	162.7	12/26/2018	53.1	12/26/2019	51.2	12/26/2020	48.07
	12/27/2017	94.5	12/27/2018	100.5	12/27/2019	59.1	12/27/2020	42.44
	12/28/2017	30.8	12/28/2018	117	12/28/2019	23	12/28/2020	103.43
	12/29/2017	34.6	12/29/2018	55.3	12/29/2019	25.8	12/29/2020	70.38
	12/30/2017	67.8	12/30/2018	55.5	12/30/2019	38.6	12/30/2020	98.49
	12/31/2017	68.9	12/31/2018	24.8	12/31/2019	53.9	12/31/2020	67.11
Januar	1/1/2018	187.89	1/1/2019	59.7	1/1/2020	54.24	1/1/2021	
	2/1/2018	92.51	1/2/2019	47.7	1/2/2020	68.73	2/1/2021	
	3/1/2018	54.24	1/3/2019	36.6	1/3/2020	128.24	3/1/2021	
	4/1/2018	39.18	1/4/2019	53.9	1/4/2020	221.3	4/1/2021	
	5/1/2018	111.01	1/5/2019	31.9	1/5/2020	25.21	5/1/2021	
	6/1/2018	104.84	1/6/2019	26.7	1/6/2020	44.09	6/1/2021	
	07/01/2018	135.14	1/7/2019	48.1	1/7/2020	94.85	7/1/2021	
	8/1/2018	188.65	1/8/2019	105.4	1/8/2020	118.45	8/1/2021	
	9/1/2018	197.13	1/9/2019	170.5	1/9/2020	153.82	9/1/2021	
	10/1/2018	145.47	1/10/2019	67.8	1/10/2020	222.16	10/1/2021	
	11/1/2018	117	1/11/2019	44.4	1/11/2020	205.84		
	12/1/2018	45.9	1/12/2019	50.6	1/12/2020	105.75		
	13/01/2018	25.39	1/13/2019	61.7	1/13/2020	139.13		
	14/01/2018	27.57	1/14/2019	90	1/14/2020	222.2		
	15/01/2018	54.05	1/15/2019	35.9	1/15/2020	175.04		
	16/01/2018	177.58	1/16/2019	50.8	1/16/2020	180.63		
	17/01/2018	105.75	1/17/2019	145.6	1/17/2020	163.43		
	18/01/2018	59.68	1/18/2019	206.2	1/18/2020	120.08		
	19/01/2018	66.03	1/19/2019	62.6	1/19/2020	56.23		
	20/01/2018	38.09	1/20/2019	73.6	1/20/2020	90.68		
	21/01/2018	101.4	1/21/2019	66.7	1/21/2020	95.94		
	22/01/2018	43.16	1/22/2019	79.6	1/22/2020	202.79		
	23/01/18	122.62	1/23/2019	124.2	1/23/2020	122.8		
	24/01/18	127.7	1/24/2019	31.4	1/24/2020	208.05		
	25/01/18	127.31	1/25/2019	38.6	1/25/2020	266.82		
	26/01/18	248.5	1/26/2019	56.6	1/26/2020	132.62		
	27/01/18	233.45	1/27/2019	184.3	1/27/2020	120.44		
	28/01/18	198.8	1/28/2019	162.9	1/28/2020	107.91		
	29/01/18	201.34	1/29/2019	65.7	1/29/2020	46.06		
	30/01/18	177.91	1/30/2019	86.7	1/30/2020	91.22		
	31/01/18	125.54	1/31/2019	102.5	1/31/2020	69.48		

The analysis of PM particles composition has shown: soot, heavy metals that have cumulative influence to human body, gaseous, endotoxins. The heavy metals time elimination from human body for Pb is for example 26 years and target values must be lower. Similar situation is with other heavy metals. The yearly trend for PM 10 particles in Užice per month is presented on Figure 1

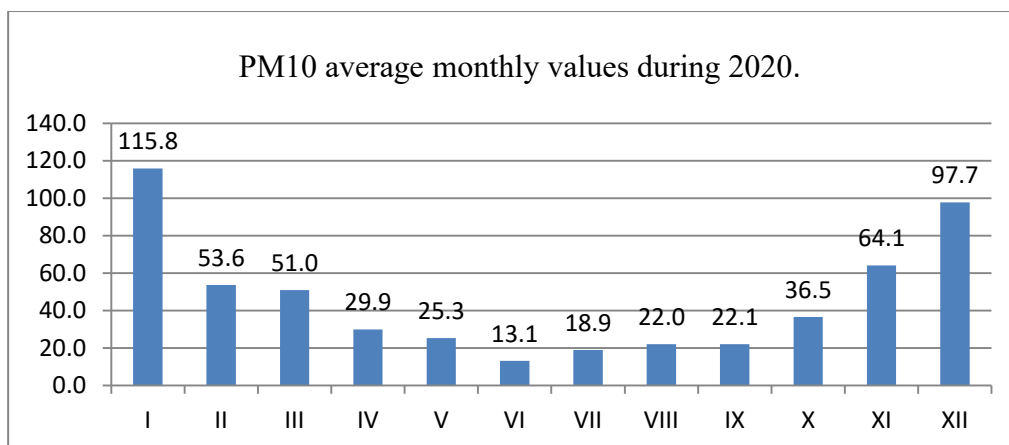


Figure 1: The average monthly values for PM 10 particles in Užice

From the annual measurements are selected January and December 2019-2020 as the months with maximum values of PM 10 particles. The table with all data are put in Supplementary Material of the Paper. The values of PM 10 are significantly lower during summer, but heavy metal, especially Ni is still variable and high during summer. In June the lowest is content of PM 10 particles, but heavy metals are present. Užice is urban area, with dominant traffic impact, Omladinska street. The heating activity on fuel oil give significant impact to air pollutants, emphasized at “Library” measuring places, while soot is dominant at “Green market” measuring places. Heating plant in the center of Užice, that are still on fuel oil are: Building Zlatibor, S building, Theatre, Library and Primary Health center, National employment service because of lack of money. The other heating plant are on natural gas and this give positive impact to inhabitants health. PM 10 particles are presented during the day with overrun for the limit values (the target value). In the morning and in the evening air pollutants are overrange usually. Daily limit for PM 10 is 50 µg/m³.

During August 2021 trend of PM 2,5 and PM 10 particles have shown that particles are present during summer period and its values vary from 17 till 7 µg/m³ for PM 10 and from 13 till 5 µg/m³ for PM 2.5 particles. As Holland National program stated the PM 2,5 and ultrafine particles are especially harmful for human health, also induce climate changes. The sources of PM 10 and PM 2, 5 particles comes from antropogen activities, also [13 M. Schaap, E.P. Weijers, D. Mooibroek, L. Nguyen, R. Hoogerbrugge, Composition and origin of Particulate Matter in the Netherlands] From the data analysed the content of PM10 particles are heavy metals Pb, As, Cd and Ni with high toxicity, soot and endotoxins and gaseous.

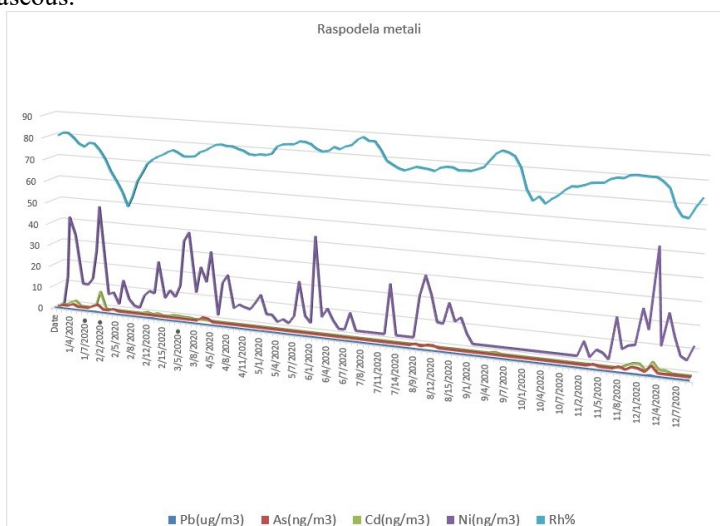


Figure 2. The concentrations of heavy metals (As, Cd, Ni, Pb) and humidity during 2020 in Užice

1. From the figure 2 PM 10 with heavy metals it is seen that on non-working days: holidays and Sundays in Serbia, the concentration of PM particles and heavy metals decreases even in the months when the heating season is not active, summer days. Mean annual concentrations of heavy metals (As, Cd, Ni, Pb) have not exceed GV, i.e. target value (CV) for the calendar year, but the heavy metal has cumulative effect and very long time of excretion from human body. The PM particles are lower

during summer, but Ni is still variable and high during summer. Nickel comes from fuel oil and diesel combustion. Heavy metals that positioned Užice on third, fourth places in Serbia are arsenic, cadmium, lead and nickel. In accordance to nickel and arsenic concentration Užice is after Zrenjanin and Bor, while Kosjerić also has these metals but it is positioned on 15th places in Serbia, (in accordance to nickel concentration after Smederevo and Pančevo, to arsenic on 5th places and cadmium to 15th places in Serbia. No daily overrange, but there is cumulative effect and action is needed to save life all inhabitants from these two towns from Zlatibor district especially during 2020 year. The situation is similar for 5 years before period. There is also benzopyrene in the air, no limit overrange. Užice is on second places in Serbia, but target value is overrange. Also there is benzopyrene in the air. In comparison with Sostarić et al [14 M. Perišić, S. Rajšić, A. Šoštarčić "Levels of PM10-bound species in Belgrade, Serbia", *Air Qual Atmos Health*, 2016] data for Belgrade traffic emphasized areas at four sampling sites affected by traffic pollution (BAS, FVM, KBC and JNA) like in Užice in Omladinska and at Library measuring places. The observed Ni concentrations exceeded the limit value of 20 ng m⁻³. High Ni concentrations characterise each mode of transportation due to the high level of Ni in diesel, petrol and fuel additives and also may be released through the engine exhaust due to wear and tear of the engine [15 Menzie, 2009]. Close to highway E75, an increase of Ni concentration was observed at the rate of 2.66 ng m⁻³ (15 %) for the entire period. Užice is also near main road Belgrade Zlatibor and Kosjerić also near Main road from Belgrade till Požega.

Soot is formed during incomplete combustion of fuels containing carbon, most often, fuel oil diesel. Soot particles can serve as cores that can absorb gas components. It contains tar substances. Soot is monitored in relation to the maximum allowed values. According to SEPA, governmental Agency for environmental measurement the center of Užice during 2019 Užice (Green market, measuring places) has been on first places in accordance to soot overrange and GVI, while during 2020 it is on second places in accordance to yearly overrange, but with increase soot concentrations. [16 Report from SEPA 2020 F. Radović, Air Quality and Pollen Allergens, Belgrade 2021.] The over range has been registered near Green Market as 63 days have overrange for soot with maximum value soot concentration of 233 (µg/m³) for 2020 year. GVI is 50 (µg/m³). During 2019 at Green Market the number of days overrange has been 52 and maximum daily value has been 223 (µg/m³). The concentration of soot increase in Užice for 5 years, from 2019 till 2020 on annual level, no matter some action have done.

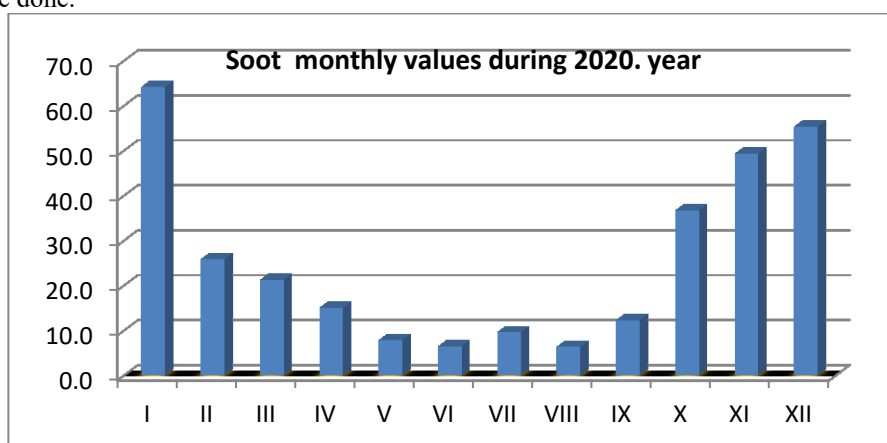


Figure 3. The average monthly concentration of soot during 2020 year

In comparison to other towns in Serbia the values of soot on measuring places Green Market is with the highest value in the center of Užice town. In Obrenovac, town with the biggest Termoelectrana Nikola Tesla with 6 blocks on charcoal, with average charcoal consumption 350-490 t per hour, values of soot in December 2019 are 120-304 µg/m³. Soot is lower in area with charcoal producing energy then in Niš and Užice. PM 10 particles are in range 85-318 µg-m³. Within PM 2.5 particles is soot, i.e. black carbon. Black carbon(BC) is a component of fine particulate matter(PM ≤ 2.5µm). Black carbon consists of pure carbon in several linked forms. It is formed through the incomplete combustion of fuels. It is one of the main types of particle in anthropogenic and naturally occurring soot. Black carbon causes human morbidity and premature mortality. Soot is ubiquitous and has large detrimental effects on human health and climate changes. [17 Y. Lin, X. Huang, Y. Liu, D. Cao, D. Lu, Z. Feng, Q. Liu, Z. Lin, G. *Anal Chem* 2021 May 4;93(17):6665-6672.]. The soot particles from different origins and with different morphologies showed highly consistent mass spectral fingerprints deriving from peak ratios of small carbon cluster anions (C₂-C₁₀-), which enabled both accurate quantification of soot in fine

particulate matter (PM 2.5) samples and label-free imaging of soot particles in biological media. By this technique investigated the suborgan distribution of soot particles in mice after exposure to PM 2.5. The lung is the main target organ for short-term inhalation exposure to soot particles. The inhalation toxicology of soot and also provides a practical novel methodological platform for identification, tracing, and toxicological studies of elemental carbon-based nanomaterials.

Recent studies report that the relationship between temperature, and mortality, including cardiovascular diseases and mortality, is influenced by climate, change location, and socioeconomic status. Climate changes manifested as increase and decrease T caused many infective diseases that caused inflammatory process in organisms [18 P. Giorgia, P. Di Giosia, M. Petrarca, "Climate Changes and Human Health: A Review of the Effect of Env Stressors on Cardiovasc Diseases, 2017, 23, 3247-3261]. Few studies have investigated the impact of temperature variability on mortality in regions with very hot and very cold seasons and impact of air pollutant that caused inflammation. The effect of very cold and very hot days increases mortality. In Chinese subjects, both extreme cold and hot temperatures have been associated with higher mortality from ischemic heart disease, with higher risk in old and female subjects

Impact of meteorological parameters to humans health is also very important in complex situation, especially for towns like Užice and Kosjerić are. The center of Užice is closed by hills and mountain slopes. The geographical configuration mean town in a valley surround by hills (Pora, Kapetanovina, Tatinac) and mountain slopes of Jelova Gora, Zabučje with altitude 700m, with river nearby and effect of climate changes. The consequences are: humidity, foggy, absence of winds, T inversion (during winter period), that contribute to the retention of harmful air pollutant in the city center. In the center of Kosjerić, town in valley of the river Skrapež surrounded by mountains over 1000 meters elevation: Povlen, Maljen, Kozomor and Subjel. The absence of winds, contribute to the retention of harmful air pollutant in the city center. In comparison to Užice geographical configuration Kosjerić is more unfavorable on the issue of air pollutant retention. Analysis of cardiovascular and pulmonary diseases for last 5 years, indicate increase, of problems during period from october till march in Užice and Kosjerić.

The meteorological condition impact to increasing air pollutants and disorder of health parameters during october –march from 2017.-2021. An air pressure value have been cca 980- 990 mbara during winter period in Užice. The daily variation in humidity for example on 7 of January have been from 55 till 77 % within one day. This variation is very negative to cardiovascular and pulmonary diseases. The temperature daily variation change from 0° C, at 15h pm till 9° C, for 7th of january 2020. These meteorological variation within one day have negative impact to human health, even if no air pollution. In combination with air pollutant from some oldfashion heating plant on fuel oil, incomplete combustion from vehicle engine and industry impact the health of older and children and inhabitants with cardiopulmonary give very negative affect. So due to high air pollution, unfavorable weather conditions, it is recommended to sensitive citizens to avoid going out in the morning and evening to prevent unfarable happened and health crisis. PM particles in Užice consist of soot in Užice, heavy metals: Pb, As, Cd, Ni as dominant species and dust, that are associated with gasses. The problem with heavy metals is their cumulative effect, bonding for HEM and many health disorders caused till time of combustion. Average value of arsenic in Užice during 2019 on measuring places Užice -Teatar was 6 ng/m³. Nickel target values is 20 ng/m³. Cadmium target values was 5 ng /m³. Lead limit value was average 500 ng/m³ and daily 1000 ng/m³. The extremely high values of PM10 data and metal are registered during January (on 3rd January, 4th, 9th January have been 189,168, 224 µg/ m³, with Ni concentration 41, 48 (ng/m³), where Ni concentration exceeded 8 times (Ni is high on working day, when traffic is on high level. Other heavy metals exceed 2,5 -2,8 times during these days. Similar situation is on 8th and 9th January. Ni concentration is variable and over the limit even when heating season is over. It is very high during march 5, 6, the concentration are 35, 40, while PM 10 particles are 44, 54 µg/m³. On 1st of june for very low PM10 value 12 µg/m³, the Ni concentration is 44(ng/m³), because of heavy traffic in the town. Heavy metals are often no overrange, but have cumulative effect to human health, especially cardiovascular, pulmonary diseases, carcinogenesis and atherosclerosis. Nickel is emitted to the atmosphere from combustion of fuel oil, car fuel and additives consist it, steel, nickel alloy production and electroplating. In urban areas, nickel levels in the ambient air range from 1-10 ng m⁻³. In industrialized areas and large cities levels in the range of 110-180 ng m⁻³ have been recorded [3]. In polluted air, the main nickel compounds appear to be nickel sulphate, nickel oxides, nickel sulphides, and to a smaller extent, elemental nickel [4 Modern toxicology]. Heating plant also emitted gaseous NO_x, SO₂, CO, CO₂. According to Nis Naftagas laboratory results of fuel oil medium S, during 2020 have shown S concentration 1.16, while % (m-m) is 14.90. Based on the measured values of mass concentrations of pollutants emitted into the air from the boiler emitter in the center of Užice (building "Zlatibor") which uses medium S fuel oil as fuel compared to the boiler where natural gas is used as fuel, SO₂ values have been seen on the fuel oil plant

emitter exceeds the limits for exhaust gases, especially for SO₂ up to 1.43, and for NO_x 2.32 times, while at the emitter where the natural gas is the value does not exceed the GVI. CO gas has not exceeded GVI.

Smoke gases is measured for cars, during technical inspection. These values are very high, i.e they exceed the limit values up to 30 times if the car does not have the dph filters and catalysators. Nitrogen gases, heavy metals, nickel, are emitted in high concentrations from cars also. One faulty car contaminated town, environmental like dozens of cars with dph filters. Also PM 10 particles are emitted from cars, so Omladinska street in the center of Užice, classified town as traffic agglomeration. A huge number of vehicles emitted an improper amount of exhaust gases. Vehicle owners have to adjust cars in order to optimized the exhaust gases of vehicle and keep inhabitants health and environment in good condition. Almost every other vehicle in Serbia pollutes the environment due to improper emissions of harmful gases. The elimination factor during the technical inspection is not emission class of the engine, but the allowed amount of exhaust gases. Cars with a Euro 3 engine on which the catalytic converter or DPF filters has been removed emit toxic gases into the air and pollute the environment. By returning the catalytic converter to the vehicle or cleaning the engine, it should be solve the problem of exhaust emissions.

Third harmful impact to air pollution comes from dust, harmful PM particles, gaseous, metals generated in industry. Companies have dedusting systems, degreasing systems, but all need to be improved as heating plant .The product of this type combustion emergent give soot, black carbon and nickel in pm 10 particles. On the contrary towns that applied for European funds as Zenica has done has even 10 times lower oxides in the air after gasification of whole town. The pm 2, 5 and ultrafine particles start measured from last year in Užice . These particles are higher problem for health of inhabitants, because these particles more easily comes into alveoles and comes into the blood and travel till vital organs such as heart, kidneys, liver. From the moment Uzice start with gasification process, car fuel in accordance with european norme the number of registered inhabitants with cardiological and pulmonary diseases slowly decreases . The data are strongly affected by industrial impact. Industry has been on lower stage of production during last years, no matter metal capacity of companies are carried out capacity expansion. From december 2019 SARS COV 2 epidemy spread all over the world so the data for 2020-2021 are not representative , because patient are asked not to used medical health , only in very critical situation. The data from primary helth care has shown that any technical improvement in function keep our inhabitants helth. 50 % decrease registered cardiovascular diseses are registered if we compred 2016-2017 with 2019- 2020 year. Sostaric et al [14 Sostaric] identify levels of population health risk, cancer caused by the inhalation of PM₁₀- bound species in urban area of Belgrade, where traffic have great impact and Ni and As metals can cause health problems. Uzice and Kosjeric are traffic and background, suburban agglomerations and air pollutants in these towns give impact to cardiovascular diseases and pulmonary diseases. During the heating season (from october till march), the quality of air is in critical zones - red and purple, which means that it is dangerous, extremely poor air quality and that inhabitants should be outdoor some days only for an hour . Registered diseases in Primary Health care in Užice collected for 5 years from 01.10.-31.03 are analysed by methods of Decriptive Statistics and presented in table 2 .

Table 2:Registered diseases in outpatient clinics in Primary Health care in Užice, for 5 years and period 01.10.-31.03. 2016 till 2021 .

Disease groups with diseases of greater importance	Autumn-winter 2016/17	Autumn-winter 2017/18	Autumn-winter 2018/19	Autumn-winter 2019/20	Autumn-winter 2020/21
Diseases of the cardiovascular system	9690	6561	4664	4887	2811
Diseases caused by hypertension	7226	4764	3140	3374	2053
Essential hypertension	7214	4743	3133	3361	2044
Conductive system disorders and cardiac arrhythmias	661	541	457	523	253
Ischemic heart disease	586	341	318	302	146
Acute myocardial infarction	134	70	52	62	40
Heart muscle disease, inflammation of the heart and heart sac, valve disease	428	292	244	228	139
Pulmonary embolism	13	7	11	8	17
Decompensated heart failure	21	4	7	4	2
Vein diseases	361	313	234	219	89
Cerebrovascular diseases	230	179	138	141	53

A stroke (cerebral infarction, bleeding)	183	109	70	70	33
Artery disease (atherosclerosis, aneurysms, emboli, thrombosis ...)	120	83	89	71	49
Diseases of the pulmonary system	16061	19481	13359	14454	9169
Diseases of the upper respiratory system	12364	15389	10921	11446	7170
Acute infections	11889	14710	10358	10840	6886
Chronic inflammation, polyps, pus..	475	679	563	606	284
Diseases of the lower respiratory system	3697	4092	2438	3008	1999
Acute bronchitis /bronchitis	1850	2122	1303	877	476
Chronic bronchitis, emphysema and obstructive pulmonary disease	547	210	204	446	59
Bronchial asthma	1063	1583	771	1078	849
Pneumonia	154	123	107	562	579

The number of people with health disorder during autumn winter period decreases from 2017-2018. the moment when gasification applied in Užice , but the data still are not good and category of air quality is still 3rd. Last two winters 2019-20, 2020-21 have decrease trend, but this data is hard to discuss because industry work with less capacity, lower number of people have been in traffic because SARS COV 19 change our way of life . Atherosclerosis, a thickening of artery walls, leading to heart attack and stroke has been attributed to approximately 75% of deaths combined air pollutants and climate change [19 B. Hennig, *Env toxicity, nutrition, and cardiovascular diseases*, 2007, 162-169]. An environmental and occupational chemical exposures have contributed to chronic heart disease. With scientific evidence supporting this fact increasing in the last few years, the necessity of a new field of study has been created termed “Environmental Cardiology” [20 Weinhold B. *Environmental cardiology: Environ Health Perspect* 2004;112(15): A880e7]. The American Heart Association have shown in a June 2004 Statement, concluding that air pollutants have great negative impact to cardiopulmonary diseases. Long-term exposure to fine particulate air pollution has been linked to increased risk of death from cardiopulmonary disease likely caused by systemic inflammation, accelerated atherosclerosis, and altered cardiac autonomic function in a large Cohort study (n = 319,000-500,000). Blood lead and cadmium, and urinary cadmium levels were associated with increased incidents of peripheral arterial diseases... Epidemiological evidence has correlated inorganic arsenic exposure with increases in carotid atherosclerosis. Arsenic exposure can result in increases in oxidant levels leading to the up-regulation of inflammatory mediating genes. Carbon Monoxide is dangerous to humans and potentially lethal because it is covalently bound to hemoglobin, formed by incomplete combustion of carbon, while carbon dioxide is formed by complete combustion of carbon, carbon monoxide combines readily with hemoglobin (Hb) to form carboxyhemoglobin (COHb), thus preventing the transfer of oxygen to tissues. The affinity of hemoglobin for CO is approximately 210 times its affinity for oxygen. The sulfur oxides from industry and heating plant tend to adhere to air particles and enter the inner respiratory tract, where they are not effectively removed. In the respiratory tract, SO₂ combines readily with water to form sulfurous acid, resulting in irritation of mucous [21 A Textbook of Modern Toxicology, W. G. Cope, R. B. Leidy, E. Hodgson *Classes of Toxicants: Chp 5 and W. G. Cope Chp 4, Exposure Classes, Toxic in Air, Water, Soil, Dom and Occ Settings*][19 B.Henning *Nutrition, Metab & Cardiovasc dis*, 17, (2007), 162-169]

Because of the long-term and widespread use of lead, it is one of the most ubiquitous of the toxic metals, that can impair renal function, interfere with the development of red blood cells, and impair the nervous system. Ingested inorganic lead is absorbed more efficiently from the GI tract of children than that of adults, and in children penetrates the blood-brain barrier. Initially, lead is distributed in the blood, liver, and kidney. The two most common routes of exposure to lead are inhalation and ingestion. It is estimated that approximately 20% of the total body burden of lead comes from inhalation. Arsenic studies have linked chronic arsenic exposure to various cancers and atherosclerosis. Inhalation exposure may result in pulmonary edema and chemical pneumonitis and cardiovascular diseases, also,

M. Miller and D.Newby from Ediburgh center for cardiovascular science published research data which state [6 M. R Miller and D.E.Newby] that diesel exhaust exposure can have detrimental effects on the cardiovascular system both: acutely and chronically. Ultrafine particles with heavy metal from diesel exhaust emissions are a major source of nanoparticles in urban environments. The PM particles, after inhalation have the capacity to induce cardiovascular substantial morbidity and

mortality. Pollutants from diesel exhaust particles exert a multitude of effects on the cardiovascular system: vascular dysfunction, increased susceptibility of the heart to ischaemic damage, and an increased tendency for thrombosis the body. Different biological pathways appears to underlie the cardiovascular actions of inhaled PM, ultrafine particles : Oxidative stress and **inflammation** remain key pathways by which inhaled PM may cause harm to the body, although these nanoparticle fractions of PM could translocate into the circulation and caused widespread effects of PM around, including myocardial infarction and stroke. Furthermore, exposure to PM has both acute (e.g. alterations in heart rate and increased blood pressure) and chronic (e.g. exacerbation of atherosclerosis) actions on the cardiovascular system. [22 Atkinson] The inflammatory parameters indicate heath disorder and correlated with all other significant parameters. The classical hypothesis is that inhaled pollutants activate inflammatory cells in the lung, leading to the release of inflammatory mediators that pass into the circulation to influence cardiovascular function. There is a convincing case to link together lung inflammation and cardiovascular disease in general. Also, markers of a systemic inflammation and oxidative stress are found in the blood after exposure to PM particles in blood humans and animal. The chemical pollutant proposed to be associated with atherosclerosis are: organic compound, arsenic (Arsenic trioxide (As_2O_3), the most prevalent in air), cadmium, suspended particles PM10, PM 2.5, sulfur dioxide, carbon disulfide, carbon monoxide, soot. Most pollutants lead to hypertension and arrhythmia. Heart damage is the most common due to damage to the endothelial barrier in blood vessels and the formation of atherosclerotic plaques, as well as stimulation of the inflammatory response. [23 A. Pulliero].

3.2. Some attempt for air pollution solutions.

Some flat filters are produced and tested with aim to be used in heating plant and industry dedusting systems. It have been worked on improving its abilities and performance in accordance with the purpose and lowering its the price.

Powders of 2 granulations were selected: 100-200 microns and 200 -300 microns, from commercial powder 316 L, austenitic non-magnetic steel and internal produced powder by atomization.

Samples have been pressed by 100 tons. Two types of edges have been tested, some correction have been done on the tools for making filters. Sintering of test flat filters samples of density 3,9 and 4,1 g/cm³, in the furnace in the atmosphere mixed gas 75% H₂ and 25% N₂ and in the furnace in the atmosphere of pure H₂. The samples were sintered to different surface and with and without "backfilling". During the sintering process under reduction atmosphere metal powder particles are joined and contact areas of the particles are enlargement, [24, M. N. Rahaman, Ceramic Processing], [25. Suk-Joong L.Kang, Sintering, Densification] Powder mass was poured in mould. The samples were dried 24h/air. After that, they were taken out of mould, taken off the crust, weight, measured their dimensions and tested its physical characteristic. Succes achieved in characteristics such as master samples based on the permeability test and pore size for densities of 3.9 and 4.1 g/cm³ (density analysis, 3.99 (3.90) g/cm³, porosity is close to the theoretically expected 49.18 (48.30%).

component. The microstructurally characterization, pore dimension have done by metallographic microscopy. The microstructures obtained from the samples prepared by standard metallographic technique were compared with those obtained in plate filter for heating plant firstly sintered with different sample size, particles, T range and different atmosphere.

Developing these filters was focus on relation between physical (relative density, pore size, shape, type of material) and mechanical properties (compression strength, area). As solution we have improved sintered filters with better permeability and lower pore dimension and multifunctional air pollutants catching, better efficiency.

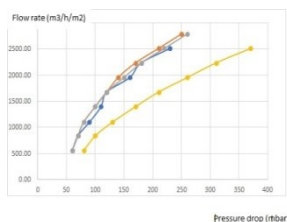


Figure 4a: Permeability material test

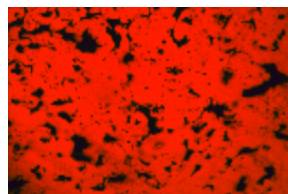


Figure 4b: Microstructure (pore structure) for 3,8 mg/cm³ density filter

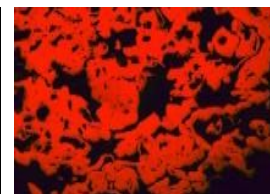


Figure 4c: Microstructure (pore structure) for 5,5 mg/cm³ density filter

Filter materials are economically available so that none of the 3 key sources of pollution would avoid their use: heating plants with fuel oil, industrial ventilation systems and car owners, truckers. These

filters should be washed and used till material is not degraded. The filter tested and captured not only PM 10 particles, PM 2.5 but also soot, gaseous and even endotoxins.

It was confirmed strong dependence of compressive strength values on density of metal and general trend of increasing compression stress by increasing density of samples for all cases.

There is significant relation between content of dispersant and density of samples for sintered powder.

4. CONCLUSION

The levels of PM10 and PM10- heavy metals (As, Cd, Ni and Pb) and soot concentrations and gaseous, and the potential adverse inhalation health outcomes, were observed in Užice and Kosjerić. Different analytical methods, including statistical have been used. The highest average PM10 and PM2.5 concentrations were obtained at the places affected by intensive traffic pollution and heating on fuel oil in Užice. Kosjerić air pollution is also caused by heating on fuel oil, intensive traffic, agriculture and industry. Arsenic, nickel, cadmium and BaP had the largest impact on the air quality and cardiopulmonary health risk. The number of primary cardiopulmonary diseases decrease in Užice, as well in Kosjerić but these two towns are still 3rd air pollution category.

Some solution are chosen in improved powder sintered filter produced for heating plant on fuel oil pollutants. Solution is in improved filtration put in heating plant, industry and cars engine.

REFERENCES

- [1.] T. Bourdrel, M-A. Bind, Y. Béjot, O. Morel, J-F, Argacha, Cardiovascular effects of air pollution, Archives of Cardiovascular Disease 110, 2017 : 634—642
- [2.] Issues in Toxicology No. 8, Environmental Cardiology Pollution and Heart Disease, Ed by A. Bhatnagar, RSC, USA, 2011
- [3.] C. Carlsten, S. Salvi, G. W.K. Wong, K.F. Chung Personal strategies to minimise effect of air pollution on respiratory health: advice for providers, patients and the public, Eur Respir J 2020; 55: 1902056, [<https://doi.org/10.1183/13993003.02056-2019>].
- [4.] A Textbook Of Modern Toxicology, 3rd edition, Ernest Hodgson Eds, A John Wiley & Sons, Inc., Publication
- [5.] Official Gazette RS, N 88/2020
- [6.] M.R, Miller, D. E. Newby Air pollution and cardiovascular disease: car sick, Cardiovascular research, pp 1-16, European Society of Cardiology, 2019
- [7.] N. H. Kamaludin, J. Jalaludin, S. B. M. Tamrin, A. Md Akim, T. Martiana, N. Widajati „Exposure to Silica, Arsenic, and Chromium (VI) in Cement Workers: A Probability Health Risk Assessment”, Aerosol and Air Quality Research, 20, 2020: 2347–2370, Special Session on Better Air Quality in Asia (III)
- [8.] G. Kovačević, V. Tomić-Spirić, J. Marinković, S. Janković, A. Ćirković, A. Milošević Djerić, M. Erić, J. Janković, Short-term effects of air pollution on exacerbations of allergic asthma in Užice region, Serbia Advances in Dermatology and Allergology 2020; XXXVII (3): 377–383 3, 2020
- [9.] T. Zhang, Y. Chen, X. Xu Health Risk Assessment of PM2.5-bound Components in Beijing, China during 2013–2015 Aerosol and Air Quality Research, 20: 1938–1949, 2020, Special Session on Better Air Quality in Asia (II)
- [10.] M. N. Todorović, M. B. Radenković, S. F. Rajšić, Lj. M. Ignjatović, Evaluation of mortality attributed to air pollution in the three most populated cities in Serbia, International Journal of Environmental Science and Technology 2019 :<https://doi.org/10.1007/s13762-019-02384-6>
- [11.] Cardiovascular diseases, “How to overcome the leading cause of death in Serbia”, Ministry of Health Serbia, 2014, [www.worldheartfederation.org/what we do /advocacy](http://www.worldheartfederation.org/what-we-do/advocacy) 25 by 25
- [12.] J. Milic, M. Curcic, Z. Brnjas, H. Carapina, J. Randjelovic, K. Krinulovic, A. Jovic „The socio-economic impact timeline in Serbia for persistent organic pollutants (POPs)”, Science of the Total Environment 688 (2019) 486–493
- [13.] M. Schaap, E.P. Weijers, D. Mooibroek, L. Nguyen, R. Hoogerbrugge, Composition and origin of Particulate Matter in the Netherlands, Netherlands Research Program on Particulate Matter Report 500099007/2010
- [14.] M. Perišić, S. Rajšić, A. Šoštarić, Z. Mijić, A. Stojić “Levels of PM10-bound species in Belgrade, Serbia: spatio-temporal distributions and related human health risk estimation, Air Qual Atmos Health, 2016]
- [15.] Menzie CA, Ziccardi LM, Lowney YW, Fairbrother A, Shock SS, Tsuji JS, Hamai D, Proctor D, Henry E, Su SH, Kierski MW, McArdle ME, Yost LJ (2009) Importance of considering the framework principles in risk assessment for metals 1. Environ Sci Tech 43(22): 8478–8482

- [16]. Report from SEPA 2020 F. Radović ed, Air Quality and Pollen Allergens In The Republic Of Serbia 2020 Years, Ministry of Environmental Protection Serbia, Belgrade 2021, ISSN 2334-8763
- [17]. Y. Lin, X. Huang, Y. Liu, D. Cao, D. Lu, Z. Feng, Q. Liu, Z. Lin, G. Jiang Anal Chem 2021 May 4;93(17):6665-6672, doi: 10.1021/acs.analchem.0c05180. Epub 2021 Apr 21.]
- [18]. P. Giorganina, P. Di Giosia, M. Petrarca, F. Lattanzi, C. A. Stamerra, C. Ferri "Climate Changes and Human Health: A Review of the Effect of Environmental Stressors on Cardiovascular Diseases Across Epidemiology and Biological Mechanisms, Current Pharmaceutical Design, 2017, 23, 3247-3261
- [19]. B. Hennig, E. Oesterling, M. Toborek, Environmental toxicity, nutrition, and cardiovascular diseases, 2007, 162-169, Environmental toxicity, nutrition, and gene interactions in the development of atherosclerosis
- [20]. Weinhold B. Environmental cardiology: getting to the heart of the matter. Environ Health Perspect 2004;112(15): A880e7]
- [21]. A Textbook of Modern Toxicology, W. G. Cope, R. B. Leidy, E. Hodgson Classes of Toxicants: Use Classes, Chapter 5 and W. G. Cope Chapter 4 , Exposure Classes, Toxicants in Air, Water, Soil, Domestic and Occupational Settings, 24 B. Henning et al Nutrition, Metabolism & Cardiovascular diseases, 17, (2007), 162-169
- [22]. Atkinson RW, Carey IM, Kent AJ, van Staa TP, Anderson HR, Cook DG. Long term exposure to outdoor air pollution and incidence of cardiovascular diseases . Epidemiology 2013;24:44-53
- [23]. A. Pulliero , R. Godschalk, M.G. Andreassi, D. Curfs, F.J. Van Schooten, A. Izzotti Environmental carcinogens and mutational pathways in atherosclerosis, International Journal of Hygiene and Environmental Health 218 (2015) 293–312
- [24] M. N. Rahaman, Ceramic Processing and Sintering, Marcell Dekker Inc , 2 nd Edition, New York
- [25]. Suk-Joong L. Kang, Sintering, Densification, Grain Growth And Microstructure, Elsevier Butterworth-Heinemann, Amsterdam 2005

