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Health risk assessment of toxic elements in sedimentable dust from landfills

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Abstract: Four monitoring campaigns of sedimentable dust were provided from two large non-sanitary landfills (Zrenjanin and Novi Sad) in Serbia during 2021. Particle size analysis by laser diffraction and inductively coupled plasma-optical emission spectrometry were carried out in order to obtain the particle size distribution (PSD) and the toxic elements (TEs) concentrations. The health risk assessment of the landfill employees was performed according to the United States Environmental Protection Agency methods based on TEs concentrations. The PSD results demonstrated that the majority of sedimentable dust samples mass were not concentrated neither within PM2.5 neither within PM10 fraction. Analysis revealed high concentration of TEs at both landfills: an extremely high concentrations of Cr and Zn in samples from Zrenjanin landfill was detected. Health risk potential of elements was as follows for both landfills: Cr > Co > Pb > Ni > Zn > Cu. According to the results, maximal hazard index for landfill employees in Zrenjanin (0.197) and Novi Sad (0.113) showed that non-cancer risk was very low. For both landfill sites, cancer risk was highest for Cr (2.75×10^{-5} for Zrenjanin and 2.02×10^{-7} for Novi Sad), though still within the defined threshold for tolerable cancer risk.

Keywords: atmospheric deposition; particle size distribution; toxic elements concentrations; hazard index; cancer risk.

INTRODUCTION

Pollution originating from landfills occupies the attention of the public, scientists, and decision-makers, since it causes environmental degradation.

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One of the main origins of pollution from landfills is the leachate that can penetrate the soil and water resources.[1] Landfill leachate contains a long list of contaminants: heavy metals, organic compounds, dissolved methane, fatty acids, sulphate, nitrate, phosphates, plastics, calcium, *etc*.[2] The dominant toxic elements (also referred as heavy metals) in leachate are cadmium, chromium, mercury, copper, zinc, lead and arsenic.[3] Likewise, landfills can cause air pollution by emitting different gases, mainly methane and carbon dioxide, that are generated due to a landfill metabolism. Dust is also of great concern when we are speaking about air pollution from landfills. Dust emission from landfills is the result of surface material resuspension related to waste transportation by heavy trucks through the landfill, waste deposition, and cover material handling.[4] Since this dust represents the soil particles from contaminated landfill areas, its composition could be complex, very often containing toxic elements. In addition, commonly, accidentally occurring fires, especially at unsanitary landfills, are sources of other potentially dangerous gases and particles of different sizes. The chemical composition of gases and particles emitted into the air during fires depends on the waste composition.[5]

Although the landfill impact on soil and groundwater has been studied intensively,[6,7] the study of atmospheric pollution from landfills has been less represented due to the complexity of such research. Atmospheric deposition processes from landfills are especially less studied, while publications concerning sedimentable dust in municipal solid waste landfills are very rare.[8] Air contamination by particles, containing toxic elements and emitted from landfills is of great concern with the respect to human health risk assessment since it could be transported to large distances.[9]

The atmospheric fate of particles is influenced by different factors like terrain configuration, meteorological parameters, properties and size of particles, *etc*. Since larger particles (>30 μm) seem to travel shorter distances, it is more likely that they will influence the environment close to the source.[10] Those coarser particles are sedimentable dust that are subject of the process of dry or wet deposition. By deposition from air, particles, and hence all their constituents (organic and organic compounds, toxic elements, *etc*.), enter the aquatic and terrestrial ecosystems, becoming available for living organisms through the food chain.[11]

Hence, humans are influenced by the particles through food, water, skin and respiratory system. The behaviour of particles after entering the human body, as well as the response that it causes, depends on the numerous parameters. In addition to the physiological parameters of the recipient human body (weight, age, *etc*.), the most important are chemical composition, size, and shape of the particles.

In recent studies, the monitoring of particles and its composition analysis provided near the landfills indicate that concentrations of cadmium, chromium, copper, manganese, nickel, and lead exceeded the USEPA standard permissible

limit.[12] Likewise, the analysis of suspended dust from a landfill near Mexico City indicated most abundant elements were silicon and aluminium.[13] In ambient air samples at different distances from the landfill, it was revealed that the highest concentrations of metals (Cd, Cu, Ni, Cr and Zn) were recorded at the sampling sites near the landfills.[14]

A studies on the exposure of landfill employees to dust reveals a higher concentration of arsenite in lung, muscle, and liver, lead in bone and blood and cadmium in kidney and liver.[4,15]

Developing countries, like the Republic of Serbia, face environmental degradation problems because of waste disposal at uncontrolled and non-sanitary landfills without prior selection standard.[16] In Serbia, there are only 12 sanitary landfills and more than 120 non-sanitary landfills. Number of uncontrolled landfills is higher than 3,500. Only 19 % of generated waste is deposited on sanitary landfills. Concerning the location, 40 % of landfills are located near settlements. Also, a huge number of accidentally occurring fires at the unsanitary landfills in Serbia are recorded in past few years, reaching the highest number in 2021.[17]

In this study, four monitoring campaigns of sedimentable dust during the summer period of 2021 at two large landfills in Serbia were provided. The aim of this study was health risk assessment of the employees at the landfills according to quantitative analysis of toxic elements (As, Cd, Co, Cr, Cu, Ni and Pb) and particle size distribution (PSD) for the first time in Serbia.

EXPERIMENTAL

Study area

Details about the study area are given in Supplementary material to this paper.

Sampling and exposure time

The dust sampling method was performed conforming to recommendations of the Environmental Protection Agency of United States[10] in accordance with the German standard VDI.[18] The Bergerhoff Gauge dust monitoring instrument was used on both locations to measure sedimentable dust. Bergerhoff method is a long-term method, where measurements are usually carried out over a 30-day period. According to the US methods, exposition time should be 30 + 2 days in a minimum of 3 campaigns and at least 2 campaigns should be in the period of May and September.

Sampling was performed during summer and early autumn of 2021, in four campaigns that represent four replicates (following the above-described method that prescribes a minimum of 3 campaigns). The beginning of sample collection was the middle of June, and the end was the middle of October 2021. Each individual campaign had a number of exposed days of 30 or 31. After a sampling period, the collected liquid samples were evaporated, and the solid residue was analysed.

Particle size distribution

Particle size distribution was determined using a Malvern Mastersizer 2000 particle size analyser. Hydro2000 Micro Precision, the dispersion unit for small amounts of a material, was used for measuring. The Malvern Mastersizer 2000 records the light pattern scattered from a

field of particles at different angles. Recorded intensity at a certain angle is the sum of the intensity of light scattered from the surface of particles and the intensity of the secondary scattered light, due to refraction when passing through the particle, which is important for the particles smaller than 50 μm. The device then uses an analytical procedure to determine the particle size distribution that creates the patterns. The composition of the examined samples is inhomogeneous, while the refractive index of dispersed material was impossible to determine precisely, so we used literature data. According to the literature data[19] the real part of the air dust refractive index is in the range 1.48–1.55. We used the value of 1.5. The wavelengths of light used during measurement were 632.8 and 740 nm. Samples were analysed in three replicates. The measurement of the samples was carried out in the dynamic mode. Measurement parameters were: pump speed, 2500 rpm; ultrasonic, off. The results were recorded as the particle volume percentage in 100 discrete size ranges between 0.02 and 200 μm.

Determination of toxic elements concentration in collected samples

All laboratory analyses were performed at the Laboratory for Soil and Agroecology of the Institute of Field and Vegetable Crops, accredited according to the standard ISO/IEC 17025:2017.[20] The samples were analysed for concentrations of As, Cd, Co, Cr, Cu, Ni, Pb and Zn after microwave digesting the samples in concentrated HNO_3 and H_2O_2 (0.3 g in 20 ml; 5:1 HNO_3/H_2O_2) by stepwise heating up to 180 °C using a Milestone Vario EL III for 55 min.

The concentration of the elements in prepared samples was determined by ICP-OES (Vista Pro-Axial, Varian) in accordance with the US EPA method 200.7:2001[21] under the following operating conditions: RF power, 1.10 kW; plasma and auxiliary gas flow rate, 15.0 and 1.50 L min^{-1}, respectively; nebulizer flow, 1.20 L min^{-1}; number of replicates, 3.

Quality assurance and quality control (QA/QC) assessments were conducted using the certified reference materials IRMM ERM-CC141 (Loam soil). The obtained limit of detection (*LOD*) from 0.03 (Cu) to 0.09 (Ni) mg L^{-1} and method detection limit (*MDL*) of 1.0 mg kg^{-1} for all elements, provided adequate sensitivity for the analysis. In this study, the percentage of recovery, defined as the ratio of measured concentrations and certified values of used reference materials, ranged from 86 to 111 %, which provided adequate analytical accuracy and precision.

Health risk assessment

Health risk assessment in humans (landfill employees) was determined according to the Exposure Factors Handbook of the Environmental Protection Agency of United States.[22] Firstly, an average daily doses (*ADD* in mg kg^{-1} day^{-1}) through three dominant exposure pathways, including ingestion (*ADD*ing), inhalation (*ADD*inh) and dermal contact (*ADD*derm), were calculated in the following manner:[23]

$$ADD\text{ing} = \frac{C \times R_{\text{ing}} \times CF \times EF \times ED}{BW \times AT} \quad (1)$$

$$ADD\text{inh} = \frac{C \times R_{\text{inh}} \times EF \times ED}{PEF \times BW \times AT} \quad (2)$$

$$ADD\text{derm} = \frac{C \times SA \times CF \times SL \times ABS \times EF \times ED}{BW \times AT} \quad (3)$$

The input parameters for the calculations of employee exposure were: C – toxic element concentration (mg kg^{-1}), R_{ing} – ingestion rate (100 mg day^{-1}), R_{inh} – inhalation rate (20 m^3 day^{-1}), EF – the exposure frequency (74 day $year^{-1}$), ED – exposure duration (20 years), BW – body weight (70 kg), AT – averaging time (365×ED days), CF – conversion factor (10^{-6} kg mg^{-1}),

PEF – particle emission factor (1.32×10^{-9} m^3 kg^{-1}), *SA* – exposed skin area (5000 cm^2), *SL* – skin adherence factor (1 mg cm^{-2} day^{-1}), *ABS* – dermal absorption factor (0.001).[24,25]

The non-carcinogenic health risk by toxic elements considered was characterized by the hazard quotient (*HQ*), representing the probability of suffering from an adverse effect. The *HQ*i is defined as the ratio of the average daily dose to its reference dose *RfD*i for the same exposure pathway:[23]

$$HQi = \frac{ADDi}{RfDi} \tag{4}$$

*RfD*i values for toxic elements considered are provided by US EPA.[25]

The sum of hazard quotient for ingestion (*HQ*ing), inhalation (*HQ*inh) and dermal esposure (*HQ*derm), named hazard index (*HI*):

$$HI = Hqing + HQinh + HQderm \tag{5}$$

has been used to assess the overall potential for noncarcinogenic health effects caused by toxic elements. Hazard index value lower or equal to unity ($HI \leq 1$) implies the absence of health risk. In opposite, hazard index greater than unity ($HI > 1$) indicates a concern for adverse effects.

Cancer risk (*CR*) is assessed by multiplying average daily dose of exposure with cancer slope factors *via* inhalation *SF*inh:

$$CR = ADD\times SFinh \tag{6}$$

Values of *SF*inh are provided by US EPA[25] per individual element. Cancer risk values below 1×10^{-6} present negligible risk, while the ones in the range of 10^{-6}–10^{-4} indicate tolerable cancer risk.[24]

RESULTS AND DISCUSSION

Particle size

The particle size distribution (PSD) allowed an estimation of the degree of dispersion of particles over the considered dimensional range. Size distribution of particles differs drastically according to whether it is calculated in terms of particle number, surface area or volume/mass.[26] Fig. 1 represents the average volume-based particle size distribution for samples collected at both landfill sites. Frequency curves are exhibited in Fig. 1. The average particle size distributions were obtained by averaging data for al campaigns at each landfill location. Individual PSD are not presented due to the fact that volume-based PSD for a certain location alters very slightly. The averaged results demonstrate that the particles whose equivalent sphere diameter was between 20 and 30 μm make up the majority of sample mass at both landfill locations. Sample from Zrenjanin (ZR) landfill showed a bimodal distribution with a significant portion of particles larger than 100 μm.

The average percentage of PM2.5 and PM10 fractions, obtained from volume-based particle size distribution cumulative curves are 4.05 and 23.82 for ZR landfill and 4.91 and 27.59 for Novi Sad (NS) landfill, respectively. The obtained results are similar on both landfill locations. It demonstrates that, despite the stochastic emission of particles on investigated landfill sites, the percentage of the mentioned fractions in sedimentable dust is very similar.

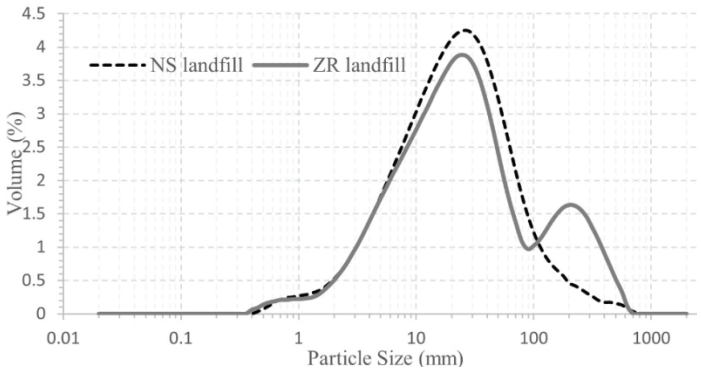

Fig. 1. Average volume-based particle size distribution on landfill sites

Average PM2.5/PM10 ratio in investigated samples was 0.178 and 0.17 for NS and ZR landfill, respectively. That is more than twice lower than found for total suspended particulate matter collected in an industrial and urban areas in Greece, where average PM2.5/PM10 ratio was within range 0.38–0.59.[27] It should be mentioned that sedimentable particles generally contain lower percentage of fine fractions that could penetrate into lungs in comparison with total suspended particles, which can be confirmed by comparing the results of this study with the results related to total suspended particles reported in the literature.[27]

Toxic element concentration

In this study, the concentration of As and Cd was not detected in accordance with set method detection limits of 1 mg kg^{-1}, therefore, the concentration of these two elements was not processed. Toxic elements concentration (Co, Cr, Cu, Ni, Pb, Zn in mg kg^{-1}) in sedimentable dust at two landfills in ZR and NS, and the literature data for landfills and urban areas around the world, were summarized in Table I.

The content of analysed toxic elements varied over a wide range concentration (Table I). Average, maximum and minimum concentrations at both landfills were of the same order of magnitude for the majority of analysed toxic elements. Concentration of Cr and Zn in samples collected at the ZR landfill had the widest range. An inconsistency was established for Cr whose maximum and average concentrations were approximately two orders of magnitude higher at ZR landfill (Table I). Hence, the highest concentrations among all investigated toxic elements were detected for Cr (14910.0 mg kg^{-1}) at ZR landfill during the campaign 4. Although Cr occurs in air through soil erosion, most come from anthropogenic sources like various industrial activities and more importantly waste burning.[32] Likewise, high concentration of Zn (1,606.0 mg kg^{-1}) was detected during the campaign 1 at the landfill in ZR. This could be explained by the fact that metallic Zn is commonly used for coating of other metals to prevent

corrosion, as well as to make batteries, thus landfills can significantly contribute to its concentration in a particulate matter.[33]

TABLE I. Toxic elements concentration (mg kg^{-1}) in atmospheric deposition samples from ZR and NS landfills and literature data

Element	Data	Sample						
		Sediment-able dust from ZR landfill	Sediment-able dust from NS landfill	Soil from landfill[28]	Fugitive dust from landfill (PM10)[13]	Urban dust in Novi Sad[29]	Urban dust in Beijing[30]	Road dust[31]
Co	Aver.	17.3	26.8	–	–	6.01	10.6	
	Max	44.2	73.9	20.41		–		
	Min	3.3	1.8	2.08		–		
Cr	Aver.	3772.3	60.6	–	70	36.1	86	80.7
	Max	14910.0	109.5	108.66		–		
	Min	4.1	16.2	13.96		–		
Cu	Aver.	50.5	99.3	–	60	50.1	138.4	43.9
	Max	90.5	130.7	470.44				
	Min	22.4	65.4	16.51				
Ni	Aver.	31.0	10.0	–	30	21	45.2	
	Max	77.9	17.7	53.74				
	Min	5.7	6.0	1.59				
Pb	Aver.	11.1	15.8	–	50	66.5	167.9	66.6
	Max	23.3	22.6	72.76				
	Min	3.0	9.6	20.97				
Zn	Aver.	464.2	263.4	–	130		722.7	215
	Max	1606.0	395.8	968.12				
	Min	54.9	186.1	21.41				

In comparison to data on toxic elements contamination in the samples from landfill soil published by Thongyuan *et al.*[28] and in fugitive dust from landfill in Mexico City,[13] it was found that average, maximum and minimum concentrations of Co, Cu, Ni, Pb and Zn are of the same order of magnitude. On contrary, average and maximum Cr concentrations at Zrenjanin landfill were two orders of magnitude higher than reported by Vega *et al.*[13] and Thongyuan *et al.*,[28] respectively (Table I).

Additionally, if we compare results from this research to the results obtained from urban dust and soil sampled at the area near studied landfills,[29] toxic elements concentrations in sedimentable dust collected at both landfill sites were significantly higher in general (Table I). This is especially noticeable for Zn and Cr concentrations at samples from ZR landfill sampling site as well as for Cr, Cu and Zn in samples from NS landfill sampling site.

All previously mentioned indicates that the examined landfills significantly contribute to the content of Cr, Zn, Cu and Co in sedimentable dust, though the

same cannot be stated for Pb and Ni. The major sources of Pb in air could be vehicles and different industrial sources.[34] Concentration of lead in urban street areas is generally high and the pollution is still present, even though leaded gasoline has not been used for a long time. This is the reason for the higher concentration of Pb in the street dust than in our samples. Nickel is one of the most common elements on Earth. Its sources in air dust could be local soil,[35] coal and petroleum combustion, as well as electronic waste.[36] Regarding nickel, it is symptomatic that its concentrations in investigated samples were not higher than its average content in the soil of Vojvodina. For this reason, nickel in investigated samples most probably originated from natural sources.

The reason for high concentration of certain elements, especially Cr and Zn, could not be explained with the high confidence, since the samples were collected over the period of one month, thus representing the average monthly concentration. However, it could be based on the fact that sampling campaigns were organized during the summer months when the landfill managing activities could be more intensive and when the landfill fires could occur more frequently because of dry periods with high temperatures. During 2021, when the monitoring campaigns were provided, more than 1715 landfill fires in Serbia were recorded. That is the highest number in the period from 2016–2021.[17] Fires could be one of the main reasons why landfills contributed to the content of Cr, Zn, Cu and Co in our samples.

Health risk assessment

Health risk assessment of landfill employees was based on TEs concentration obtained by dust analysis. An average daily doses (*ADD* in mg kg^{-1} day^{-1}), the non-carcinogenic health risk by toxic elements by the hazard quotient (*HQ*), hazard index (*HI*) and cancer risk (*CR*) were assessed.

According to the results, *ADD* of employees at the landfill in ZR (Table II) was the highest for Cr (4.54×10^{-4} mg kg^{-1} day^{-1}). The lowest total *ADD* was obtained for Pb (7.09×10^{-7} mg kg^{-1} day^{-1}). Most of the toxic elements (Co, Cu and Ni) showed the same magnitude of total maximal exposure amount (10^{-6} mg kg^{-1} day^{-1}) that is an order of magnitude lower than found for Zn (10^{-5} mg kg^{-1} day^{-1}) and two orders of magnitude lower than found for Cr (10^{-4} mg kg^{-1} day^{-1}).

At the landfill in NS (Table III), maximal total daily exposure was the highest for Zn (1.21×10^{-5} mg kg^{-1} day^{-1}) and the lowest for Ni (5.38×10^{-7} mg kg^{-1} day^{-1}). Toxic elements Co, Cr and Cu demonstrated the same magnitude of total maximal exposure amount (10^{-6} mg kg^{-1} day^{-1}) which is still lower in comparison to the magnitude of total exposure amount of Zn (10^{-5} mg kg^{-1} day^{-1}).

Results of the *HQ* values of different exposure pathways and *HI* for both landfills are presented in Tables IV and V.

TABLE II. Average daily doses (*ADD* in mg kg^{-1} day^{-1}) for employees at ZR landfill

Element	Data	Data type			
		*ADD*inh	*ADD*ing	*ADD*derm	Total exposure
Co	Aver.	7.59×10^{-10}	5.01×10^{-7}	2.50×10^{-8}	5.27×10^{-7}
	Max	1.94×10^{-9}	1.28×10^{-6}	6.40×10^{-8}	1.35×10^{-6}
	Min	1.45×10^{-10}	9.56×10^{-8}	4.78×10^{-9}	1.01×10^{-7}
Cr	Aver.	1.66×10^{-7}	1.09×10^{-4}	5.46×10^{-6}	1.15×10^{-4}
	Max	6.54×10^{-7}	4.32×10^{-4}	2.16×10^{-5}	4.54×10^{-4}
	Min	1.80×10^{-10}	1.19×10^{-7}	5.95×10^{-9}	1.25×10^{-7}
Cu	Aver.	2.22×10^{-9}	1.46×10^{-6}	7.32×10^{-8}	1.54×10^{-6}
	Max	3.97×10^{-9}	2.62×10^{-6}	1.31×10^{-7}	2.76×10^{-6}
	Min	9.84×10^{-10}	6.49×10^{-7}	3.25×10^{-8}	6.83×10^{-7}
Ni	Aver.	1.36×10^{-9}	8.97×10^{-7}	4.48×10^{-8}	9.43×10^{-7}
	Max	3.42×10^{-9}	2.26×10^{-6}	1.13×10^{-7}	2.37×10^{-6}
	Min	2.52×10^{-10}	1.66×10^{-7}	8.31×10^{-9}	1.75×10^{-7}
Pb	Aver.	4.87×10^{-10}	3.21×10^{-7}	1.61×10^{-8}	3.38×10^{-7}
	Max	1.02×10^{-9}	6.74×10^{-7}	3.37×10^{-8}	7.09×10^{-7}
	Min	1.32×10^{-10}	8.70×10^{-8}	4.35×10^{-9}	9.15×10^{-8}
Zn	Aver.	2.04×10^{-8}	1.34×10^{-5}	6.72×10^{-7}	1.41×10^{-5}
	Max	7.05×10^{-8}	4.65×10^{-5}	2.33×10^{-6}	4.89×10^{-5}
	Min	2.41×10^{-9}	1.59×10^{-6}	7.94×10^{-8}	1.67×10^{-6}

TABLE III. Average Daily Doses (ADD in mg kg^{-1} day^{-1}) for employees at NS landfill

Element	Data	Data type			
		*ADD*inh	*ADD*ing	*ADD*derm	Total exposure
Co	Aver.	1.18×10^{-9}	7.77×10^{-7}	3.89×10^{-8}	8.17×10^{-7}
	Max	3.24×10^{-9}	2.14×10^{-6}	1.07×10^{-7}	2.25×10^{-6}
	Min	8.11×10^{-11}	5.35×10^{-8}	2.67×10^{-9}	5.63×10^{-8}
Cr	Aver.	2.66×10^{-9}	1.75×10^{-6}	8.77×10^{-8}	1.85×10^{-6}
	Max	4.81×10^{-9}	3.17×10^{-6}	1.59×10^{-7}	3.33×10^{-6}
	Min	7.10×10^{-10}	4.69×10^{-7}	2.34×10^{-8}	4.93×10^{-7}
Cu	Aver.	4.36×10^{-9}	2.88×10^{-6}	1.44×10^{-7}	3.03×10^{-6}
	Max	5.74×10^{-9}	3.79×10^{-6}	1.89×10^{-7}	3.98×10^{-6}
	Min	2.87×10^{-9}	1.90×10^{-6}	9.48×10^{-8}	1.99×10^{-6}
Ni	Aver.	4.37×10^{-10}	2.88×10^{-7}	1.44×10^{-8}	3.03×10^{-7}
	Max	7.76×10^{-10}	5.12×10^{-7}	2.56×10^{-8}	5.38×10^{-7}
	Min	2.64×10^{-10}	1.74×10^{-7}	8.72×10^{-9}	1.83×10^{-7}
Pb	Aver.	6.93×10^{-10}	4.57×10^{-7}	2.29×10^{-8}	4.81×10^{-7}
	Max	9.92×10^{-10}	6.55×10^{-7}	3.27×10^{-8}	6.88×10^{-7}
	Min	4.23×10^{-10}	2.79×10^{-7}	1.40×10^{-8}	2.94×10^{-7}
Zn	Aver.	1.16×10^{-8}	7.63×10^{-6}	3.81×10^{-7}	8.02×10^{-6}
	Max	1.74×10^{-8}	1.15×10^{-5}	5.73×10^{-7}	1.21×10^{-5}
	Min	8.17×10^{-9}	5.39×10^{-6}	2.69×10^{-7}	5.67×10^{-6}

According to the results, total (maximal) *HI* for landfill employees in ZR (0.197) and NS(0.113) demonstrated low non-cancer risk. Also, it could be noted that ingestion is the most possible pathway. Hence, in comparison to other path-

ways of exposure, ingestion exposure index for employees at NSlandfill has more than 98 % share.

TABLE IV. Hazard quotients (*HQ*) and hazard indexes (*HI*) for ZR landfill

Element	Data	Data type			
		*HQ*inh	*HQ*ing	*HQ*derm	*HI*
Co	Aver.	1.33×10^{-4}	2.50×10^{-5}	1.57×10^{-6}	1.60×10^{-4}
	Max	3.40×10^{-4}	6.40×10^{-5}	4.00×10^{-6}	4.08×10^{-4}
	Min	2.54×10^{-5}	4.78×10^{-6}	2.99×10^{-7}	3.04×10^{-5}
Cr	Aver.	5.79×10^{-3}	2.19×10^{-2}	2.19×10^{-2}	4.95×10^{-2}
	Max	2.29×10^{-2}	8.64×10^{-2}	8.64×10^{-2}	1.96×10^{-1}
	Min	6.30×10^{-6}	2.38×10^{-5}	2.38×10^{-5}	5.39×10^{-5}
Cu	Aver.	5.28×10^{-8}	3.96×10^{-5}	3.85×10^{-5}	7.81×10^{-5}
	Max	9.46×10^{-8}	7.08×10^{-5}	6.90×10^{-5}	1.40×10^{-4}
	Min	2.34×10^{-8}	1.75×10^{-5}	1.71×10^{-5}	3.47×10^{-5}
Ni	Aver.	5.23×10^{-8}	4.48×10^{-5}	4.48×10^{-5}	8.97×10^{-5}
	Max	1.32×10^{-7}	1.13×10^{-4}	1.13×10^{-4}	2.26×10^{-4}
	Min	9.69×10^{-9}	8.31×10^{-6}	8.31×10^{-6}	1.66×10^{-5}
Pb	Aver.	1.38×10^{-7}	9.18×10^{-5}	3.09×10^{-5}	1.23×10^{-4}
	Max	2.90×10^{-7}	1.93×10^{-4}	6.48×10^{-5}	2.58×10^{-4}
	Min	3.74×10^{-8}	2.49×10^{-5}	8.36×10^{-6}	3.33×10^{-5}
Zn	Aver.	6.79×10^{-8}	4.48×10^{-5}	1.12×10^{-5}	5.61×10^{-5}
	Max	2.35×10^{-7}	1.55×10^{-4}	3.88×10^{-5}	1.94×10^{-4}
	Min	8.02×10^{-9}	5.30×10^{-6}	1.32×10^{-6}	6.63×10^{-6}
Total	Aver.	5.92×10^{-3}	2.21×10^{-2}	2.20×10^{-2}	5.00×10^{-2}
	Max	2.32×10^{-2}	8.70×10^{-2}	8.67×10^{-2}	1.97×10^{-1}
	Min	3.17×10^{-5}	8.46×10^{-5}	5.92×10^{-5}	1.76×10^{-4}

Health risk potential of elements for ZR and NSis as follows: Cr > Co > Pb > Ni > Zn > Cu.

Results for cancer risk for Co, Cr and Ni are presented in Table VI. Results revealed that the highest cancer risk were calculated at the ZR landfill. At this site, the highest *CR* was calculated for Cr (of 2.75×10^{-5}). At the landfill of NS, the highest *CR* was calculated also for Cr (2.02×10^{-7}). However, calculated *CR* for selected toxic elements were in the range of defined threshold of 10^{-6}–10^{-4} that indicates tolerable cancer risk. In the present study, the health risk assessment was completed concerning toxic elements concentration within sedimentable dust at landfills. However, it is known that toxic elements are preferentially bound to fine dust particle size fractions[37] while sedimentable dust consists of bigger particles that tend to sediment by gravity in general. This was also indicative when our results were compared with total suspended particulate matter collected in an industrial and urban areas;[27] average PM2.5/PM10 ratio at landfills was significantly lower indicating lower PM2.5 and higher PM10 content within

investigated samples. Therefore, concerning total suspended particulate matter, health risk would probably be higher than reported here.

TABLE V. Hazard quotients (*HQ*) and hazard indexes (*HI*) for NS landfill

Element	Data	Data type			
		*HQ*inh	*HQ*ing	*HQ*derm	*HI*
Co	Aver.	2.06×10^{-4}	3.89×10^{-5}	2.43×10^{-6}	2.48×10^{-4}
	Max	5.68×10^{-4}	1.07×10^{-4}	6.69×10^{-6}	6.82×10^{-4}
	Min	1.42×10^{-5}	2.67×10^{-6}	1.67×10^{-7}	1.70×10^{-5}
Cr	Aver.	9.30×10^{-5}	6.14×10^{-2}	3.51×10^{-4}	6.18×10^{-2}
	Max	1.68×10^{-4}	1.11×10^{-1}	6.34×10^{-4}	1.12×10^{-1}
	Min	2.48×10^{-5}	1.64×10^{-2}	9.38×10^{-5}	1.65×10^{-2}
Cu	Aver.	1.04×10^{-7}	7.78×10^{-5}	7.57×10^{-5}	1.54×10^{-4}
	Max	1.37×10^{-7}	1.02×10^{-4}	9.96×10^{-5}	2.02×10^{-4}
	Min	6.84×10^{-8}	5.12×10^{-5}	4.99×10^{-5}	1.01×10^{-4}
Ni	Aver.	1.68×10^{-8}	1.44×10^{-5}	1.44×10^{-5}	2.88×10^{-5}
	Max	2.98×10^{-8}	2.56×10^{-5}	2.56×10^{-5}	5.12×10^{-5}
	Min	1.02×10^{-8}	8.72×10^{-6}	8.72×10^{-6}	1.74×10^{-5}
Pb	Aver.	1.97×10^{-7}	1.31×10^{-4}	4.40×10^{-5}	1.75×10^{-4}
	Max	2.82×10^{-7}	1.87×10^{-4}	6.29×10^{-5}	2.50×10^{-4}
	Min	1.20×10^{-7}	7.98×10^{-5}	2.68×10^{-5}	1.07×10^{-4}
Zn	Aver.	3.85×10^{-8}	2.54×10^{-5}	6.36×10^{-6}	3.18×10^{-5}
	Max	5.79×10^{-8}	3.82×10^{-5}	9.55×10^{-6}	4.78×10^{-5}
	Min	2.72×10^{-8}	1.80×10^{-5}	4.49×10^{-6}	2.25×10^{-5}
Total	Aver.	3.00×10^{-4}	6.16×10^{-2}	4.94×10^{-4}	6.24×10^{-2}
	Max	7.36×10^{-4}	1.11×10^{-1}	8.39×10^{-4}	1.13×10^{-1}
	Min	3.93×10^{-5}	1.66×10^{-2}	1.84×10^{-4}	1.68×10^{-2}

TABLE VI. Cancer risk for Co, Cr and Ni for ZR and NS landfills

Metal	ZR landfill	NS landfill
Co	1.90×10^{-8}	3.18×10^{-8}
Cr	2.75×10^{-5}	2.02×10^{-7}
Ni	2.87×10^{-9}	6.52×10^{-10}

CONCLUSION

In this research, a sedimentable dust samples were collected at two large landfills in Serbia during the 4 summer monitoring campaigns, in order to analyse particle size distribution and toxic elements content (As, Cd, Co, Cr, Cu, Ni, Pb, Zn), as well to assess health risk for landfill employees. Since the concentration of As and Cd were not detected in accordance with the set method, the detection limits for these two elements were not taken in consideration.

The results of particle size distribution analysis demonstrate that the particles whose equivalent sphere diameter was between 20–30 μm make up the majority of sample mass at both landfill locations, though the sample from Zrenjanin landfill showed a bimodal distribution with a significant portion of particles larger

than 100 μm. Average PM2.5/PM10 ratio in investigated samples was 0.178 and 0.17 for Novi Sad and Zrenjanin landfills, respectively.

Analysis revealed high concentration of toxic elements in samples at both landfills. Additionally, an extremely high concentration of Cr and Zn in samples from the landfill in Zrenjanin was detected. The high concentration of certain elements (Cr, Zn Cu and Co) was attributed to the frequently occurring landfill fires.

Concerning health risk assessment, we have found that *HI* were in order of magnitude E-01 that indicates that there is low non-cancer risk for the employees at both landfill sites. In general, the highest *CR* was calculated for the employees at Zrenjanin landfill. For both landfill sites, *CR* is highest for Cr, but still within the defined threshold for tolerable cancer risk. If the risk evaluation for total suspended particles is conducted, we assume that the health risk would probably be higher than reported here due to the fact that total suspended particles, in comparison with sedimentable particles, generally contain higher percentage of fine fraction that could penetrate to lungs and that is generally enriched with toxic elements.

Since the study proved the influence of landfill to enrichment dust by toxic elements, especially Cr and Zn, future research is necessary in order to measure toxic elements concentrations in sedimentable, PM2.5, PM10 and total suspended dust during organized campaigns at city landfills.

SUPPLEMENTARY MATERIAL

Additional data and information are available electronically at the pages of journal website: https://www.shd-pub.org.rs/index.php/JSCS/article/view/12335, or from the corresponding author on request.

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ИЗВОД

ПРОЦЕНА ЗДРАВСТВЕНОГ РИЗИКА ОД ТОКСИЧНИХ ЕЛЕМЕНАТА У ТАЛОЖНОЈ ПРАШИНИ СА ДЕПОНИЈА

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На две велике несанитарне депоније у Србији (Зрењанин и Нови Сад) спроведене су четири кампање мониторинга таложне прашине. Анализа расподеле величине честица урађена је ласерском дифракцијом, док је концентрација токсичних елемената (ТЕ) одређена помоћу оптичке емисионе спектрометрије са индуктивно спрегнутом плазмом. Процена ризика по здравље запослених на депонијама спроведена је на основу концентрација ТЕ према методама Агенције за заштиту животне средине Сједињених Америчких Држава. Резултати расподеле величине честица су показали да највећи део

узорака таложне прашине не припада ни PM2,5 ни PM10 фракцији. Анализа је показала високу концентрацију ТЕ на обе депоније: установљена је изузетно висока концентрација Cr и Zn у узорцима са зрењанинске депоније. Потенцијал анализираних токсичних елемената у погледу ризика по здравље за обе депоније је следећи: Cr > Co > Pb > Ni > Zn > Cu. Према резултатима, укупни (максимални) индекс опасности за запослене на депонијама у Зрењанину (0,197) и Новом Саду (0,113) показао је да је ризик од канцера веома низак. За обе депоније, ризик од канцера је био највећи за Cr ($2{,}75\times10^{-5}$ за Зрењанин и $2{,}02\times10^{-7}$ за Нови Сад), чија је вредност такође у оквиру дефинисаног прага толеранције за ризик од канцера.

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