

**IS KRAGUJEVAC CITY STILL A “HOT SPOT” AREA, TWENTY YEARS AFTER  
THE BOMBING?**

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## **ABSTRACT**

After NATO bombing of Serbia in 1999, UNEP has identified Kragujevac as one of the four heavily polluted environmental “hot spots”. Damaging of industrial and military targets caused the release of substantial amounts of hazardous chemical substances into the environment. This study was conducted in order to assess the exposure of residents of Kragujevac city to persistent soil pollutants, twenty years after NATO air campaign. The paper reports the results of measuring radionuclides, polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs) and heavy metals (As, Cd, Co, Cr, Cu, Mn, Ni, Pb, Zn, and Hg) in soil samples collected from two depths (0-15 cm and 15-30 cm) at 30 locations along the riverbank of the Lepenica River. The average specific activities of  $^{226}\text{Ra}$ ,  $^{232}\text{Th}$ ,  $^{40}\text{K}$  and  $^{137}\text{Cs}$  were comparable to average worldwide values; excess lifetime cancer risk (ELCR) from natural radionuclides ranged from  $1.1 \cdot 10^{-4}$  to  $3.3 \cdot 10^{-4}$ . The measured concentrations of As, Co, Cr, Cu, and Ni exceeded the limit values in most of the samples. Non-carcinogenic risk (hazard quotient and hazard index) and carcinogenic risk from heavy metals were assessed. Total hazard index was 0.257 and 2.16 for adults and children, respectively. Sum of measured PAHs ranged from 110 to 1026  $\mu\text{g kg}^{-1}$ . Sum of PCBs exceeded the limit value of 20  $\mu\text{g kg}^{-1}$  in all samples (it ranged from 48.8 to 196.8  $\mu\text{g kg}^{-1}$ ), but it was still below the remediation level. The differences between two layers with respect to all measured variables were not statistically significant.

**Keywords:** soil; radioactivity; PAHs; PCBs; heavy metals

## 1. INTRODUCTION

Damaging of military and industrial targets in the former Yugoslavia during NATO air campaign in the spring of 1999 caused the release of substantial amounts of hazardous chemical substances into the environment. A large number of facilities such as petrochemical, chemical, and plastic plants, fuel storage tanks, refineries, automobile plants, machine industry, food-processing plants, heating plants, electric power transformers, water-treatment plants, etc. were destroyed (Vukmirovic et al., 2001). According to UNEP/UNCHS Balkans Task Force report from 1999, Kragujevac was identified as one of the four heavily polluted environmental “hot spots” that posed a high risk to the health of the local population (UNEP/UNCHS, 1999). The Lepanica River (a tributary of the Morava River which flows into the Danube) runs through industrial areas located in the city center and it collects both, the industrial and municipal wastewaters. Besides, the river flows in the close vicinity of automobile and arms factories (former Zastava complex) which were targeted twice during NATO air strikes in 1999. The bombing caused heavy damage to the power station, car assembly line, paint hall, truck plant, etc. Damaging of transformers containing PCB oil caused leaking of several tones of PCBs into the Morava River (UNEP, 2004). According to APOPSMAL (2005), 3000 L of Pyralene was spilled in Zastava factory, causing an ecological disaster. Soil, air and water were extensively contaminated by persistent organic pollutants and heavy metals. Implementation of the UNEP Clean-up Programme in the Zastava complex took place by 2004.

Human activities cause environmental pollution with heavy metals and persistent organic pollutants (POPs) such as polycyclic aromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs). PAHs are a group of stable organic substances that can occur naturally, but they

are predominantly produced during the processes of burning fossil fuels and other organic matters (Simoneit, 1977; Wakeham et al., 1980a,b). They have been identified as carcinogenic, mutagenic and teratogenic agents (Hoffman and Wynder, 1971; Grimmer, 1983; Perera, 1997). PCBs are a family of highly toxic compounds consisting of two benzene rings in which chlorine replaces two or more hydrogen atoms. They have low water solubility and volatility and they are resistant to biotic and abiotic degradation (Valera et al., 2013). Organohalogenes can enter human body through direct skin contact, air breathing, water drinking, and through food chains. These chemicals can be accumulated in tissues causing reproductive, neurotoxic, immunotoxic, endocrine, and behavioral abnormalities, as well as carcinogenic effects (Kodavanti et al., 2008). The use and manufacture of PCBs are principally prohibited in most of the developed countries. Heavy metals also present a significant menace to local ecosystems and human health, due to their toxicity and persistence in nature. They are produced by traffic, fossil fuel combustion, industrial and residential activities (Biasioli et al., 2006; Kong et al., 2011). Heavy metals and POPs accumulate in soil and they can also be released back into the atmosphere, depending on soil characteristics and environmental conditions.

Human exposure to natural radiation mainly results from gamma radiation emitted by terrestrial radionuclides in the series of  $^{238}\text{U}$  and  $^{232}\text{Th}$  and natural  $^{40}\text{K}$  (UNSCEAR, 2000). Anthropogenic radionuclides coming from nuclear tests and accidents contribute less than 0.5% of the total annual dose (UNSCEAR, 2000). The most important artificial radionuclide  $^{137}\text{Cs}$  ( $T_{1/2} = 30.1$  y), originating mainly from Chernobyl nuclear accident, can still be found as a persistent environmental contaminant in most of the European countries.

The aim of this paper was to present the results of measuring radioactivity, POPs and heavy metal contents in soil samples collected along the riverbank of the Lepenica River. The study was

conducted in order to access the exposure of residents of Kragujevac city to persistent soil pollutants almost twenty years after NATO aggression.

## 2. MATERIALS AND METHODS

### 2.1 Study area, sampling and preparation

With a population of about 150 000 (2011 census), Kragujevac (43° 59' N; 20° 53' E) is one of the biggest cities in Serbia, and the administrative center of Šumadija District. It lies at 180 meters above the sea level and it is located in the valley of the Lepenica River, a small tributary of the Velika Morava, which in turn flows into Danube. This region has a continental climate and the average annual rainfall of 618 mm. Kragujevac is known for its automobile (Fiat Chrysler Automobiles Serbia - FCAS) and munitions (Zastava Arms) industry. Besides, there are several minor industrial facilities for producing asphalt materials, panel furniture, technical chains, paints and varnishes, etc.

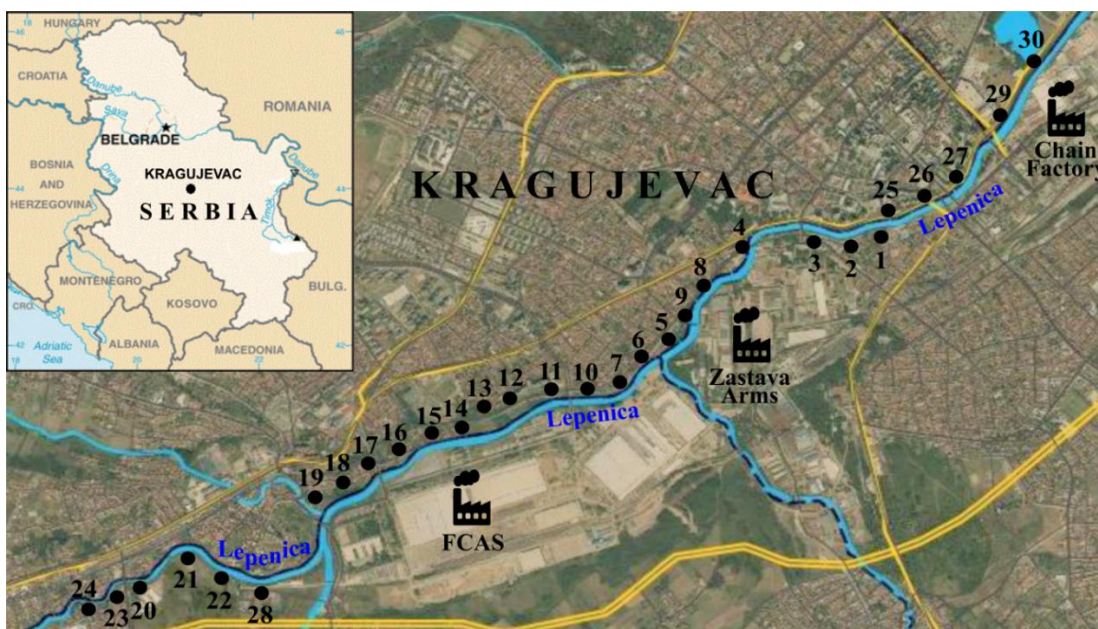


Fig. 1. Map of the study area

Samples of soil were collected from 30 locations along the riverbank of the Lepenica River, near the main industrial facilities surrounded by highly populated city areas (Fig. 1). Sampling was performed during the autumn of 2017. The total of 60 samples were taken from two depths (0–15 and 15–30 cm) by metal spade, applying the template method (IAEA, 2004). They were cleaned from plant roots, grass and stones, packed, and transported to the laboratory.

## ***2.2 Gamma spectrometry***

Soil samples were air-dried to constant weight, homogenized, sealed in Marinelli beakers, and stored for a month before measuring, in order to ensure the radioactive equilibrium between  $^{226}\text{Ra}$  and its progeny. The specific activities of  $^{226}\text{Ra}$ ,  $^{232}\text{Th}$ ,  $^{40}\text{K}$  and  $^{137}\text{Cs}$  were measured using coaxial HPGe spectrometer (GEM30-70 ORTEC, 30% relative efficiency and 1.65 keV FWHM for  $^{60}\text{Co}$  at 1.33 MeV) shielded with 10 cm lead to reduce the background. The system was calibrated using standard mixture of gamma-emitting isotopes (MBSS 2) provided by the Czech Metrology Institute. Gamma spectrometric measurement of each sample was performed for 6 h.

## ***2.3 Heavy metals***

Heavy metal concentrations were determined by USEPA Method 3051A (Milestone Ethos 1 microwave sample preparation system) and ICP-OES method (Varian Vista Pro-axial). Mercury content was determined using Direct Mercury Analyzer DMA 80 Milestone in accordance with

US EPA Method 7473. The limit of detection (LOD) for mercury content was  $3.3 \mu\text{g kg}^{-1}$ . Detailed description of the measuring procedures applied was given by Stevanović et al. (2018).

#### ***2.4 Polycyclic aromatic hydrocarbons (PAHs)***

Polycyclic aromatic hydrocarbons were extracted from soil samples using standard US EPA 3540C method for Soxhlet extraction. 10 g of dried soil sample was mixed with 5 g of anhydrous sodium sulfate and placed in the Soxhlet timble. The extraction solvent was dichloromethane (200 mL). Solvent was heated to reflux and Soxhlet extraction was performed for 24 h. After the extraction, the solvent was removed from the extracts by using rotary evaporator and then extracts were diluted in 2 mL of cyclohexane. Cleaning of the concentrated extracts was performed using silica gel filled glass column with anhydrous sodium sulfate on the top. Silica gel was conditioned prior adding extract with 10 mL of dichlormethane and 40 mL of n-pentane.

After adding the sample extract in cyclohexane on the top of the silica packed column, it was eluted with 25 mL of n-pentane and 25 mL of pentane/dichloromethane (3/2 v/v). The first eluted fraction was discarded due to containing n-alkanes and the second fraction containing PAHs was collected and vacuum-evaporated and solvent-exchanged to acetonitrile. Extract in acetonitrile was after that concentrated to 1 mL under a stream of nitrogen before analysis by GC/MS. The analysis of PAHs in prepared soil samples was performed on a Agilent 6890 CG-5975MSD system equipped with a HP-5MS capillary column. 1  $\mu\text{L}$  of sample extract was injected in a system in splitless mode and helium was used as a carrier gas. Temperature program used for chromatographic separation was following: the initial temperature of  $60\text{ }^{\circ}\text{C}$  with 2 min hold, than increased to  $120\text{ }^{\circ}\text{C}$  at a rate of  $30\text{ }^{\circ}\text{C min}^{-1}$ , then increased to  $300\text{ }^{\circ}\text{C}$  at a rate of  $5\text{ }^{\circ}\text{C min}^{-1}$  with 15 min hold. The inlet temperature was  $260\text{ }^{\circ}\text{C}$  and the interface and ion source were maintained at  $295\text{ }^{\circ}\text{C}$  and  $230$ , respectively. The 16 analyzed PAHs were: naphtalene, acenaphthene, acenaphthylene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, chrysene, benzo[k]fluoranthene, benzo[a]anthracene, benzo[b]fluoranthene, benzo[a]pyrene, dibenzo[a,h]anthracene, benzo[g,h,i]perylene indeno[1,2,3-cd]pyrene. The detection limits of the applied method for individual PAHs ranged between  $0.6$  and  $4.4 \mu\text{g kg}^{-1}$ .

Quality control was performed by analysis of blank and certified reference soil samples CRM-170 provided by Fluka. The recoveries for PAHs were in the range of 85-110%.

### ***2.5 Polychlorinated biphenyls (PCBs)***

Quick Easy Cheap Effective Rugged Safe (QuEChERS) method (Anastassiades et al. 2003; He et al. 2015) has been applied for extracting of PCBs from samples. The analysis was performed with an Agilent 7890B Gas Chromatography with Electron Capture Detector (GC-ECD). The 30 m long column HP-5, with a diameter of 0.32 mm and a 25  $\mu\text{m}$  thick film of stationary phase was used for analyte separation. The injection volume was 1.0  $\mu\text{L}$  in a split mode 10:1. Working conditions of the GC system were set as follows: injector at 170  $^{\circ}\text{C}$ , detector at 300  $^{\circ}\text{C}$ , initial oven temperature at 40  $^{\circ}\text{C}$ , for 2.0 min, heating to 120  $^{\circ}\text{C}$  at a rate 8  $^{\circ}\text{C min}^{-1}$ , then to 190  $^{\circ}\text{C}$  at a rate 5  $^{\circ}\text{C min}^{-1}$ , with a final 5 min hold. Split injection mode 10:1 with flow of 1.4  $\text{mL min}^{-1}$  was used. To reduce background errors, procedure blanks, laboratory blanks, standard-addition in matrixes and blanks, duplicated samples were analyzed regularly in the process of data acquisition. For quantification by GC-ECD individual target PCB calibration curves were in a linear response ( $r^2 > 0.999$ ). Target compounds were under the limit of detection in blanks. Based on standard surrogate of 2,4,5,6-tetrachloro-m-xylene (5  $\text{mg L}^{-1}$ , 20 mL in each sample) concentrations of PCBs were determined. To calculate surrogate recoveries and target compounds 10 mL internal standard solutions (10  $\text{mg L}^{-1}$  concentrated) of o-Nitrobromobenzene and PCB-209 were injected to samples before analysis. Surrogate recoveries in samples ranged from 75.0% to 99.5%, and the recoveries from spiked matrixes were greater than 90%. Based on their retention times (tR) identification of PCB congeners was solely.



### 3. RESULTS AND DISCUSSION

#### 3.1 Radioactivity

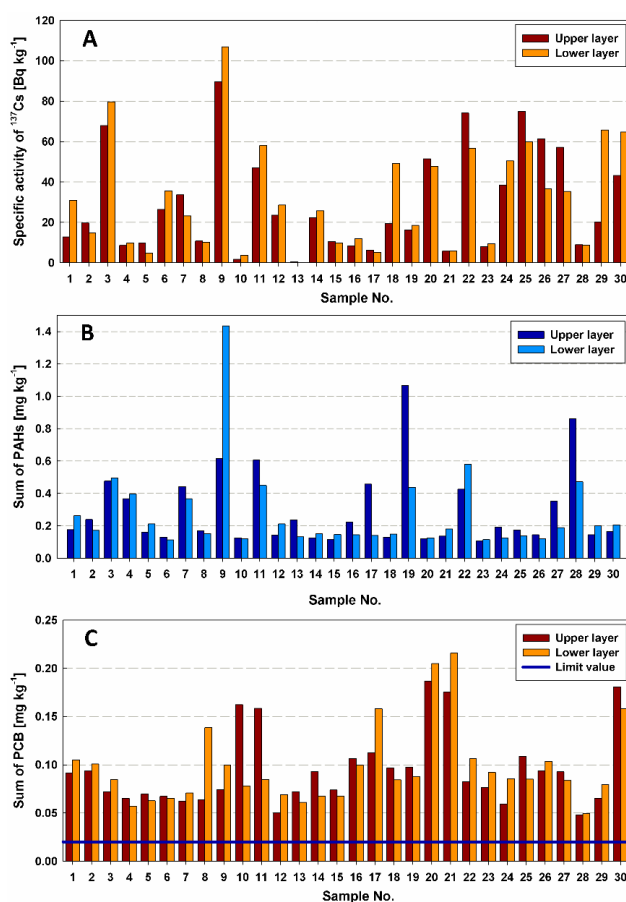
Table 1 presents descriptive statistics of two-layer-averaged specific activities (obtained by averaging the values measured in two layers) of radionuclides. The specific activities of  $^{137}\text{Cs}$  measured in the upper (0-15 cm) and the lower (15-30 cm) layers of soil were presented in Fig. 2A. Two-layer-averaged specific activities of  $^{226}\text{Ra}$ ,  $^{232}\text{Th}$ ,  $^{40}\text{K}$  and  $^{137}\text{Cs}$  were in the ranges of 15.7-33.1, 13.1-54.1, 199-620 and 0.29-98.35  $\text{Bq kg}^{-1}$ , respectively. These results are in line with the average worldwide values (UNSCEAR, 2008) as well as with the values reported from other regions of Serbia (Jankovic Mandic and Dragovic, 2010; Forkapic et al., 2017). The results are also comparable to the values previously measured in other parts of Kragujevac city (Milenkovic et al., 2015; Stajic et al., 2016).

**Table 1.** Descriptive statistics of two-layer-averaged specific activities of radionuclides ( $\text{Bq kg}^{-1}$ ), PCBs ( $\mu\text{g kg}^{-1}$ ) and sum of PAHs ( $\mu\text{g kg}^{-1}$ )

		Min	Max	Median	Mean	SD	Skewness	Kurtosis	Normality p*
Radionuclides	$^{226}\text{Ra}$	15.75	33.05	25.00	24.84	4.24	0.033	-0.044	0.764
	$^{232}\text{Th}$	13.10	54.10	34.27	34.81	7.07	-0.011	3.673	0.009
	$^{40}\text{K}$	199.00	620.50	424.5	432.30	87.31	0.033	1.509	0.109
	$^{137}\text{Cs}$	0.29	98.35	25.07	30.79	24.90	0.870	0.216	0.015
	ELCR	$1.1 \cdot 10^{-4}$	$3.3 \cdot 10^{-4}$	$2.4 \cdot 10^{-4}$	$2.4 \cdot 10^{-4}$	$0.4 \cdot 10^{-4}$	-0.304	2.175	0.099
P	PCB10	4.9	21.3	12.1	13.1	4.0	0.400	-0.293	0.397

<b>PCB28</b>	8.2	79.6	25.7	27.9	15.7	2.338	6.269	0.000
<b>PCB52</b>	6.9	32.0	10.0	11.4	5.6	2.948	8.929	0.000
<b>PCB153</b>	3.1	54.2	11.3	13.7	10.8	2.159	5.920	0.000
<b>PCB138</b>	3.6	53.0	11.9	19.2	15.4	1.172	0.030	0.000
<b>PCB180</b>	2.9	28.6	11.4	10.7	5.7	1.027	1.907	0.030
<b>ΣPCBs</b>	48.8	196.8	89.3	95.9	36.7	1.583	2.332	0.000
<b>ΣPAHs</b>	110	1026	183.5	282.5	221.7	1.910	3.528	0.000

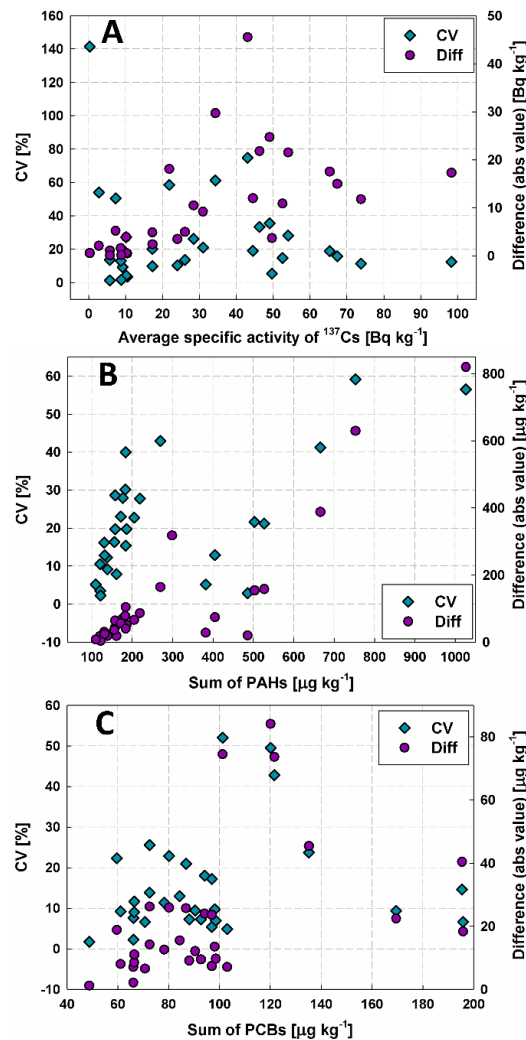
\* Shapiro-Wilk normality test



**Fig. 2.**  $^{137}\text{Cs}$  (A), sum of PAHs (B) and sum of PCBs (C) in two layers of soil

According to Shapiro-Wilk normality test, total specific activities of  $^{226}\text{Ra}$  and  $^{40}\text{K}$  ( $p=0.764$  and  $0.109$ , respectively) have normal distribution in differ to  $^{232}\text{Th}$  ( $p=0.009$ ) and  $^{137}\text{Cs}$

( $p=0.015$ ). The differences between two layers in the activities of natural radionuclides were negligible; coefficients of variation (CV) for  $^{226}\text{Ra}$ ,  $^{232}\text{Th}$  and  $^{40}\text{K}$  ranged between 0 – 21%, 1 – 23% and 0 – 31%, respectively. Non-parametric Wilcoxon test was used to compare specific activities of  $^{137}\text{Cs}$  in the upper and lower layers of soil. The difference between two layers was not statistically significant ( $Z=-0.919$  and  $p=0.358$ ). However, considerable variations between  $^{137}\text{Cs}$  specific activities of two layers was observed in a large number of locations. Coefficient of variation ranged from 1% to 141%, as presented in Fig. 3A.



**Fig. 3.** Coefficient of variation, CV (left y-axis), and difference in absolute value (right y-axis) of  $^{137}\text{Cs}$  (A) sum of PAHs (B) and sum of PCBs (C) in two layers of soil

### 3.1.1 Excess lifetime cancer risk (ELCR)

Excess lifetime cancer risk outdoors was calculated as:

$$ELCR = D_E \times DL \times PC \quad (1)$$

where  $DL$  is average duration of life (70 y) and  $PC$  is the nominal probability coefficient for detriment-adjusted cancer risk of  $5.5 \cdot 10^{-2} \text{ Sv}^{-1}$  (ICRP, 2007).  $D_E$  is annual effective dose calculated as follows:

$$D_E = DCF \times \dot{D} \times t \times p \quad (2)$$

where DCF is the dose conversion factor ( $0.7 \text{ Sv Gy}^{-1}$ );  $t$  is the annual exposure time (8760 h) and  $p = 0.2$  is the outdoor occupancy factor.  $\dot{D}$  ( $\text{nGy h}^{-1}$ ) is the external gamma dose rate in air at 1 m above ground level, calculated according to the formula (UNSCEAR, 2008):

$$\dot{D} = 0.462A_{Ra} + 0.604A_{Th} + 0.0417A_K \quad (3)$$

where  $A_{Ra}$ ,  $A_{Th}$  and  $A_K$  are the values of specific activities  $^{226}\text{Ra}$ ,  $^{232}\text{Th}$  and  $^{40}\text{K}$  ( $\text{Bq kg}^{-1}$ ), respectively.

The excess lifetime cancer risk ( $ELCR$ ) ranged from  $1.1 \cdot 10^{-4}$  to  $3.3 \cdot 10^{-4}$ , with a mean of  $2.4 \cdot 10^{-4}$  (Table 1). This mean value is slightly lower than the worldwide average of  $2.54 \cdot 10^{-4}$ , (UNSCEAR, 2008). The results were calculated using two-layer-averaged specific activities of radionuclides.

### *3.2 Heavy metals*

Descriptive statistics of heavy metals in the upper and lower layers of soil are presented in Table 2 while the results of correlation analyses are shown in Table S3. Cadmium concentrations were below minimum detectable value ( $1.5 \text{ mg kg}^{-1}$ ) in all samples. Wilcoxon test was used to investigate the difference between the upper and lower layers of soil with respect to heavy metals concentrations. There is no statistically significant difference between two layers except for B ( $Z=-2.973$  and  $p=0.003$ ). According to Luo et al. (2012), concentrations of As, Cd, Co, Cr, Cu, Ni, Pb, and Zn in 9954 soil samples from 34 European cities had median values of  $13 \text{ mg kg}^{-1}$ ,  $0.95 \text{ mg kg}^{-1}$ ,  $6.4 \text{ mg kg}^{-1}$ ,  $59 \text{ mg kg}^{-1}$ ,  $46 \text{ mg kg}^{-1}$ ,  $22 \text{ mg kg}^{-1}$ ,  $102 \text{ mg kg}^{-1}$ , and  $130 \text{ mg kg}^{-1}$ , respectively. Compared to this values, median concentrations of As, Pb and Zn in analyzed soils of Kragujevac were lower than in other European cities. Median concentration of Cu was similar to its concentration in European urban soils, but the concentrations of Co, Cr and Ni were 2 or 3 times higher than European average.

According to Dutch standard for soil (VROM, 2000) and Serbian Soil Quality Regulation, (Official Gazette, 2018), limit values for soil which indicate sustainable soil quality for Cr, Cu, Ni, Pb, Zn, Hg, As and Co are 100, 36, 35, 85, 140, 0.3, 29 and  $9 \text{ mg kg}^{-1}$ , respectively. Exceeding the limit value indicates the level of contamination that distorts ecological balance and implies further investigations as well as limitations in the soil management (Official Gazette, 2018). Although the concentrations of Co, Ni and Cr are higher than limit values, their medians are similar to their mean values with low skewness indicating consistency in concentrations and normal distribution. High SD values are often reliable indicator of anthropogenic activities (Manta et al., 2002,

Mihailovic et al., 2015) but on the other hand, positive correlation between Cr and Ni concentrations in soils can indicate their natural origin (Ajmone -Marsan et al., 2008). In our research, anthropogenic origin cannot be assumed due to strong positive correlation (Spearman  $\rho = 0.969$ ) between Cr and Ni concentrations which indicates natural origin of Cr and Ni in analyzed soils, probably from the parental rock. Strong positive correlations at the 0.01 significance level were also observed between the pairs: Ni-Co, Cr-Co, Mn-Co, Mn-Cr, and Ni-Mn. Zn was also strongly correlated with B, Cu and Pb. These strong correlations among the metals suggests their common origin and similar geochemical affinities in soils.

**Table 2.** Descriptive statistics of heavy metals measured in two layers

		Min	Max	Median	Mean	SD	Skewness	Kurtosis	Normality p*
<b>Upper layer</b>	<b>As</b>	5.95	15.33	9.54	9.87	1.63	1.009	3.982	0.008
	<b>Co</b>	2.69	20.84	13.94	13.67	3.23	-1.051	3.912	0.037
	<b>Cr</b>	39.23	189.10	121.65	118.70	33.32	-0.260	0.650	0.407
	<b>Cu</b>	21.32	250.80	40.41	47.65	39.91	4.844	25.168	0.000
	<b>Mn</b>	352.00	876.20	578.75	600.25	114.21	0.612	0.667	0.135
	<b>Ni</b>	28.64	145.20	93.57	92.03	25.74	-0.363	0.541	0.616
	<b>Pb</b>	17.88	240.60	26.60	39.77	42.35	4.053	18.385	0.000
	<b>Zn</b>	71.95	260.10	111.35	115.44	41.07	2.144	5.510	0.000
	<b>Hg</b>	0.09	1.16	0.20	0.27	0.22	2.684	8.868	0.000
<b>Lower layer</b>	<b>As</b>	7.00	14.14	9.77	9.99	1.71	0.732	0.426	0.161
	<b>Co</b>	3.81	17.89	13.88	13.59	2.95	-1.777	4.370	0.000
	<b>Cr</b>	43.27	178.60	124.05	119.75	33.14	-0.755	0.179	0.092
	<b>Cu</b>	17.43	564.40	38.80	58.74	96.60	5.285	28.510	0.000

<b>Mn</b>	386.90	886.40	575.45	599.07	115.74	0.847	0.777	0.102
<b>Ni</b>	29.75	139.40	96.95	93.62	24.93	-0.793	0.594	0.168
<b>Pb</b>	15.19	274.60	28.25	42.68	48.58	4.119	18.919	0.000
<b>Zn</b>	61.74	299.40	99.35	116.84	45.46	2.459	8.284	0.000
<b>Hg</b>	0.07	1.47	0.21	0.28	0.26	3.414	14.388	0.000

\* Shapiro-Wilk normality test

The highest concentrations of heavy metals were detected in two soil samples taken at the sampling site no. 11. Concentration of Pb was 3 times higher and concentration of Zn was 2 times higher than intervention value while the concentration of Cu exceeded the remediation value for almost double. Lead, Zn and Cu are considered to be typical “urban” metals as they are emitted in large quantities by anthropogenic activities that are concentrated in urban areas (De Miguel et al., 1998). Since such high concentrations of Pb, Cu and Zn are not detected at other sampling sites in the vicinity of sampling site 11, high concentrations of Pb, Cu and Zn at the sampling site 11 probably originate from some other source of pollution other than Fiat Chrysler Automobiles Serbia (FCAS) and munitions industry (Zastava Arms). After the NATO bombing in 1999, Balkans Task Force also reported relatively high concentrations of Ni ( $330 \text{ mg kg}^{-1}$ ) and Cr ( $550 \text{ mg kg}^{-1}$ ) in the sediment from the Lepenica River, 4 km down the Zastava factory (BTF, 1999). However, BTF experts concluded that these concentrations are probably the result of long-term industrial pollution rather than war destructions (UNEP/UNCHS, 1999).

### 3.2.1 Health risk assessment from heavy metals

Non-carcinogenic risk and carcinogenic risk were used to assess health effects of exposure of children and adults to heavy metals in soil. US Environmental Protection Agency (USEPA, 2001) model was applied.

Non-carcinogenic risk to population was estimated using the hazard quotient (HQ) and the hazard index (HI). Three exposure pathways were considered: ingestion, air inhalation and dermal contact. The average daily doses (ADDs) from these three main paths were calculated for adults and children, using the following equations (Chen et al., 2015; Qing et al., 2015; Haribala et al., 2016):

$$ADD_{ing} = C \times \frac{IngR \times EF \times ED}{BW \times AT} \times 10^{-6} \quad (4)$$

$$ADD_{inh} = C \times \frac{InhR \times EF \times ED}{PEF \times BW \times AT} \quad (5)$$

$$ADD_{dermal} = C \times \frac{SA \times AF \times ABS \times EF \times ED}{BW \times AT} \times 10^{-6} \quad (6)$$

where  $ADD_{ing}$ ,  $ADD_{inh}$  and  $ADD_{dermal}$  are the average daily intake from soil ingestion, inhalation and dermal absorption in  $mg\ kg^{-1}\ day^{-1}$ ;  $C$  is the concentration of metal in soil ( $mg\ kg^{-1}$ );  $IngR$  ( $IngR = 100\ mg\ d^{-1}$  for adults and  $IngR = 200\ mg\ d^{-1}$  for children) and  $InhR$  ( $InhR = 20\ m^3\ d^{-1}$  for adults and  $InhR = 7.6\ m^3\ d^{-1}$  for children) are the ingestion and inhalation rates, respectively;  $EF$  is the exposure frequency ( $EF = 350\ d\ y^{-1}$ );  $ED$  is exposure duration ( $ED = 30\ y$  for adults and  $ED = 6\ y$  for children);  $BW$  is the body weight of exposed individual ( $BW = 70\ kg$  for adults and  $BW = 15\ kg$  for children);  $AT$  is the averaging time ( $AT = 365 \times ED\ d$ );  $PEF$  is the emission factor ( $PEF = 1.36 \times 10^9\ m^3\ kg^{-1}$ );  $SA$  is the surface area of the exposed skin ( $SA = 1530\ cm^2$  for adults and  $SA = 860\ cm^2$  for children);  $AF$  is the adherence factor ( $AF = 0.07\ mg\ cm^{-2}\ day^{-1}$  for adults and  $AF =$



0.2 mg cm<sup>-2</sup> day<sup>-1</sup> for children); *ABS* is the dermal absorption factor (0.04, 0.1, 0.35, 0.02, 0.03, 0.05, and 0.006 for Cr, Cu, Ni, Zn, As, Hg, and Pb, respectively).

**Table 3.** Non-carcinogenic and carcinogenic health risks of heavy metals in soil.

Non-carcinogenic risk								
Metals	HQ <sub>ing</sub>		HQ <sub>inh</sub>		HQ <sub>der</sub>		HI	
	Child	Adult	Child	Adult	Child	Adult	Child	Adult
As	4.23E-01	4.53E-02	1.18E-05	6.64E-06	2.66E-02	3.55E-03	4.50E-01	4.89E-02
Cr	5.08E-01	5.44E-02	1.42E-05	8.01E-06	8.74E-01	1.17E-01	1.38E+00	1.71E-01
Cu	1.70E-02	1.82E-03	4.73E-07	2.67E-07	4.87E-03	6.50E-04	2.19E-02	2.47E-03
Ni	5.93E-02	6.36E-03	1.61E-06	9.08E-07	6.61E-02	8.83E-03	1.25E-01	1.52E-02
Pb	1.51E-01	1.61E-02	4.18E-06	2.36E-06	5.18E-03	6.91E-04	1.56E-01	1.68E-02
Zn	4.95E-03	5.30E-04	1.38E-07	7.80E-08	4.26E-04	5.68E-05	5.38E-03	5.87E-04
Hg	1.18E-02	1.26E-03	1.15E-06	6.49E-07	7.22E-03	9.64E-04	1.90E-02	2.22E-03
Carcinogenic risk								
Metals	CR <sub>ing</sub>		CR <sub>inh</sub>		CR <sub>der</sub>		TCR	
	Child	Adult	Child	Adult	Child	Adult	Child	Adult
As	1.63E-05	8.74E-06	4.59E-09	1.29E-08	1.03E-06	6.85E-07	1.73E-05	9.44E-06
Cr	6.53E-05	3.50E-05	1.53E-07	4.32E-07	-	-	6.55E-05	3.54E-05
Ni	-	-	2.39E-09	6.73E-09	-	-	2.39E-09	6.73E-09
Pb	3.84E-07	2.06E-07	-	-	-	-	3.84E-07	2.06E-07

Average daily doses for each metal are divided by the reference doses, *RfD* (given in Table S1) to calculate hazard quotient *HQ* (*HQ*<sub>ing</sub> for ingestion, *HQ*<sub>inh</sub> for inhalation, and *HQ*<sub>der</sub> for dermal exposure). Hazard index (*HI*) for each element is calculated by summing *HQ*s related to different exposure pathways. The results are presented in Table 3 for adults and children. The contribution of different exposure pathways of heavy metals increases following the order: inhalation < dermal

contact < ingestion. Total *HI* values were 0.257 and 2.16 for adults and children, respectively. The biggest contribution to total *HI* is associated with Cr and As content. The values of *HI* greater than 1 indicate that population may experience non-carcinogenic harmful health effects (USEPA, 2001). Children are more sensitive to heavy metal pollutants in soil due to intensive body growth and their behavioral habits.

Carcinogenic risk (*CR*) indicates the probability of an individual to develop any type of cancer due to lifetime exposure to carcinogenic hazards (Li et al., 2014).  $CR_i$  for each exposure pathway (*i*) was obtained by multiplying average daily doses with corresponding slope factor  $SF_i$ . The average daily doses were calculated using Eqs. 4-6 for the same values of parameters except for *AT* which now takes the value of  $70 \times 365$  d. Carcinogenic slope factors are given in Table S1. Table 3 presents the results of calculating carcinogenic risk from ingestion, inhalation and dermal exposure, as well as the total carcinogenic risk (TCR) obtained as the sum of these three. If CR is less than  $10^{-6}$ , the carcinogenic risk can be considered negligible while CR values within a range from  $10^{-6}$  to  $10^{-4}$  indicate an acceptable or tolerable risk to human health. CR above  $10^{-4}$  is associated with a high risk of developing cancer in humans (Wu et al., 2015).

### ***3.3 Polycyclic aromatic hydrocarbons (PAHs)***

The sum of 16 PAHs analyzed in 60 soil samples varied from 106 to 1436  $\mu\text{g kg}^{-1}$  with the average value 282.5  $\mu\text{g kg}^{-1}$  which is lower than average PAHs concentrations detected in urban soils of other European cities such as Belgrade (375.2  $\mu\text{g kg}^{-1}$ , Crnković et al., 2007), Ljubljana, Slovenia (989.5  $\mu\text{g kg}^{-1}$ ), Torino, Italy (857.6  $\mu\text{g kg}^{-1}$ ) (Morillo et al., 2007) and Taragona, Spain (736.2  $\mu\text{g kg}^{-1}$ ).

kg<sup>-1</sup>, Nadal et al., 2004). Descriptive statistics of two-layer-averaged concentration of PAHs are presented in Table 1.

According to Dutch standard for soil (VROM, 2000) and Serbian Soil Quality Regulation, (Official Gazette, 2018) limit value for PAHs in soil is 1000 µg kg<sup>-1</sup>. Concentrations higher than the limit value indicate anthropogenic influence on soils. In our research, only two samples, taken at the sampling sites 9 and 19 contained PAHs in concentrations slightly higher than the limit value which implicates that soils in Kragujevac are not polluted with PAHs.

Aislabie et al. (1999) indicated that naphthalene, phenanthrene, and perylene are produced biologically in addition to their presence in the exhaust fume of combustion processes. Wilcke (2007) concluded that the composition of PAH mixtures in soils are dominated by background and anthropogenic source patterns. Background pattern is dominated by natural PAHs (naphthalene, phenanthrene, and perylene) produced biologically or released by vegetation fires or volcanic exhalations. Anthropogenic source pattern results from the combustion of fossil fuels dominated by the presence of a number of high-molecular weight PAHs. Since the concentration of naphthalene in analyzed soil samples was below detection limit and concentration of phenanthrene was low compared to total PAHs concentrations it can be conclude that PAHs in analyzed soils follow anthropogenic pattern.

Based on their origin, PAHs can also be divided into two groups: pyrogenic and petrogenic (Hylland, 2006). Pyrogenic PAHs are released during incomplete combustion of organic material (forest fires, tobacco smoke etc.) while the petrogenic PAHs can be found in oil and oil products (Feng et al., 2009, Lang et al., 1962, Wakeham et al., 1980). Pyrogenic PAHs are composed of larger ring systems compared to petrogenic PAHs. Petrogenic PAHs are naturally present in crude oil (Laughlin and Neff, 1979, Harvey, 1996, Achten and Hofmann, 2010).

Pyrogenic/petrogenic origin of PAHs can be determined based on low molecular weight/high molecular weight PAH ratio. Low molecular weight PAHs are constituted from 2 or 3 rings, while high-molecular PAHs are composed of 4 and more rings. LMW/HMW ratio in all analyzed samples was significantly lower than 1 (Table S2) which indicate pyrogenic origin of PAHs in soils probably due to incomplete combustion of fossil fuels.

Of 16 analyzed PAHs, seven are considered to be carcinogenic according to IARC (International Agency for Research on Cancer) classification. The sum of carcinogenic PAHs in analyzed soils was ranging from not detected to 520  $\mu\text{g kg}^{-1}$  (Fig. 2B) with the average value of 100  $\mu\text{g kg}^{-1}$  which is almost three times lower than in other European cities (Menzie et al. 1992). The highest concentration of carcinogenic PAHs was detected at sampling site 9, near the Zastava Arm factory (Table S2).

Coefficients of variation (CV) and the absolute differences between two layers in the sum of PAHs were presented on Fig. 3B. Wilcoxon test was used to investigate the difference between the sum of PAHs in the upper and the lower layers of soil. The difference was not statistically significant ( $Z=-0.699$  and  $p=0.484$ ).

### ***3.4 Polychlorinated biphenyls (PCBs)***

Table 1 presents descriptive statistics of two-layer-averaged values of PCBs. The sum of PCBs (PCB 10, PCB 28, PCB 52, PCB 138, PCB 153 and PCB 180) ranged between 48.8 and 196.8  $\mu\text{g kg}^{-1}$  with a mean value of 95.9  $\mu\text{g kg}^{-1}$  (Fig. 2C). The highest sum of PCBs was detected in the samples 20 and 21. These samples were collected near the facilities of Fiat's cooperator company "Sigit" producing rubber and plastic parts. Formerly, military barracks were located at

this site. Coefficients of variation (CV) and the absolute differences between two layers in the sum of PCBs were presented on Fig. 3C. CV ranged between 2% and 52%. Wilcoxon test indicated no statistically significant difference between the sum of PCBs in the upper and the lower layers of soil ( $Z=-0.915$  and  $p=0.360$ ).

According to the Soil Regulation, published in the Official Gazette (2018), the maximum limit value of the total content of PCB congeners (PCB 28, PCB 52, PCB 101, PCB 118, PCB 138, PCB 153 and PCB 180) is  $20 \mu\text{g kg}^{-1}$  and the value of  $1000 \mu\text{g kg}^{-1}$  imposes remediation requirement. PCB 101 and PCB 118 were not measured in this study. However, sum of the remaining five congeners (PCB 28, PCB 52, PCB 138, PCB 153 and PCB 180) still exceeds the limit of  $20 \mu\text{g kg}^{-1}$ . Individual concentrations of these five PCBs were generally higher than the values reported from England, France, Russia and Turkey (listed in Table 4). According to the study of Li et al. (2010), the sum of PCBs in European soil ranges between  $0.047$  to  $97 \mu\text{g kg}^{-1}$ , with the average of  $7.5 \mu\text{g kg}^{-1}$ , which is far below the values measured in this study.

There are reasons to believe that the high levels of PCBs are probably related to the NATO air strikes in 1999. Several studies conducted after the bombing reported a high contamination of Zastava complex and the Lepenica River by many hazardous substances particularly by persistent organic pollutants. According to UNEP/UNCHS Balkans Task Force report from 1999, samples of soil/waste collected around damaged transformers in the power plant and the paint hall of the Zastava factory contained very high levels of PCBs ( $>1 \text{ g kg}^{-1}$ ). A relatively high PCB (the sum of the 7 congeners) concentration was also found in the sediment samples collected at the mouth of the Lepenica River ( $52 \mu\text{g kg}^{-1}$ ) and in the Velika Morava downstream of the Lepenica confluence ( $22 \mu\text{g kg}^{-1}$ ) (UNEP/UNCHS, 1999). The concentration of  $2400 \mu\text{g kg}^{-1}$  was measured in the sediment of Lepenica 4 km downstream of the Zastava factory, while the sediment upstream

of Kragujevac contained a very low level of PCBs (UNEP/UNCHS, 1999). According to these reports, PCB concentration in the Velika Morava upstream of the Lepenica mouth was also below detection limits (BTF, 1999). A study conducted in 2003/2004 by Klanova et al. (2007) reported that the sum of seven PCB congeners measured in the top layer of soil from Zastava factory was as high as 1300  $\mu\text{g kg}^{-1}$ . According to Bartoš et al. (2009), the overall risk of carcinogenic diseases due to inhalation of airborne organic pollutants in the factory (in the early summers of 2003 and 2004) was assessed to be 4.5 times higher than the EPA limit value. Such an increased risk was mainly caused by PCB contamination.

According to UNEP's Balkan's Task Force, some of the workers who took part in cleanup action in the Zastava factory became ill. However, long-term health effects to the workers or the general population are still unknown due to the lack of studies investigating this issue. Besides, it is difficult to estimate the exact contribution of the war destruction to the environmental contamination since there was no systematic monitoring of pollution in this area before the conflict.

**Table 4.** Comparison of individual PCB congeners measured in this study and the values reported from other countries (in  $\mu\text{g kg}^{-1}$ )

<b>Author</b>	<b>Location</b>	<b>PCB28</b>	<b>PCB52</b>	<b>PCB153</b>	<b>PCB138</b>	<b>PCB180</b>
Vane et al. 2014	England	0.8	3.0	5.1	5.9	1.4
Wilcke et al. 2006	Russia	0.6	1.8	4.3	6.1	0.9
Motelay-Massei et al. 2004	France	-	3.58	5.15	1.48	6.05
Kaya et al. 2012	Turkey	3.6	2.1	1.6	2.3	1.1
This study	Serbia	27.9	11.4	13.7	19.2	10.7

#### 4. CONCLUSION

The levels of PAHs and radionuclides measured in soil indicate no significant contamination. The concentrations of As, Co, Cr, Cu, and Ni exceed the limit values established by Serbian official regulations in many samples, but these levels were still typical for industrial areas. Ingestion is the dominant pathway of exposure to all heavy metals, followed by dermal absorption and inhalation. Non-carcinogenic risk from heavy metals was assessed through total hazard index which was calculated to be 0.257 and 2.16 for adults and children, respectively. The biggest contribution to total hazard index came from Cr and As. On the other hand, the sum of PCBs ranges from 48.8 to 196.8  $\mu\text{g kg}^{-1}$  and it is rather high in comparison to the values reported from other European countries. These values also exceed the regulative limit value of 20  $\mu\text{g kg}^{-1}$  in all samples. It cannot be stated with certainty whether these elevated values are the consequence of NATO bombing or the local industry (or probably both). However, this level of contamination distorts ecological balance and implies further investigations in order to assess and control environmental pollution and the exposure of the local population.

Most of the samples contained As, Co, Cr, Cu, and Ni in concentrations that exceed the maximum limit values established by Serbian official regulations. However, the intervention level was exceeded only in one sample (for Cu).

Although the coefficient of variation was rather high in some cases, the differences between two layers with respect to all measured variables were not statistically significant.

## **Acknowledgement**

The present work was supported by the Ministry of Education, Science and Technological Development of the Republic of Serbia, under the Projects No. 171021, 176006, 176019.

**Declaration of interests:** none

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