



Pollution indices and sources appointment of heavy metal pollution of agricultural soils near the thermal power plant

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Abstract Alluvial soils of valleys of the Danube and Mlave rivers represent priority development areas with favorable conditions for life, agriculture and tourism in eastern Serbia. Operation of the thermal power plant Kostolac results in the emission of potentially toxic pollutants into the air, water and land. The goals were to determine the soil pollution with inorganic pollutants using different pollution indices, to identify of the sources of pollutants by means of principal component analysis and the loading of each factor for individual element assessed by multi-linear regression analyses. Chemical characteristics of the studied area resulted in division of the area into four impact zones upon the distance from main pollutants (power plant blocks and ash disposal dumps). There was no established soil pollution with potentially toxic elements in bulk of the agricultural territory. Two principal components (PC1 and PC2) explained about 73% of variance. Three studied

elements (As, Cu and Pb) showed anthropogenic origin of their most concentrations in soil, while other elements (Cd, Co, Cr, Ni and Zn) were of a natural (geological) origin. Single pollution index showed moderate pollution level by Ni. Integrated Nemerow pollution index showed low to no pollution levels, indicating slight ecological risk. There were no established limitations for agricultural production in the studied area, except for the only spot polluted by As due to the great flooding event in the studied year.

Keywords Heavy metals · Pollution indices · Thermal power plant · Ecological risk · PCA · MLRA

Introduction

The ecological crisis, which is becoming more intense, is correlated with the socio-economic development of the region. Permanent growth of the human population accompanied with urbanization and the development of economic sectors (mining, energy, industry, transport) generates a series of environmental problems, which can be local (unregulated dumps, emissions of heavy metals from an industrial facilities) (Alloway 1995), regional (eutrophication and pollution of international rivers) or global (climate change, the destruction of stratospheric ozone depletion, soil erosion, etc.) (Dutch Target and Intervention Values 2000). Coal combustion in thermal power plants

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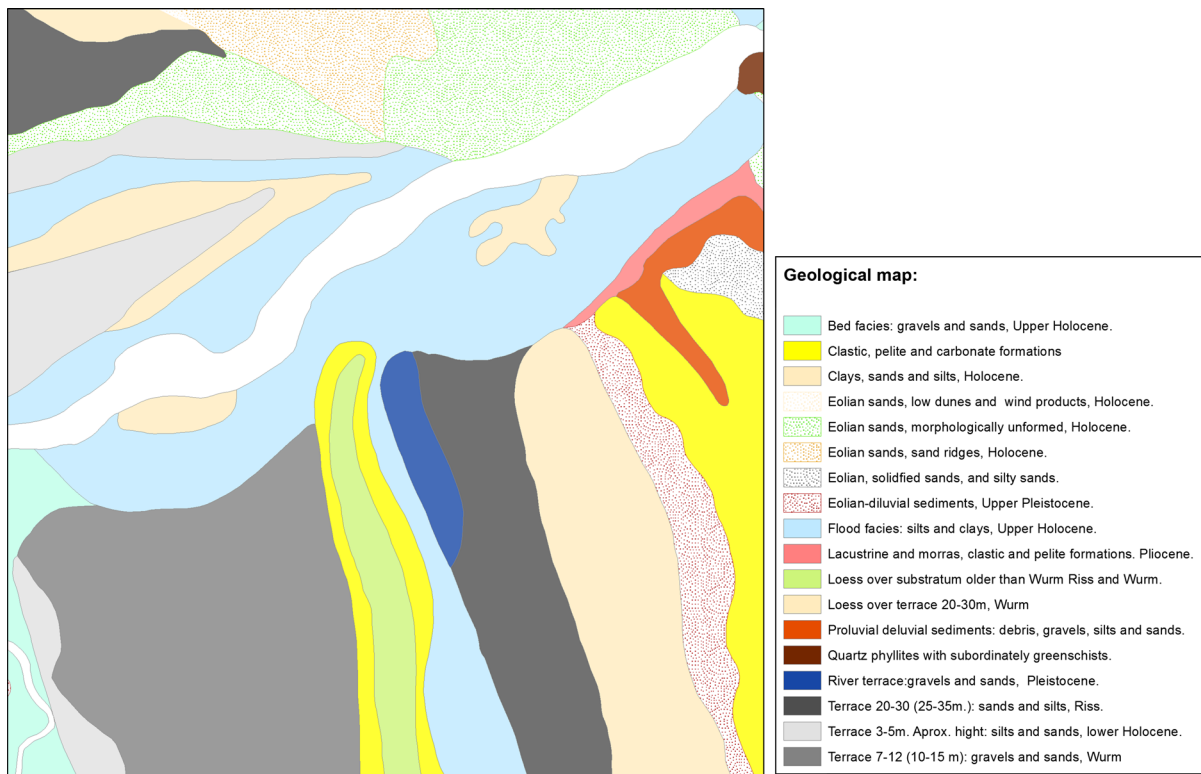


Fig. 1 Geological map of the studied area around thermal power plant Kostolac

produces huge amounts of ash, which is a source, from both air and damp, of inorganic pollutants of the area surrounding the power plant (Adriano et al. 2002; Dragovic et al. 2013).

Exposition of soil to permanent accumulation of toxic and hazardous microelements of anthropogenic origin may deteriorate its quality, causing chemical, biological and physical degradations, which might result in deterioration of crop quality and thus affect the food safety. The creation of anthropogenic landscapes, such as the disposal sites of ash from thermal electric plants, leads to extremely heavy stress for plant survival (Pavlović et al. 2004). The activities of the thermal power plant and disposal of ash might put in a risk quality of agricultural production in the surrounding area due to the emission of potentially toxic and hazardous elements. In EU countries, about 137,000 km² of agricultural land contains relatively high concentrations of heavy metals (Toth et al. 2016).

Some microelements, including heavy metals, are essential for metabolism of plants and animals at low concentrations. However, they become toxic for living organisms when their concentration exceeds a specific

threshold (Alloway 1995; Kabata-Pendias and Pendias 2001; Prem Kishor et al. 2010).

However, numerous studies have reported successful usage of fly ash for improving soil's physical, chemical and biological characteristics as soil ameliorant (Phung et al. 1979; Adriano et al. 2002; Inam 2007; Prem Kishor et al. 2010). But the question is whether a permanent exposure of agricultural lands to airborne microelement deposition and exposure to potential contamination from ash-dumps will have overall negative or positive effects.

This study was done in the territory of Kostolac coal basin and power plant in eastern Serbia (TPP Kostolac). Alluvial soils of the river valleys of the studied area represent priority development areas with highly favorable conditions for life, agriculture, tourism, etc. (Official gazette of RS 88/2010). Currently, the ash from TPP is dumped over an area of 250 ha with 2–30 m of thickness. This resulted in ash dump rising above the level of the Danube and surrounding terrain, which intensifies the processes of aeolian and hydro-erosion and the process of ash scattering. Therefore, a permanent control of soil pollution state, as well as

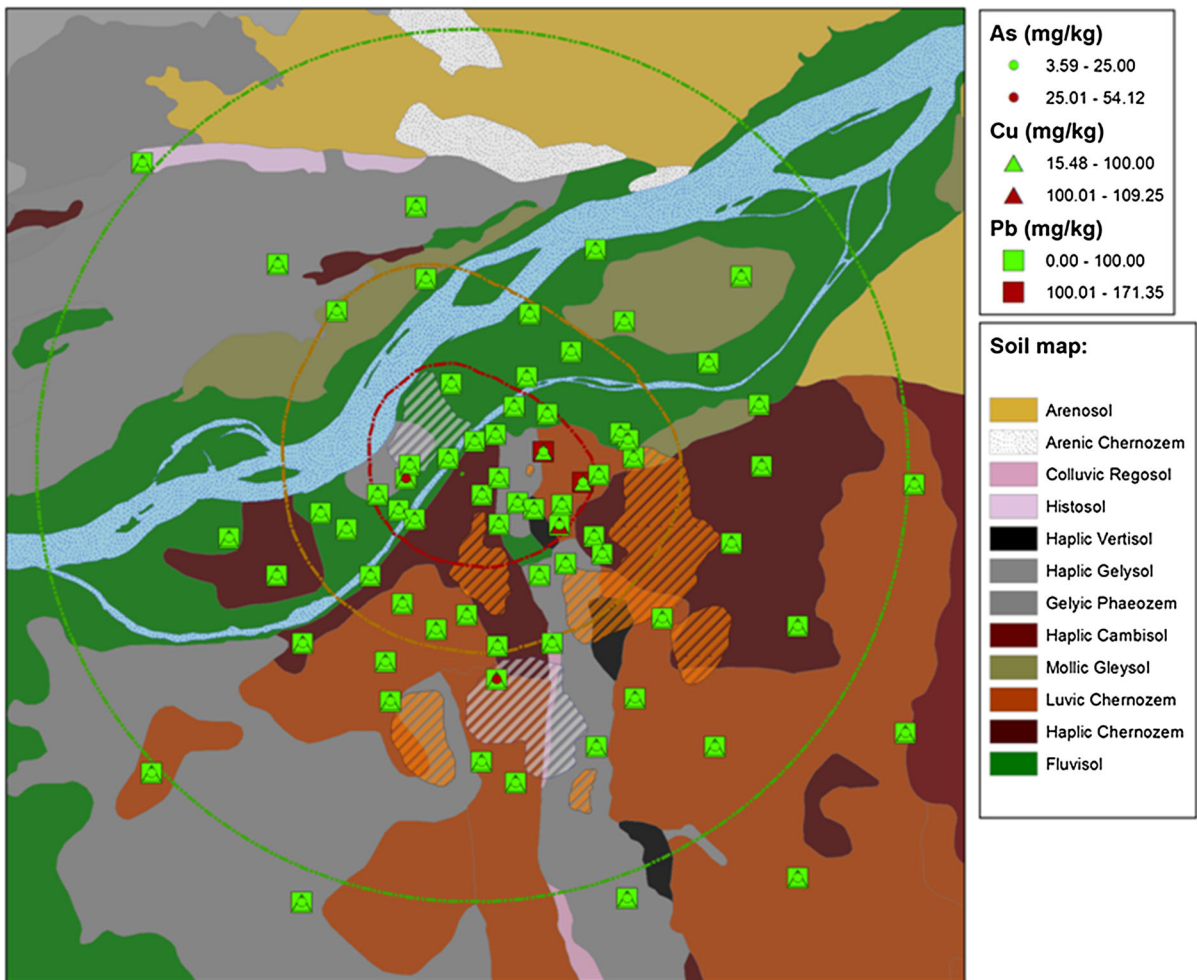


Fig. 2 Locations of sampling points and zones of impact of thermal power plant, Kostolac, Serbia. *Note:* the intervals for As, Cu and Pb concentrations were selected based on the MAC and Remediation values (Official gazette of RS 88/2010)

monitoring changes in soil’s physical, chemical and biological characteristics, especially the soil in agricultural use is a high-priority task. These goals cannot be achieved without reliable information from the systematic data set about the state, trends and changes in the environment.

This paper presents a part of soil monitoring project around TPP Kostolac focused on the objectives determination of soil pollution state by the most important inorganic pollutants (total concentrations of As, Cd, Co, Cr, Cu, Ni, Pb and Zn); identification of the areas of vulnerability (distance from the source of pollutants); appointment of the sources of pollutants (natural or anthropogenic); quantification of their concentrations in agricultural soils around the thermal power plant Kostolac (TE-KO) in Serbia.

Materials and methods

Studied area

The thermal power plant Kostolac is situated in the eastern part of Serbia on the Danube river bank and occupies an area of about 400 km² (Electric Power Industry of Serbia, Power Plants and Mines Kostolac, TE-KO). The investigated area covered about 450 km² and extends in a radius of about 12 km from the town Kostolac. The area is rich in lignite and located at 44°43’N latitude and 21°14’E longitude (Fig. 1). The TPP Kostolac has two thermal power plants (A and B) with the production of nearly 63,743 GWh that makes almost 11 percent of the total electric power production in Serbia. The Kostolac TPPs

produce and dump hydraulically about 2×10^6 t of ash and slag.

Geology and pedology of the studied area

The large part of the area is occupied by alluvial plains and river terraces of the Danube, Velika Morava and Mlava, where mostly Fluvisol and Chernozem soils were formed, and in lesser degree the soils of heavier texture (Gleysols and Gleyic Phaeozems) (Figs. 1, 2). The part between the alluvium of Morava and Mlava rivers consists of sand and clay (tertiary, pliocene) and loess (quaternary, pleistocene), where Cambisols, Vertisols and Chernozem were formed. Eastern part of the Mlava River is a loess terrace (Pleistocene), where Chernozem soils were formed. The northeastern part of the area forms the periphery of the Deliblatsko-Ramian sandstone, where the Arenic and Chernozem soils were formed. So, the soils of the studied area are predominately represented by Fluvisol, Chernozem and Gleyic Phaeozem (WRB 2006). The climate in Kostolac area is characterized with relatively cold winters and warm summers. Mean annual air temperature is 10.9 °C, and mean annual amount of precipitation is about 650–700 mm.

Wind direction

The relative proximity of the Djerdap Gorge (Iron Gate) that is the exit door of the wind from southeast, whose speed exceeds 90 km/h, has a significant effect on the climate of the Kostolac area. In average, this wind occurs about 100 days of a year. The strongest winds come from southeast and east to southeast. The western wind, southeast and south winds are the most frequent. The smallest frequency has the wind from the north–northeast direction. It is a cold, very squally southeastern wind that starts in the Carpathian Mountains and follows the Danube northwest through the Iron Gate region where it gains a jet effect.

Soil sampling and preparation

On the studied area, 70 measuring points were sampled in 2014. Each soil sample represents the average of 5 subsamples and represents about 25 m³ of soil, according to the regulation (Official Gazette 2010). Soil samples were air-dried and sieved through a sieve of 2 mm. Further, for the analysis of

microelements, the sample was sieved through 150- μ m mesh. In the 2014 sampling year, there was a big flooding in some parts of the studied area, including damp areas.

Soil sampling points were distributed in the way to cover all main soil types that are under agricultural use with consideration of the dominant wind direction, which comes from the southeast.

Analytical methods

Soil pH was determined with a glass electrode pH meter (1:2.5 water solution). The soil's total C and N were measured with an elemental CNS analyzer (Elementary Analyses system GmbH, Hanau, Germany) (Nelson and Sommers 1996), and CaCO₃ volumetrically with Scheibler calcimeter. Available P and K were determined by Al method of Egner–Riehm (1958).

Total content of microelements (As, Cr, Ni, Pb, Cu, Zn, Cd, Co) in the soil was extracted by digestion with *aqua regia* (L.) (ISO 11466:1005, 1995) and determined on ICAP 6300 optical emission spectrometer (Thermo Electron Corporation, Cambridge, UK). All chemical analyses were performed in two analytical replications. For verification of the results, the referent soil was determined for the microelements (reference ERM-CC141 loam soil, Belgium, with exact concentration of microelements soluble in *aqua regia* to determine accuracy of measuring apparatus). Lower limits of detection for the elements were: 0.6436 (As), 0.0326 (Co), 0.0166 (Cd), 0.2897 (Cr), 2.3233 (Cu), 0.2239 (Ni), 2.8597 (Pb), 8.5106 (Zn), 81.4905 (Fe) mg/kg.

The SPSS statistical software version 20 was used for paired *t* test, linear squares regression (R^2), Kaiser–Meyer–Olkin Measure and Bartlett's test as pre-factor analysis; Pearson correlation analysis (*r*) was used to test differences in means. Results of statistical tests were considered significant at $P < 0.05$. Principal component analysis (PCA) with Varimax with Kaiser Normalization rotation method was applied to distinguish the sources of possible pollutions (SPSS 2010). Multi-linear regression was used to identify the factor loads for individual microelements.

Soil pollution indices

The indices of soil pollution (P_i), enrichment factor (EF) and potential ecological risks (RI) were calculated for individual microelements.

The *single pollution index* by an individual element was calculated according to the equation (Hu et al. 2013):

$$P_i = \frac{C_i}{S_i} \tag{1}$$

where C_i is individual metal concentration in a soil; S_i is its reference value, which is a baseline concentration below which the element assumes not to affect natural properties of soil:

$$S_i = \frac{LV * [A + (B * clay) + (C * organic\ matter)]}{[A + (B * 25) + (C * 10)]} \tag{2}$$

where LV is a limit value specified on the Standards for Soil Quality of Serbia (Official gazette of RS 88/2010). A, B and C are the constants upon the type of trace elements given by European Union and Serbian legislations (Dutch Target and Intervention Values 2000).

Degree of overall pollution of the surface soil by hazardous and harmful microelements was assessed by *Nemerow pollution index* (PI_N):

$$PI_N = \sqrt{\frac{PI_{ave}^2 + PI_{max}^2}{2}} \tag{3}$$

where PI_{ave} and PI_{max} are the mean and maximum of single pollution indices (P_i) for individual microelements.

For quantitative assessment of the contribution of anthropogenic sources to the concentrations obtained

in the surface soil, the enrichment factors (EF) of studied microelements were calculated as:

$$EF = \frac{C_i/C_r}{B_i/B_r} \tag{4}$$

where C_i and C_r are concentrations of the target and reference microelement, respectively, and B_i and B_r are the background concentrations of the target and reference microelements, respectively. Background concentrations for individual elements for given area were defined as the lower of the maximum detected levels or two times the mean. Enrichment factors for studied microelements were calculated using Fe as the reference metal.

Potential ecological risk indices were defined as RI index and calculated as the sum of risk factors of microelements:

$$RI = \sum E_i \tag{5}$$

where E_i is the single risk factor for individual microelement i , which is defined as:

$$E_i = T_i * f_i \tag{6}$$

where T_i is the toxic response factor for microelements (Hu et al. 2013): As—10, Cd—30, Cr—2, Cu—5, Ni—5, Pb—5 and Zn—1; The f_i was assessed as the ratio of C_i and B_i (see description for the Eq. 4).

For comparison of the level of soil contamination, the pollution indices were classified into five classes (Wu et al. 2014) (Table 1).

The Kaiser–Meyer–Olkin measure and Bartlett’s test were performed to prove the suitability of the results for factor analysis (PCA).

Principal component analysis (PCA) is a useful tool to reduce the total data set and to distinguish soil pollution sources (Wu et al. 2014). Factor loadings present the correlation coefficient between the

Table 1 Adjusted grading standard of soil pollution indices by microelements (heavy metals) in soil

Class	P_i^*	EF**	Pollution degree	PI_N	Pollution degree	E_i	RI	Risk degree
1	< 1	< 2	Unpolluted	≤ 0.7	No pollution	< 30	< 40	Slight
2	1–3	2–5	Moderately polluted	0.7–1	Warning line of pollution	30–60	40–80	Medium
3	3–6	5–20	Considerably polluted	1–2	Low pollution	60–120	80–160	Strong
4	6–12	20–40	Highly polluted	2–3	Moderate pollution	120–240	160–320	Very strong
5	> 12	> 40	Extremely polluted	> 3	High pollution	> 240	> 320	Extremely strong

P_i single pollution index; EF enrichment factor; PI_N Nemerow pollution index; E_i potential ecological risk of a single element; RI comprehensive ecological risk

Table 2 Main agrochemical parameters according to the zones of impacts in vegetation season (V)

Statistics	pH (KCl)	Total N	Total C	Total S	Organic C	CaCO ₃	Available P ₂ O ₅	Available K ₂ O
<i>Impact zone I</i>								
Max	7.60	0.25	3.71	0.13	3.06	10.08	100.40	38.78
Min	5.60	0.09	1.29	0.04	0.89	0.00	1.71	15.80
Mean	7.01a [†]	0.17a	2.45a	0.08a	2.02a	3.44a	35.63a	26.32a
SD	0.41	0.05	0.66	0.02	0.50	2.62	33.24	6.92
<i>Impact zone II</i>								
Max	7.40	0.31	3.44	0.13	3.28	7.63	92.07	38.60
Min	5.80	0.10	1.31	0.05	1.19	0.00	2.71	8.40
Mean	6.93a	0.19a	2.35a	0.08a	2.06a	2.39a	18.94b	19.84b
SD	0.48	0.06	0.60	0.02	0.53	2.08	19.71	8.25
<i>Impact zone III</i>								
Max	7.55	0.38	5.50	0.14	5.39	12.10	90.15	38.40
Min	5.10	0.09	1.13	0.05	0.95	0.00	1.23	12.40
Mean	6.71a	0.21a	2.62a	0.07a	2.34a	2.34a	13.88b	20.69b
SD	0.66	0.07	1.00	0.02	0.95	2.95	18.65	6.19
<i>Impact zone IV</i>								
Max	7.05	1.28	15.24	0.19	15.18	1.30	76.81	39.00
Min	5.65	0.14	1.47	0.06	1.44	0.00	1.42	13.60
Mean	6.52ab	0.36b	3.82b	0.10a	3.77b	0.42b	21.30b	24.49a
SD	0.50	0.38	4.64	0.04	4.64	0.51	25.83	10.12

[†]The different letters within the column indicate statistically significant differences between the means determined by LSD analysis at 0.05 levels

variables and the factors. Squared factor loading is a percent in variance where the variable can be explained by a factor.

Results and discussion

Zones of impacts upon distance from the pollution sources

Pattern of distribution of studied PTE and main soil agrochemical properties allowed to divide the studied area into four zones, depending on a distance from the pollutants (the central point between Kostolac ash dumps and two power plant blocks (Fig. 2). The first impact zone was within a radius of 0–2.5 km from the source of pollution and included 18 measuring points. The second impact zone was within a radius of 2.5–5 km from the source of pollution and included 19 measuring points. The third impact zone was within a radius of 5–10 km from the source of pollution and

included 21 measuring points. And the fourth zone was beyond the 10 km in radius from the main pollutants and included seven measuring points that showed no anthropogenic influence in the content of PTE.

Main agrochemical parameters

Soil pH showed that the soils of the area have a favorable acidity for plant growth, from slightly acidic to neutral. There was an observed trend of increase in impact zone I (7.03) in comparison with zone IV (6.17). About 80% of the soil samples showed good supply of total carbon (above 1.7%). Differences were observed in the content of total and organic carbon between zone I and zone IV (2.45–3.82%). Contents of N and available forms P and K did not change significantly between the zones as indicated by the same letters in Table 2.

The difference in soil acidity occurred due to various factors such as soil diversity, because different

Table 3 Basic statistics of total content of microelements in soil influenced by distance from the pollutant (impact zones), mg/kg

	1st zone			2nd zone			3rd zone			4th zone										
	Mean	Min	Max	SD	CV	Mean	Min	Max	SD	CV	Mean	Min	Max	SD	CV					
As	10.44a	4.89	54.12	11.00	1.05	7.92b	3.82	16.96	3.64	0.46	7.27b	4.06	12.33	2.18	0.30	7.41b	3.59	12.39	2.86	0.39
Cd	0.35a	0.16	0.64	0.12	0.35	0.36a	0.13	0.98	0.20	0.55	0.38a	0.19	0.81	0.17	0.45	0.51b	0.34	0.88	0.17	0.33
Co	15.43a	8.52	21.88	4.13	0.27	14.5a	8.75	26.34	4.81	0.33	14.1a	8.21	20.96	3.10	0.22	13.1a	4.72	20.17	4.09	0.31
Cr	53.72a	25.57	99.66	22.10	0.41	55.2a	29.46	125.35	28.14	0.51	49.5a	33.32	85.05	16.88	0.34	42.7a	23.83	92.20	20.01	0.47
Cu	42.58a	20.39	109.25	26.55	0.62	26.4b	15.48	46.72	8.82	0.33	25.7b	18.39	35.13	5.16	0.20	26.6b	18.53	42.66	8.25	0.31
Ni	79.45a	32.64	145.37	40.77	0.51	72.9a	32.44	170.21	42.78	0.59	60.9a	31.81	137.61	28.05	0.46	49.9b	22.97	132.96	32.09	0.64
Pb	41.81a	4.77	171.35	42.02	1.01	25.0b	6.63	68.45	19.05	0.76	20.3b	8.50	53.65	12.15	0.60	19.4b	10.36	57.15	14.57	0.75
Zn	78.31a	50.69	125.02	20.80	0.27	72.8a	41.71	139.89	26.34	0.36	68.0a	48.02	116.97	17.36	0.26	68.8a	33.06	130.39	27.69	0.40

The different letter in a row signifies the significant difference of mean comparison

types of soil naturally vary in acidity due to the soil texture, organic matter content and other agrochemical parameters, but also possible anthropogenic impact. Because the low-S coals produce alkaline ashes (Carlson and Adriano 1993) (the ash pH in H₂O was 9.0–9.4, and pH in KCl was around 8.6) their application increases soil pH (Chang et al. 1977). In our study, increase in soil pH in zone I versus zone IV (Table 2) occurred due to the hydroxide and carbonate salts in fly ash neutralize soil acidity (Cetin and Pehlivan 2007). Some studies reported successful use of fly ash for neutralizing soil acidity (Phung et al. 1979) and improving soil properties (Adriano et al. 2002; Inam 2007).

Usually, the N and C from coal are volatilized during combustion (Carlson and Adriano 1993), and therefore, there was no observed effect of fly ash on soil’s total N and total and organic C content (Table 2). The significantly higher content of N and C in the zone IV is explained by the types of soil in this zone that is predominantly represented by Chernozem and Gleyic Phaeozem, which are genetically better supplied with organic matter. However, some researchers working on the utilization of fly ash showed its significant effect on C-sequestration, for example, using coal fly ash in place of agricultural lime for minimizing global warming. West and McBride (2005) showed that 1 ton of fly ash could sequester up to 26 kg of CO₂, i.e., 38.18 ton of fly ash per tons of CO₂ sequestered.

Concentrations of potentially toxic elements

During the burn of fossil fuel, the smoke (As, Sb, Cd, Cr, F, Hg, Cl), small particles of dust (As, Sb, Be, Cd, Cr, Ni, Cu, Zn, Co, Pb, Mn, P and radionuclide) and ash from dams (As and B) that are in the immediate vicinity may contain many harmful microelements; therefore, it is necessary to test the anthropogenic impacts on the soil around the plants (Adriano et al. 2002; Dragovic et al. 2013). The total contents of the microelements in studied soils are shown in Table 3.

Arsenic (As): the established background concentrations of As on the soils formed on big river valleys in Serbia are 12.9 mg/kg. The average concentrations of As were 10.44, 7.92, 7.27 and 7.41 mg/kg for the zones I, II, III and IV, respectively, and were below the MAC, except one sample in impact zone I near the dam (Fig. 2). Observed differences between the

Table 4 Single pollution index (P_i), single ecological risk (E_i), integrated Nemerow pollution index (NIPI) and overall potential ecological risk (RI)

	As	Cd	Cr	Cu	Ni	Pb	Zn	NIPI
<i>Pollution index by individual microelements (P_i)</i>								
1st zone	0.420	0.547	0.530	1.354	2.289	0.537	0.599	1.511
2nd zone	0.285	0.548	0.502	0.7800	1.861	0.302	0.526	0.746
3rd zone	0.267	0.577	0.460	0.759	1.629	0.254	0.490	0.867
4th zone	0.233	0.662	0.328	0.651	0.999	0.203	0.396	0.533
<i>Single ecological risk by individual microelements (E_i)</i>								
1st zone	0.432	25.45	0.017	0.189	0.163	0.097	0.006	26.356
2nd zone	0.293	25.48	0.016	0.109	0.133	0.054	0.006	26.088
3rd zone	0.274	26.85	0.015	0.106	0.116	0.046	0.005	27.415
4th zone	0.239	30.80	0.011	0.091	0.071	0.037	0.004	31.252

Table 5 Enrichment factors for individual microelements (EF)

	As	Cd	Co	Cr	Cu	Ni	Pb	Zn
<i>1st zone</i>								
Mean	1.264	0.686	1.011	1.026	1.527	1.317	2.056	1.034
Min	0.672	0.344	0.773	0.774	0.767	0.661	0.182	0.764
Max	5.877	1.253	1.452	1.455	3.927	2.319	9.127	1.566
Median	0.941	0.574	0.948	0.941	1.032	1.087	0.910	0.957
SD	1.154	0.272	0.168	0.222	1.105	0.536	2.543	0.230
<i>2nd zone</i>								
Mean	0.969	0.674	0.958	1.062	0.919	1.202	1.015	0.960
Min	0.684	0.351	0.825	0.756	0.727	0.721	0.417	0.736
Max	1.434	1.177	1.185	1.456	1.856	1.988	2.084	1.293
Median	0.905	0.596	0.943	1.021	0.880	1.143	0.762	0.969
SD	0.204	0.242	0.083	0.249	0.249	0.401	0.517	0.160
<i>3rd zone</i>								
Mean	0.895	0.695	0.922	0.958	0.872	1.021	0.853	0.881
Min	0.579	0.377	0.636	0.721	0.703	0.647	0.481	0.727
Max	1.396	1.097	1.296	1.585	1.205	2.234	2.211	1.200
Median	0.833	0.800	0.914	0.876	0.829	0.858	0.720	0.813
SD	0.186	0.241	0.129	0.213	0.156	0.377	0.414	0.145
<i>4th zone</i>								
Mean	1.069	1.025	0.913	0.891	0.979	0.892	0.897	0.951
Min	0.592	0.889	0.545	0.757	0.743	0.658	0.537	0.759
Max	2.714	1.341	1.074	1.480	1.361	1.858	2.028	1.381
Median	0.869	0.986	0.966	0.795	0.940	0.770	0.661	0.876
SD	0.636	0.140	0.154	0.227	0.192	0.370	0.497	0.200

Table 6 Kaiser–Meyer–Olkin measure and Bartlett’s test

Kaiser–Meyer–Olkin measure of sampling adequacy		0.735
Bartlett’s test of sphericity	Approx. Chi square	486.593
	<i>df</i>	28
	Sig.	0.000

zones of impact were statistically confirmed and irregularly accumulated due to irregular locations of the dams, which have determinant influence on the As distribution in soil (Li et al. 2017). Another reason is a greater mobility of As in soil under changed redox condition due to the flooding in 2014, when As in the dam was transformed into more mobile three-valent form (Adriano 2001).

Cadmium (Cd): significantly higher concentrations of Cd in zone IV are most probably explained by the redistribution of Cd in soil around the main pollutant sources, because Cd, due to its higher solubility in river flow and river sediments, is deposited in areas close to the bank (Mitchell et al. 2016). Another reason might be due to emissions of trace elements that are predominantly associated with the particulate phase rather than with the vapor phase, where the smallest particles enriched in some of these elements (As, B, Cd, Cu, Pb, Sb and Zn) were air-transported (Wu et al. 2013) and deposited in the zone IV. The MLR analysis clearly shows that very small percent of Cd is explained with two components, implying the impact of flooding since the Cd is highly soluble in sediments (Mitchell et al. 2016).

Chromium (Cr): average content of Cr that was determined by geological substrate of the soils formed in valleys of big rivers in Serbia is 57.8 mg/kg. In our study, average concentration of Cr was about 49 mg/kg. Chromium concentration was not influenced by the distance from the pollutant sources indicating the geological origin of Cr that is confirmed by 61.48% of PC1 loading.

Copper (Cu): average concentrations of Cu in studied soils were 42.58, 26.38, 25.69 mg/kg, respectively, in the impact zones and 26.55 mg/kg in zone IV, showing that only zone I had concentrations of Cu higher than natural background (34.2 mg/kg) in studied soils. Content of Cu in our research was about 2–4 times higher than reported by Ozkul (2016). As PCA analyses showed, the most of Cu is of anthropogenic origin. This might be due to very intensive agricultural

production with application of chemicals that often contains copper compounds in the studied area.

Nickel (Ni): average concentration of Ni in soils of big river valleys in Serbia is 75.75 mg/kg. Average concentrations of total Ni in studied soils were 79.45, 72.88, 60.86 and 49.93 mg/kg in zones I, II, III and IV of impact. About 40% of soil samples showed concentrations of Ni exceeding MAC but below remediation values. The largest accumulation of Ni in the zones of impact might indicate the anthropogenic origin of the Ni, because this metal is relatively heavy and is not transformed into gas like As during the burning thus precipitating close to the chimney (Helble et al. 1996).

Lead (Pb): average natural concentration of Pb in river valleys in Serbia is 53 mg/kg. Although studied soils showed average content of Pb much lower than the natural background, almost twice higher concentration of Pb was observed in zone I of impact than in the other zones, indicating an anthropogenic origin of Pb accumulation in zone I. Three samples from zone I showed concentrations of total Pb between 85 and 170 mg/kg that is near and little above of MAC value. Although Zhai et al. (2009) found moderate contamination with Pb of mine-plant soil due to the influence of traffic using leaded petroleum, in our case, this option is excluded since the studied agricultural soils were not affected to the permanent heavy traffic.

Zinc (Zn): average natural concentrations of Zn in river valleys in Serbia are 70.8 mg/kg (Mrvic et al. 2013). In the studied soil, average Zn concentrations were 78.31, 72.85, 68.00 and 68.84 mg/kg, in zones I, II, III and IV of impact. No sample exceeded the MAC concentration of Zn.

Except Ni, only few samples showed somewhat higher concentrations of certain trace elements: one sample showed total Zn value lower than MAC; two samples showed Pb concentration exceeding MAC in zone I; one sample showed concentration of Cr and Cu above MAC.

About 40% of samples have total content of Ni above MAC but below the remediation value. Most of the contaminated sites are located on the Fluvisols mainly along Danube river bank. Total Ni content showed the highest concentrations in the soils of zone I.

An influence of distance from the pollutant was observed for the Cu, Ni and Pb, where Cu and Pb showed significant decrease in the zones II, III and IV

Table 7 Total variance and component matrixes (three factors selected) for microelements

Component	Initial eigenvalues			Extraction sums of squared loadings			Rotation sums of squared loadings		
	Total	% of Variance	Cumulative %	Total	% of Variance	Cumulative %	Total	% of Variance	Cumulative %
<i>(a) Total variance explained*</i>									
1	4.54	56.793	56.793	4.54	56.793	56.793	3.922	49.03	49.027
2	1.34	16.772	73.565	1.34	16.772	73.565	1.963	24.54	73.565
3	0.963	12.039	85.605						
4	0.598	7.476	93.081						
5	0.272	3.397	96.478						
6	0.189	2.361	98.839						
7	0.058	.719	99.559						
8	0.035	.441	100.000						
Element	Component matrix ^a **			Rotated component matrix ^{***}					
	PC1		PC2	PC1		PC2			
<i>(b) Component matrixes</i>									
As	0.511		0.307	0.323		0.500			
Cd	0.667		− 0.105	0.645		0.199			
Co	0.903		− 0.296	0.941		0.132			
Cr	0.945		− 0.241	0.954		0.200			
Cu	0.413		0.845	− 0.002		0.941			
Ni	0.899		− 0.281	0.931		0.143			
Pb	0.560		0.545	0.262		0.736			
Zn	0.915		0.008	0.818		0.410			

*Extraction method: principal component analysis

**Extraction method: principal component analysis. a. 2 components extracted

***Extraction method: principal component analysis. Rotation method: Varimax with Kaiser Normalization. Rotation converged in 3 iterations

compared to the zone I of impact, while concentrations of Ni were similar in the zones I, II and III and significantly less in zone IV (Table 3).

For tracking the sources of microelements accumulation and the level of their ecological risks in the soils around the thermal plant, an assessment of pollution indices and PCA analyses were performed.

Pollution indices

A single pollution index (P_i) showed that the soils in the zones I, II and III are moderately polluted with Ni ($P_i > 1$), and the soil in the zone I is moderately polluted with Cu. The integrated Nemerow pollution index (NIPI) allowed to identify the classes of pollution for the impact zones, where the zone I is low polluted (NIPI = 1–2), the zones I and III are in

the warning line of pollution (0.7–1), and the zone IV is unpolluted (< 0.7) (Table 4).

A single ecological risk factor showed that only Cd showed medium risk level in the impact zone IV ($E_i = 30.8$); it was near the border of non-polluted ($E_i < 30$). The overall ecological risk (RI) for all the zones was classified as a slight risk level, that is, the least risk class (RI < 40).

An enrichment factor (EF) revealed a moderate pollution with Pb (EF > 2) in zone I, and two samples showed the EF between 5 and 20 that is classified as considerable pollution (Table 5). The same samples showed moderate pollution with Cu as assessed by EF (2–5).

The pollution and risk indices showed no pollution with As, except the enrichment factor (EF) with maximum value in zone I 5.88, which classifies the

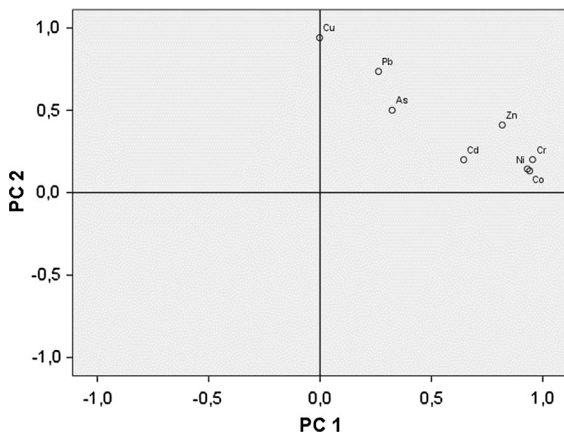
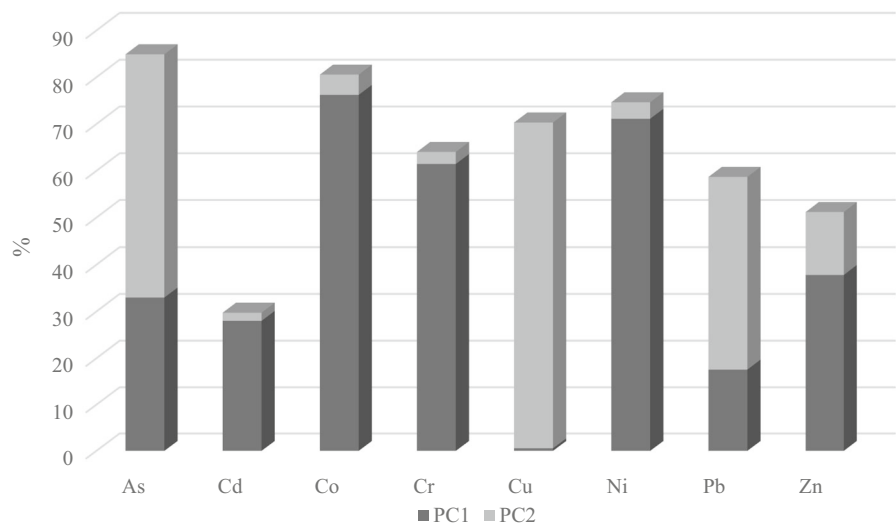


Fig. 3 PCA loadings of the microelements assessed by multivariate analysis of microelements in 0–30 cm soil surface in coal mining and thermal power plant Kostolac

soil into considerable polluted level due to the only sample containing 54.12 mg As/kg soil that was near the remediation value (55 mg/kg) (Official gazette of RS 88/2010) and far above the mean range for soil at world scale (4.8–8.4 mg/kg, Kabata-Pendias and Mukherjee 2007). On zone IV, the maximum EF value was 2.7, what classifies the soil as moderately polluted (EF = 2–5).

The presence of As in zone IV can be explained firstly, by its air deposition with fly ash since gaseous As is easily transported and deposited by air and due to the flooding in 2014 when dissolved As migrated from the damp with withdrawing water (Adriano 2001) and secondly by its geological origin.

Fig. 4 Loadings of factors for individual elements assessed by multi-linear regression analysis



According to the single pollution index (P_i) and the enrichment factor (EF), zone I is considered as moderately polluted with Cu. However, there was no observed pollution risk (E_i) by Cu, because only 16% of samples showed concentrations above MAC, but below the remediation value.

As expected, pollution index (P_i) for Ni in zones I, II and III showed moderate pollution level. Moreover, mainly due to the values of Ni, the NIPI showed low pollution level in zone I and warning line pollution in zones II and III. Similarly, mainly Ni determined that overall ecological risk (RI) showed slight risk level for zones I, II and III, while Cd was responsible for the slight ecological risk in zone IV. The obtained content of the studied microelements and their EF are within a range of other similar studies (Saha et al. 2017), except Ni, whose higher concentration is appeared to be of geological origin in most of the samples as explained in the next section.

Identification of the sources of heavy metals by principal component analysis (PCA)

The Kaiser–Meyer–Olkin measure and Bartlett’s test showed suitability of the PTE data for factor analysis (Table 6) (Hinton et al. 2004).

PCA results showed that eigenvalues of the two components explain 73.565% of all data variation (Table 7). In the rotated component matrix, the first PC (PC1) variance of 49% included Cd, Co, Cr, Ni and Zn, while the second PC (PC2) variance of 24.54%

Table 8 Correlation coefficients between microelements in 0–30 cm surface soil

	As	Cd	Co	Cr	Cu	Ni	Pb	Zn
As	1							
Cd	0.200	1						
Co	0.379**	0.528**	1					
Cr	0.435**	0.568**	0.916**	1				
Cu	0.459**	0.135	0.176	0.197	1			
Ni	0.388**	0.446**	0.937**	0.935**	0.155	1		
Pb	0.113	0.371**	0.306*	0.376**	0.555**	0.361**	1	
Zn	0.351**	0.636**	0.766**	0.860**	0.374**	0.757**	0.538**	1

The values < 0.19 are regarded as very weak, 0.2–0.39 as weak, 0.40–0.59 as moderate, 0.6–0.79 as strong, > 0.8 as very strong correlation (Baxton 2008)

*Correlation is significant at the 0.05 level (2-tailed)

**Correlation is significant at the 0.01 level (2-tailed)

included As, Cu and Pb. The PC1 factor is defined as a natural factor, because the variability of microelements is controlled by geological substrate, while the PC2 is responsible for the anthropogenic factor.

It is conventionally accepted that factor loadings greater than 0.71 are considered excellent, and those less than 0.32 are considered as very poor (Nowak 1998). In our study, Co, Cr, Ni and Zn in PC1 rotated matrix had greater than 0.71 loadings, while Cu and Pb showed greater than 0.71 loading in PC2 rotated matrix. But it should be noted that the results of PCA did not include some factors that could have an impact as well (meteorological factor, decomposition factor, etc.).

Multi-linear regression analyses of PCA loadings revealed the loads of the components for the individual microelements (Figs. 3, 4). The Cu, Pb and As located in the upper left corner in Fig. 3, which correspond to 69.78% of Cu, 41.11% of Pb and 51.92% of As, accumulated in soil due to anthropogenic activities, while 0.56%, 17.59% and 32.99%, respectively, accumulated due to natural factor (Fig. 4).

Rotated component matrix of PCA analyses confirmed an anthropogenic source for Cu and Pb accumulation, which is also confirmed by the component loadings for individual microelements, while anthropogenic source of As is supported by 0.5 value in PC2 rotated matrix, and natural source of As is supported by 0.323 in PC1 rotated matrix. The anthropogenic origin of these three elements is also

confirmed by their close correlations. So, Cu was correlated only with As, Pb and Zn (Table 8).

PC1 is a factor of natural source, and PC2 is the factor of anthropogenic source of microelements.

High content of Ni in impact zones is of geological origin for 71.14% samples as shown in PCA, with 0.93 Varimax with Kaiser Normalization value. High concentration of As in the only sample (54.12 mg/kg) that is near the remediation value (55 mg/kg) is located near the damp, which determined that the PCA showed anthropogenic contamination with As of about 52% of samples. Hu et al. (2018) found that As, Pb and Cu in agricultural soils were mainly originated from mining activities in China.

In this study, anthropogenic origin of Cu accumulation might be due to the two sources: the air deposition from fly ash and the agricultural activities such as use of Cu-containing fertilization and pest control (Facchinelli et al. 2001). There are other reported investigations confirming that sources of Cu and Pb accumulation are often due to the anthropogenic sources via application of manure, sewage sludge and coal burning (Yang et al. 2014), while Ni is more associated with parent rocks.

Although the concentrations of Cd in zone IV showed medium pollution level as assessed by Ei index, there is no anthropogenic influence of Cd accumulation that is supported by the 28% loading of PC1 that corresponds to the geological substrate, and 1.74% is determined by PC2 corresponding to anthropogenic factor. Cadmium is present in coal fossil fuel

(Yang et al. 2014; Hu et al. 2018), what explains the medium pollution level assessed by single pollution index (Pi) in zone IV.

There were high correlation coefficients between the studied microelements, where all the correlations were positive (Table 7). Except Cu, all studied microelements were correlated significantly at $p < 0.01$ level. Copper was correlated only with As ($p < 0.01$), Pb ($p < 0.01$) and Zn ($p < 0.01$). Close correlations between Co, Cr, Ni and Zn indicate and confirm similar origin of these metals, which as assessed by PCA is from natural source. This is well correlated with the results of PCA loadings confirming an anthropogenic origin of Cu, As and Pb in top soils on the territory surrounding the thermal power plant. The absence of correlation between As and Pb that usually well correlated both geologically and anthropogenically, was due to the flooding when the dissolved As spatially redistributed over the area, while Pb opposite to As was most affected by zones of impacts. Arsenic behavior was observed to be remarkably different from other heavy metals in other studies. Hu et al. (2013) found that PCA and cluster analyses showed significantly different sources for As, where about 66.5% of soil samples showed deficiency to minimal enrichment of As, while As was present at significant to extremely high enrichment levels in 10.1% of the samples. In our study, the Varimax value with Kaiser Normalization for As showed that As loaded on both factor 1 (0.323) and factor 2 (0.500) with less than 0.71 value, but higher than 0.3. Enrichment maximum values higher than 2 were observed in zones I and IV, that may explain such loading of As. High concentration of As in zone I might relate to the power plant emissions and ash deposit, while moderately polluted EF in zone IV might be caused by both agricultural activities (fertilization, pest control) and air deposition due to power plant activities as well as by competition between phosphorus and arsenic ions (Peryea 1998). Addition of phosphate to As-contaminated soils might induce arsenate replacement through competitive anion exchange (Peryea 1998), thereby enhancing As release into the soil solutions. Phosphate fertilizers influence leaching of lead and arsenic in a soil contaminated with lead arsenate.

Conclusions

There were no established soil pollution and any limitations for agricultural production in the studied area, except for the one spot polluted by As.

Zone I showed to be the most vulnerable to potential contamination of soil by inorganic pollutants, namely by As, Cu and Pb, partly due to the operation of the thermal power plant and partly due to the other agricultural activities, such as fertilization.

PCA isolated two principal components that explained 73% of variance of the sources of studied microelements where As, Cu and Pb showed an anthropogenic origin for most of their content, while other elements (Cd, Co, Cr, Ni and Zn) were mostly of a geological origin. Although higher concentrations of Ni were of geological origin, this element due to its heavy weight is air-deposited close to the pollutant; therefore, it is necessary to closely monitor its concentration in zone I of impact.

The recommendations include permanent monitoring of heavy metal concentrations in soil, water and agricultural crop production around the Kostolac coal power plant with a focus on zone I of impact and hot spots that are potentially risky. This study has been continuing to establish the long-term effect of the thermal power plant on soil biological characteristics and plant by analyzing DTPA soluble form of potentially toxic and hazardous elements.

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