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Research on Power Plant Ash Impact on the Quality of Soil in Kostolac and Gacko Coal Basins

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Abstract: Increased concentrations of heavy metals in ash can adversely affect the microbiological and pedogenetic processes in soil. The aim of this paper is to determine the impact of ash from unburned coal generated in the Kostolac and Gacko coal basins on the quality of soil in the surrounding environment. The investigation included the surface soil layer that was sampled and tested during 2016 and 2017. A total of 30 samples of Kostolac soil and 9 samples of Gacko soil were analyzed for the content of 8 heavy metals: Cu, Pb, Cd, Zn, Hg, As, Cr and Ni. The analyses were carried out by inductively coupled plasma mass spectrometry (ICPMS) technique according to the EPA 6020A method and the following conclusions were made: Kostolac coal ash affects the quality of the surrounding soil in terms of Ni, Cu and Cr as evidenced by the moderately strong correlation of the Ni-Cu pair (k = 0.71), as well as the Cu-Cr pair (k = 0.73) and strong correlation of the Ni-Cr pair (k = 0.82), while the high recorded concentration of Pb, Hg, As and Zn is attributed to other sources of pollution, such as the traffic network and intensive farming activities, and in some cases, its impact is only local. All recorded concentrations of heavy metals are within the remediation values. The effect of ash on soil contamination in the surroundings of the Gacko coal basin is limited to Ni and Cd, with a strong correlation coefficient of this pair (k = 0.82). The recorded overrun of maximum allowed concentration of Cr is evidenced in only 2 samples, and in terms of this element the contamination of the Gacko soil can be considered to be local. It is concluded that prevailing winds play a part in soil pollution. Cluster analysis showed that Ni, Cr and Zn have very similar values in analyzed soil samples from both basins, while a cluster composed of only Hg, in the case of Gacko, indicates lower contamination with Hg compared to the other heavy metals.

Keywords: soil; ash; heavy metals; Kostolac coal basin; Gacko coal basin

1. Introduction

Coal is one of the most commonly used natural resources for electricity generation, which greatly contributes to environmental pollution, including the occurrence of acid rain and the greenhouse effect which causes temperatures to rise. As a natural resource, coal started forming over a few million years ago and as such it does not pose any environmental risk. However, coal-related activities, which are likely to lead to adverse environmental impacts, are coal mining, coal preparation and cleaning, storage and finally combustion for electricity generation [1]. The combustion of coal in power plants results in the emission of a wide range of pollutants, which once released into the air as transport medium reach the surrounding land where they are deposited and remain for years.

One of the main problems associated with electricity generation from coal-combustion is the so-called "energy-waste" issue. In our region, fly ash, bottom ash and unburned coal residues are considered as energy waste and they are very easily dispersed during and after deposition due to their fine granular size [2].

When analyzing the potentially harmful environmental impact of ash, it primarily applies to the ash disposed of in landfill sites, since only a small portion (about 1%) of total ash generated during coal combustion is released into the atmosphere through power plant stacks [3].

Even though the long-term effects of ash on soil chemical properties have not been sufficiently investigated, it is well known that these effects may be good and bad, such as improvement of physicochemical soil properties and heavy metal pollution of soil [4]. For example, changes in soil quality under the influence of ash can directly or indirectly affect the microbiological activity and a plant's root system [5]. Ash contains elements that are favorable for soil and plants, such as phosphorous, calcium and other nutrients required for plant growth and for increasing the water retention capacity of soil, and it does not fall into hazardous waste according to European Directive 2001/118/EC [6]. While containing elements that can be useful to soil and plants, ash gathered in heaps on landfills acts as an aggressive and adverse factor toward ecosystems [7]. The reason for such a controversial impact of ash on soil lies in the fact that some heavy metals and potentially toxic elements are found in unburned coal material. Ash constituents such as boron (B), arsenic (As), selenium (Se), molybdenum (Mo), vanadium (V), aluminum (Al) and cadmium (Cd) are considered to be extremely dangerous for plants, if accumulated in their habitat [5]. At increased concentrations, heavy metals affect primarily the microbiological characteristics of soil and necessarily disturb the soil's structure. The heavy metals accumulated in the soil also reach the plants and are inevitably transferred to animals and humans through the food chain.

This paper is focused precisely on coal ash and its intention is to determine if and to what extent ash as a residual of coal combustion in the power plants of the Kostolac and Gacko coal basins affects the quality of soil in the surrounding area. Serbia, (excluding Kosovo and Metohia) generates annually 5.5 million tons of ash, while in Bosnia and Herzegovina this quantity is about 1.8 million tons [8]. It must be emphasized that the quantities generated in the coal-fired power plants of the Kostolac Basin and Gacko basin, which are among the largest coal basins in Serbia and Bosnia and Herzegovina respectively, greatly contribute to these figures and therefore potentially pose a great danger primarily for the working environment, and then for the environment in general, since when it comes to mining, these two are often practically inseparable. In addition to this, the investigation described in this paper can also have a bearing on decision-making relating to the construction of new coal-fired power plants, such as, for example, CFPP Stavalj, in the southwest of Serbia [9].

Similar investigations were carried out in Croatia [10] and considered the impact of the coal-fired power plant in Plomin on the surrounding land. The samples taken were analyzed rare earth elements (REE) concentrations. The results show that the thermal power plant evidently has an impact on the surrounding land, but as expected the content of these metals decreases with the distance from the power plant. The results also demonstrate that fly ash emission from the power plant is more pronounced in the prevailing wind direction.

Mandal and Sengupta [11] analyzed soil contamination by heavy metals in the vicinity of coal-fired power plants in India. They sampled the soil in the area surrounding the ash landfill and analyzed the content of some heavy metals whose concentrations were consequently elevated. As there are no other industrial pollutants in the vicinity of the site, elevated concentrations of heavy metals in the soil were attributed to the impact of the ash landfill [11]. As in the case of Croatia, pollution is particularly pronounced in the prevailing wind direction.

Similar investigations were carried out in Slovakia where it was found that the concentration of arsenic in the soil near the thermal power plant was increased. Over its period of operation the power plant has contributed to raised levels of soil arsenic in the local soils, though not substantially of other elements, such as zinc, lead, copper, chromium and cadmium. Airborne arsenic emissions are controlled now, but concern remains regarding soil arsenic concentrations and fugitive emissions from the plant. It was concluded that arsenic concentrations in the soil were reduced to a radius of up to 5 km [12]. When it comes to distances at which heavy metal emissions from coal-fired power plants affect the quality of the land, Mehra et al. [13] have established from analyzing the land surrounding the Delhi Thermal Power Plant that this distance is about 4 km, hile Agrawal et al. [14] have determined even more precisely that the concentration of heavy metals is between 2 and 4 km in relation to the power plant, in the prevailing wind direction.

The concentration of heavy metals is up to 10 times higher in ash than in the coal from which it was generated. It is due to the loss of organic components during volatilization and enrichment of inorganic heavy metals [15]. Depending on the origin of coal, its pre-combustion preparation and combustion technology, the chemical characteristics of fly ash and bottom ash can vary significantly [16]. Table 1 shows the maximum values of investigated heavy metals in ash that were obtained from the chemical analyses made within the framework of numerous studies carried out worldwide [17], as well as the results of analyses of Gacko and Kostolac ashes that were made for the purposes of this paper. Collected data are shown together to compare local and worldwide results.

Table 1. Maximum values of investigated heavy metals in ash [17].

Chemical Element (mg/kg)	Cu	Pb	Cd	Zn	Hg	As	Cr	Ni
Ash, worldwide	N/D	35	<250	950	<4	4000	270	700
Ash, Kostolac	281	45	0.87	189	1.3	141.2	428.3	219
Ash, Gacko	550.3	56.5	5.9	374	0.2	94	482.1	505.2

Based on the data presented in Table 1 it is possible to conclude that the maximum concentrations of cadmium (Cd), zinc (Zn), arsenic (As) and nickel (Ni) in Kostolac and Gacko ashes are far below the maximum values of these elements as recorded worldwide. However, this cannot be applied to lead (Pb) and chromium (Cr) concentrations. Also, if we compare ashes themselves, much higher values of Cu, Cd, Zn and Ni and slightly higher values of Pb and Cr are recorded in Gacko ash, while much higher values of Hg and As are recorded in Kostolac ash.

The aim of this paper is to:

- Determine the impact of ash from unburned coal generated in the Kostolac and Gacko coal basins on the quality of soil in the surrounding environment, and
- Evaluate how tolerable the determined impact is, compared to the permissible concentration prescribed by the relevant legislation.

2. Materials and Methods

Kostolac coal basin specifically designates the area of the Municipality of Pozarevac and is located in the northeast of Serbia, about 90 km east of Belgrade, Figure 1a. This basin extends over an area of 100 km^2. Kostolac coal basin occurs in Upper Miocene (Pontian, $M_3{}^2$). Soft brown coal is related to sandy-clayey sediments, i.e., to clastic depositional environments. According to the huminite/vitrinite reflectance (Rr) of coals from Kostolac coal basin have been classified as soft (Low-Rank C, ECE-UN, 1998–2000). The mean the huminite/vitrinite reflectance (Rr) of the soft brown coal (M_1) is 0.30% ± 0.03% Rr [18]. Coal from Kostolac coal basin is mainly used in the coal-fired power station, while smaller amounts are supplied to the open market. The Coal-Fired Power Station Kostolac (TEKO) consists of two production plants—TEKO A and B, which participate in the annual electricity production of the Republic of Serbia with about 14%. To produce energy the plants burn lignite from the Drmno mine, generating large quantities of fly and bottom ash, which is disposed of in nearby landfills. Annual production of ash in the Coal-Fired Power Station Kostolac is about 740,000 tons. The plants TEKO A and B have two currently active landfills of fly and bottom ash. The landfill Central Kostolac Island (SKO) has been active since the beginning of operations of the Kostolac coal-fired power plants and it is scheduled for use for next 5 years. It consists of 3 cells, A, B and C, with a total area of about 276 ha. Since May 2015, cell B, measuring 56 ha, has the status of an operating landfill cell, and cell C, which had previously been active, has now become an emergency backup landfill cell. Cell A is backfilled to the maximum and partly reclaimed. Since 2011, another landfill has been activated in the abandoned surface mine Cirikovac, which was used for fly and bottom ash disposal from TEKO B. Cirikovac landfill occupies 20 ha of hydro-technically treated and hydro-isolated area, with a view to using all 130 hectares in future and it is scheduled for use during next 20 years [19]. Kostolac ash falls into the category of silicate ashes with SiO_2 content of over 50% [2].

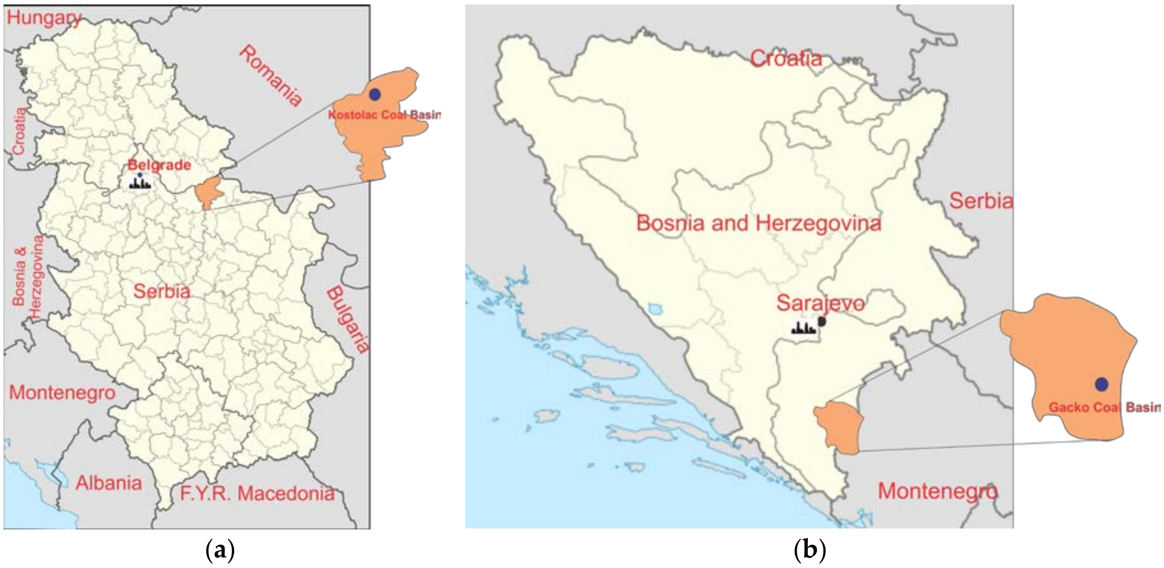

Figure 1. Map of Serbia with the location of the Kostolac coal basin (**a**); Map of Bosnia and Herzegovina with the location of the Gacko coal basin (**b**).

Gacko coal basin is located in Gacko Polje in the southeastern part of Bosnia and Herzegovina in the Republic of Srpska, approximately 140 km south of Sarajevo, Figure 1b. It extends over an area of about 40 km^2 at an altitude of about 940 m, in a typical karst area. The optimum climatic conditions of the Middle Miocene (Langhian, Badenian, $M_2{}^1$) stimulated formation of a perennial lake in the Gacko Basin. The lignites in the lower part of the basin infill indicate a vast swamp environment dominated by taxodiacean forests that extended across the whole basin. Coal is represented by a soft-brown coal (lignite) with the following average quality values at the studied site: total moisture 37.4% a.r., ash 15.1% a.r., total sulfur 1.22% a.r. and net caloric value 9.623 kJ/kg [20]. Annual production of ash in the Gacko Coal-Fired Power Station is about 400,000 tons [21,22]. Gacko ash falls into the category of calcium ashes with CaO content of over 60% [2]. The currently active landfill has been used for fly and bottom ash disposal since 1995 and is situated in the excavated area of the surface mine Gracanica, and currently consists of two active ash cells. The landfill is located west of Gacko City and of the Gacko Coal-Fired Power Station, at approximately 1000 m of airline distance.

Gacko coal basin is surrounded by pastures and meadows, while in the vicinity of the Kostolac coal basin there are agricultural lands with intensive farming that belong to the farmstead of Hrastovaca.

This paper presents the results of chemical analyses made on soil samples collected in the vicinity of subject locations to establish the content of the following heavy metals: copper (Cu), lead (Pb), cadmium (Cd), zinc (Zn), mercury (Hg), arsenic (As) (Cr) and nickel (Ni), and determine the potential soil contamination caused by the presence of ash. Since the petrographic characteristics of lignite coal seams are very similar in these two basins, it seemed appropriate to make a comparative analysis of their respective impacts. Both groups of results were compared to the permissible concentration prescribed by the relevant legislation.

For Kostolac coal basin, the basic document used to compare the results obtained with the permissible concentration of elements in soil is the "Regulation on the program of systematic monitoring of soil quality, the indicators for risk assessment of the soil degradation and methodology for development of remediation programs" [23], and for Gacko coal basin the "Rule book on allowed quantities of hazardous and noxious materials in agricultural land and water for irrigation and methods for their examination" [24].

During 2016, in the surrounding area of Kostolac coal basin a total of 30 samples were taken from the surface soil layer and during 2017, 4 samples were collected in the vicinity of Gacko coal basin. The sampling activities were performed by the Geoing Group from Belgrade and the laboratory analyses were carried out in the laboratory of the Institute of Mining and Metallurgy in Bor. Samples were collected from the study area according to prevailing wind direction. Before sampling, surface litter was scraped away, at each area. Topsoil samples were collected with a shovel, packed into plastic bags, labeled and transported to the laboratory. The weight of each sample was approximately 1 kg. Since heavy metals are usually deposited in the surface soil layers that are suitable for growing agricultural crops [25], this 30 cm thick surface soil layer was precisely the subject of investigation in this paper.

Before the laboratory work, samples were air dried for 3 days. The analyses were carried out by inductively coupled plasma mass spectrometry (ICPMS) technique according to the EPA 6020A method. The recording was performed on Agilent 7700 (Agilent Technologies, Santa Clara, CA, USA). Samples were dissolved in aqua regia (recommended for soil samples) in duplicate (0.5 g of soil sample + 10 mL AR ($HCl:HNO_3$ = 3:1). The mercury content (Hg) is determined by the atomic absorption spectrophotometer (FIMS 100, Perkin Elmer, Waltham, MA, USA). The reagents used were HNO_3 (p.a.), HCl (p.a.) and the standard Hg solution of 1000 ppm.

Over the period 2011–2013, within the framework of the biological reclamation of the surface mine Gracanica [26], 5 samples were collected from the soil in Gacko surroundings. The samples were tested in the laboratory of the Agriculture Institute of Republic of Srpska in Banja Luka and the results of chemical analyzes were combined with the results of the new tests (Table 3). The locations of soil samples collected in the vicinity of Kostolac and Gacko Basins are shown in Figure 2a,b.

All samples were analyzed for concentrations of 8 elements: copper (Cu), lead (Pb), cadmium (Cd), zinc (Zn), mercury (Hg), arsenic (As), chromium (Cr) and nickel (Ni).

The results were statistically processed using PAST 3.14 software (Natural History Museum, University of Oslo, Oslo, Norway) and Microsoft Excel. The basic descriptive statistical parameters, correlation tests with level of significance set at $p < 0.05$ and cluster analysis was performed in each case.

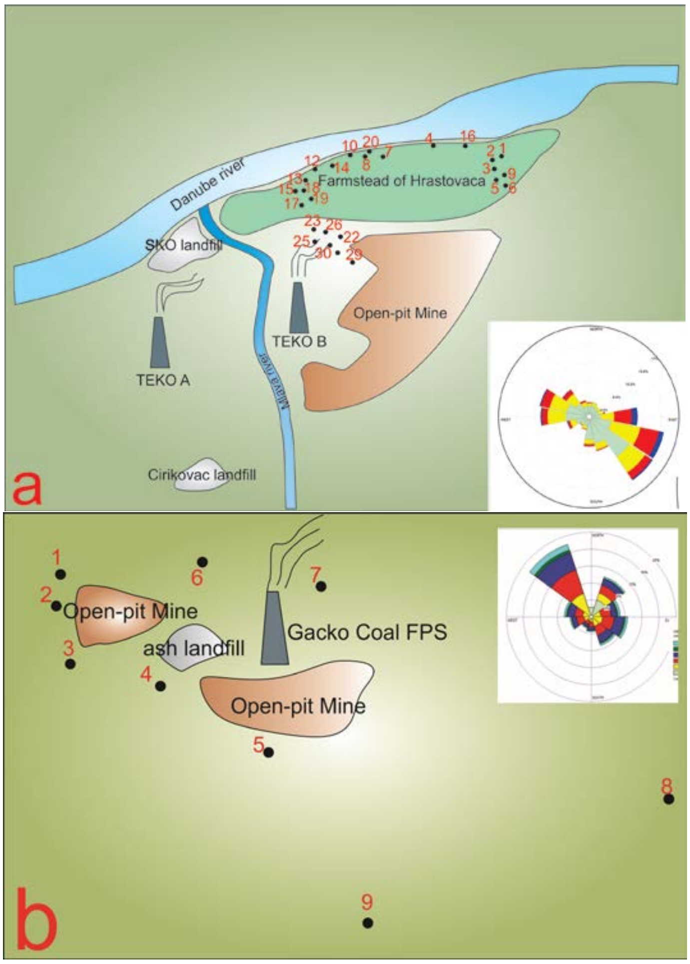

Figure 2. The locations of soil samples collected in the vicinity of Kostolac coal basin (**a**) and Gacko coal basin (**b**).

3. Results

Tables 2 and 3 show the results of chemical analysis of heavy metal content in soil samples near the Kostolac and Gacko basins for copper (Cu), lead (Pb), cadmium (Cd), zinc (Zn), mercury (Hg), arsenic (As), chromium (Cr) and nickel (Ni). The results are compared with the prescribed limit values in compliance with relevant legislation.

The results in Table 2 show non-permissible concentration in Kostolac soil for copper (Cu), lead (Pb), zinc (Zn), arsenic (As), chromium (Cr) and nickel (Ni), but at the same time their content is lower than prescribed remedial values for stated elements according to the stipulations laid down in the "Regulation" [23].

The results in Table 3 show non-permissible concentrations for cadmium (Cd), chromium (Cr) and nickel (Ni) in Gacko soil, according to the "Rule book" [24].

Table 2. Results of chemical analyses of heavy metal content in soil samples collected in the surroundings of Kostolac coal basin.

Chemical Element (mg/kg)	Cu	Pb	Cd	Zn	Hg	As	Cr	Ni
Annual values	36	85	0.8	140	0.3	29	100	35
Remediation values	190	530	12	720	10	55	380	210
1	92	68.2	0.4	109.5	0.24	21.3	88.4	140.8
2	57.3	88	0.61	130.7	0.19	28.4	113	185.3
3	50	77.1	0.5	114	0.17	25.5	95.4	162.1
4	52	94	0.68	143	0.25	33.4	106.4	175
5	45	71	0.44	100.1	0.2	25	94	161.5
6	56.1	72.2	0.56	98.5	0.22	22	84.1	148.4
7	47.3	78.4	0.67	129.5	0.22	26	94	155.5
8	32	69.1	0.55	97.8	0.24	21	71.2	112.2
9	30	59	0.45	71.6	0.21	18.5	68.4	103
10	19	33	0.27	48.9	0.15	11.1	43	62.2
11	28.1	57.5	0.43	80.7	0.21	17	59.2	94
12	25	49	0.35	77	0.19	16.3	51.2	85
13	20	41.4	0.28	67.9	0.14	14	53	80
14	17.4	40.5	0.3	66	0.15	13.5	45	70
15	246	53.4	0.35	82.3	0.27	16	57.5	86.3
16	40.5	86.2	0.77	129.9	0.21	25	82.2	135
17	32.1	69	0.43	101.5	0.11	23.3	77.4	130
18	47	90	0.54	132.5	0.21	25.5	103.1	161.1
19	30	62.1	0.37	87.2	0.41	20	67	116
20	10	34.7	0.41	69.2	0.16	21	44.4	75.2
21	20.2	78	0.33	83.5	0.14	20.1	67	110.1
22	42	81.2	0.4	94.2	0.26	22.2	91	129
23	64	123	0.49	118.7	0.34	27	107	158.3
24	40	91.4	0.45	99.2	0.26	27	102	149.2
25	42.1	80	0.33	86.4	0.24	21.1	88	126
26	32	70	0.24	65.3	0.36	17	82	126
27	37	61	0.36	88.9	0.52	23	100	144
28	32.2	28	0.23	59.4	0.1	17.3	92.5	140
29	34	89	0.34	84	0.39	15.3	83	107
30	38	235.3	0.26	59.3	4.1	14	67.2	94

Table 3. Results of chemical analyses of heavy metal content in soil samples collected in the surroundings of Gacko coal basin.

Chemical Element (mg/kg)	Cu	Pb	Cd	Zn	Hg	As	Cr	Ni
Limit value [1] (mg/kg)	90	100	1	150	1	15	80	50
1	46	20	1.7	88	0.05	4.5	88	119
2	49	25	1.6	83	0.05	2.5	82	104
3	36	19	1.9	70	0.05	5.5	80	111
4	21	23	2	85	0.05	3.5	72	107
5	27	21	1.8	80	0.05	4.2	76	116
6	66	28	1.5	45	0.05	13.7	50.4	89
7	56.3	32	1.1	91.3	0.05	5.4	28	42.1
8	46	30.3	0.92	51.2	0.05	8.4	28.3	28.2
9	45	31.2	1	29.4	0.05	8.5	40.4	52

[1] For powdery-loamy soil according to the "Rule book" ("Official Gazette of the Republic of Srpska") [24].

Figure 3a,b shows the graphical presentation of the basic descriptive statistical parameters of the concentrations present in the soil samples collected in the coal basins that are investigated here: median, standard deviation and range. The largest variation intervals, if we consider the outliers, can be noticed in the case of lead (Pb) (in Kostolac), Figure 3a. Generally, if we compare the results of soil analyses from these two coal basins, the concentrations of almost all the analyzed heavy metals are higher in Kostolac, although Gacko ash has higher concentrations of half of analyzed heavy metals, Table 1.

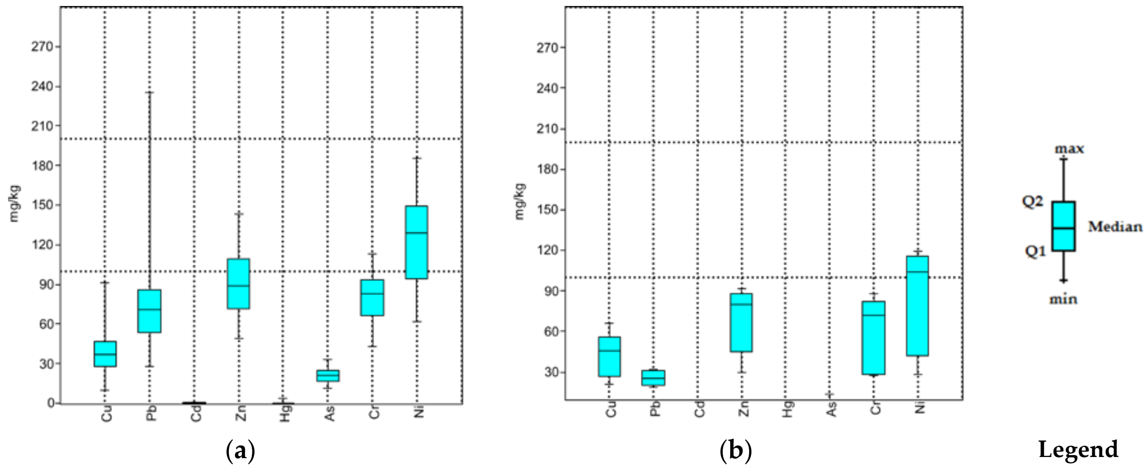

Figure 3. Graphical presentation of descriptive statistical parameters of analyzed concentrations of elements in Kostolac soil (**a**) and Gacko soil (**b**).

In order to get a better understanding of the results obtained, it was decided to determine their distribution and test their correlation. The Shapiro-Wilk test was applied to test the data normality [27], considering that the available sample was small (<50) [28]. For data normality testing the usual significance threshold of $\alpha = 0.05$ was applied and finally the null hypothesis was set up:

H_0—The sample is from normal distribution.

If $p > \alpha$, the null hypothesis is accepted and assumes that data have a normal distribution, otherwise it is rejected.

From the data presented in Table 4, one can draw the conclusion that in the case of Kostolac soil, 6 of 8 variables have normal distribution, whereas in the case of Gacko soil, all the 8 variables have normal distribution. However, since the soil analysis data for selected chemical elements were obtained from a relatively small number of samples; i.e., 30 samples of Kostolac soil and 9 samples of Gacko soil, it was necessary to adopt the nonparametric statistical procedures, which are usually recommended in such situations [29]. Therefore, for data correlation analysis, it was appropriate to apply a non-parametric correlation method—Kendall's Tau matrix.

Table 4. The Shapiro-Wilk normality test applied on the results of heavy metal content in the surroundings of Kostolac and Gacko coal basins.

Chemical Element	Cu	Pb	Cd	Zn	Hg	As	Cr	Ni
				Kostolac soil				
Shapiro-Wilk W	0.934	0.7362	0.9486	0.9642	0.2796	0.9808	0.9547	0.9721
p (normal)	0.06259	5.483×10^{-6}	0.1548	0.3954	4.771×10^{-11}	0.8475	0.2252	0.5993
				Gacko soil				
Shapiro-Wilk W	0.9656	0.9042	0.9087	0.8732	1	0.8764	0.8696	0.8433
p (normal)	0.8548	0.2776	0.3068	0.1332	1	0.1438	0.1218	0.06279

The null hypothesis was set up to perform correlation testing:

H_0—There is no correlation between variables.

If $p > \alpha$, the null hypothesis is adopted and it can be considered that there is no correlation between the two variables, otherwise it is rejected. The correlation coefficient (k) indicates correlation strength and sign. Finally, $\alpha = 0.05$ is adopted as the significance threshold and Kendall's Tau correlation matrix was calculated.

In the case of the Kostolac soil (Table 5), there is a positive strong correlation between the Cr-Ni pair ($k = 0.82$), while between the pairs of elements that are in bold there is a moderate positive correlation.

Table 5. The Kendall's Tau correlation matrix for the case of the Kostolac soil.

Chemical Element	Cu	Pb	Cd	Zn	Hg	As	Cr	Ni
Cu		0.00013217	0.0014736	1.3112×10^{-5}	0.14637	1.3282×10^{-5}	1.5379×10^{-8}	3.7686×10^{-8}
Pb	0.49252		0.0010912	1.2365×10^{-5}	0.010556	6.065×10^{-5}	5.7341×10^{-5}	0.003847
Cd	0.40973	0.42082		1.9516×10^{-7}	0.7704	2.605×10^{-6}	0.0035716	0.00043627
Zn	0.56157	0.56322	0.67053		0.5256	1.893×10^{-8}	6.0626×10^{-6}	1.7189×10^{-7}
Hg	0.18716	0.32948	0.037605	0.081787		0.63611	0.16162	0.54953
As	0.5612	0.51673	0.60557	0.72434	0.060966		1.6084×10^{-7}	1.5377×10^{-8}
Cr	0.72895	0.51843	0.37544	0.58295	0.18035	0.67514		1.7259×10^{-10}
Ni	0.70886	0.45747	0.45319	0.67356	0.077113	0.72895	0.82258	

It is interesting that all analyzed element pairs showed a positive correlation, which indicates their possible common origin [30], especially in the case of Cr-Ni.

In case of Gacko soil, the results are more variable and fewer elements are in correlation, if compared to Kostolac soil. There is a strong positive correlation in the case of the following pair:

- Cr-Ni ($k = 0.87$), and
- Cd-Ni ($k = 0.82$).

A strong negative correlation exists between pairs:

- Pb-Ni ($k = -0.90$), and
- Pb-Cr ($k = -0.85$).

Moderate positive correlation was observed in the pair Cd-Cr ($k = 0.65$), while a moderate negative correlation was found for Pb-Cd pair ($k = -0.61$).

As opposed to Kostolac soil, in Gacko soil it is possible to observe a lot of element pairs that have no common origin, which can be determined with certainty, given the high negative correlation coefficient, which is most often in the case of lead with other heavy metals.

Cluster analysis (CA) of heavy metals values in soil samples was performed with the aim to optimize the heterogeneity between elements, as well as the homogeneity within them [31]. Ward's method based on Euclidean distance measure was used. Data were log-transformed prior to analysis. The results are presented as dendrograms (Figure 4a,b).

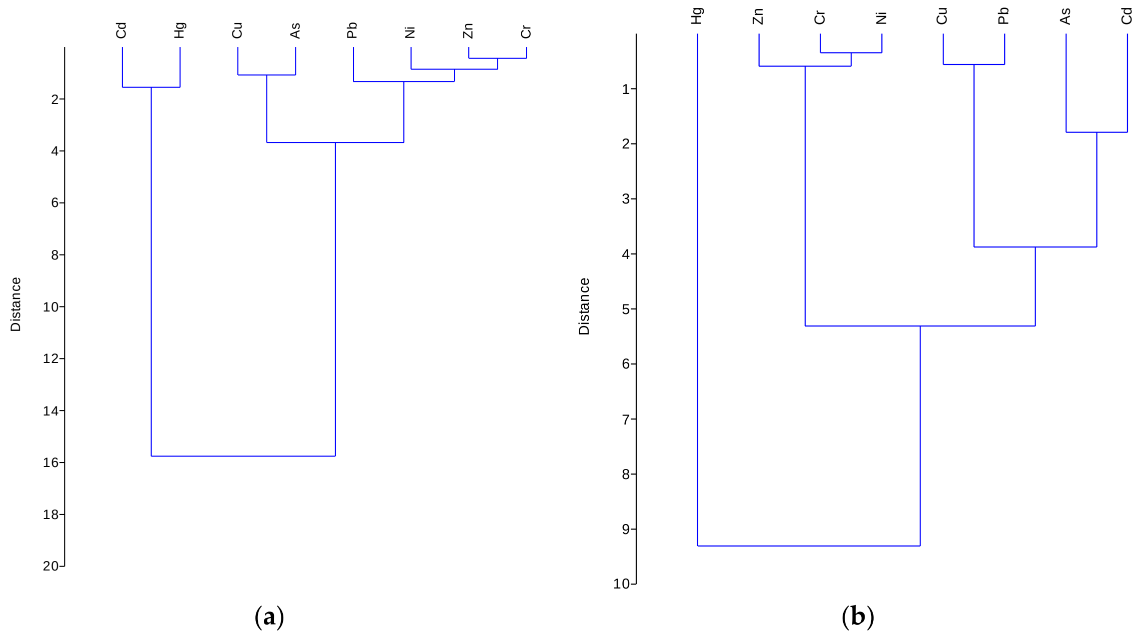

Figure 4. Dendrogram derived from the CA of analyzed concentrations of elements in Kostolac soil (**a**) and Gacko soil (**b**).

Two clusters can be noticed in the case of Kostolac soil, Figure 4a. The first cluster includes Cd and Hg, while Cu, As, Pb, Ni, Zn and Cr are grouped in the second cluster, which is composed of two sub-clusters. The first sub-cluster includes Cu and As, while the second one is composed of strong association between Zn and Cr, which are associated with Ni and Pb at later stages.

Two clusters can be noticed in the case of Gacko soil, too. The first cluster includes only Hg, Figure 4b. The second cluster consists of all other heavy metals, Zn, Cr, Ni, Cu, Pb, As and Cd. This cluster includes 3 sub-clusters. Strong association is observed between Cr and Ni, which are associated with Zn at later stage. Also, two sub-clusters can be noticed between Cu and Pb and As and Cd. Elements from the same clusters have very similar concentrations.

4. Discussion

In the case of Kostolac soil the concentrations of nickel (Ni), copper (Cu) and lead (Pb) were the most critical (see Table 2), while in Gacko soil this was the case with nickel (Ni) and cadmium (Cd) (see Table 3).

In the samples of soil collected in both basins, nickel (Ni) is the element that particularly stands out for its high concentrations. Nickel (Ni) values in almost all the samples substantially exceed the limit values. The primary minerals from magmatic wall-rocks, which are the parent substrate from which the soil profile has developed, represent the natural source of nickel in the soil [32]. Other sources of nickel are coal-fired power stations and agricultural activities that include the use of waste slurries, phosphorus fertilizers, pesticides, etc. In the world, the average concentration of Ni in the soil is determined at 40 mg/kg of soil [33], while in most cases the concentrations range from 10 to 50 mg/kg [34]. Also, organic matter has an extraordinary ability to absorb nickel, and as such it can be brought into connection with ash [35]. Although the origin of Ni in the soil is very variable and it is difficult to focus on just one source of emission, the impact of ash is undeniable.

In the area surrounding the Kostolac coal basin, nickel was previously shown to have an increased concentration, but its usual concentration ranged from 50 to 100 mg/kg [36]. In this case, we have a very evident impact of Kostolac coal-fired power stations with ash landfills and also the influence of the farmstead of Hrastovaca, which has been active since 1980 and is engaged in crop farming, livestock rearing and seed production. In the case of Gacko, since we have predominantly pasture areas with no major agricultural activities for the moment, the impact can be attributed only to coal combustion activities and by-products.

The element that exceeds the limit value in 15 samples collected from the Kostolac soil is copper. The average copper content in the lithosphere is 70 mg/kg and in the Earth's crust it ranges from 24 to 55 mg/kg [37]. The correlation coefficient of 0.71 for the pair Cu-Ni indicates their common origin and the fact that Kostolac ash is their main source. The samples collected from Gacko soil did not show an exceeding of the limit value of this heavy metal.

Chromium is released into the environment primarily from coal combustion processes and it can reach the soil through disposal of waste slurry. Increased chromium content in soil surface layers was recorded in the vicinity of anthropogenic sources, for example in the vicinity of industrial waste disposal sites and in agricultural land after the use of phosphate fertilizers [35]. Other smaller sources include wear or Cr-containing asbestos brake linings in vehicles, which can have impact on roadside soils [37]. A strong correlation of the Ni-Cr pair was evidenced in soil samples collected from the land that surrounds both coal basins, indicating their common origin. Interestingly, the high concentration of these heavy metals in the soil is a very common occurrence in the vicinity of coal-fired power plants and many studies concluded that lignite combustion and its unburned residuals are responsible for this situation [38–41]. Since the limit value of chromium is exceeded in only 5/30 samples collected from Kostolac soil and in 2/9 samples collected from Gacko soil, when it comes to chromium, the impact of coal ash on the soil quality in analyzed coal basins cannot be estimated as significant. For both of basins, Cr, Ni, and Zn are in the same sub-cluster, which means that their values are very similar.

In the area of Kostolac basin, the dominant winds are from south-southeast, west and west-northwest direction. The assumption is that increased concentrations of Ni, Cu and Cr in the soil are due to west wind, on whose path is the SKO landfill.

For better clarity of obtained results, Figure 5a,b show the maximum recorded concentrations of the heavy metals analyzed in Kostolac and Gacko ash and soil, from which it is possible to notice some particularities. Higher maximum concentrations of lead and mercury were recorded in Kostolac soil samples, which was not to be expected. This difference is particularly pronounced in the case of lead.

As seen from Figure 5b, such particularities cannot be noticed in the Gacko soil, except in the case of Hg, whose concentration is just a little higher in the soil.

The lead concentrations in the soil near the traffic routes reach values of several hundreds and even over 1000 mg/kg. In addition to combustion of leaded petrol in internal combustion engines, the agricultural use of waste slurries also contributes to the contamination of soil. In the past, a significant source of lead in the soil was the use of lead-arsenates as insecticides [35].

Although unburned coal residues and mineral fertilizers usually represent the main source of mercury in the soil, pesticides can also be a significant source. However, it is very important to emphasize that mercury has the tendency to transform and volatilize in the presence of microorganisms in the soil [42]. The lack of significant correlation between Hg and the other heavy elements suggests that its sources were quite different from those of the others. This is the case for both basins.

In the area surrounding the analyzed soil in Kostolac, there is a network of local roads with active traffic. It is a well-known fact that lead is retained at a distance of 100 m from busy traffic roads. Besides, a large number of samples taken in the vicinity of Kostolac coal basin were collected at the farmstead of Hrastovaca.

On account of that, it could be concluded that apart from ash disposed of at the landfills, there are other emission sources that could also be responsible for Pb and Hg concentrations.

The concentrations of arsenic and zinc are only slightly above the limit values in only one Kostolac soil sample (see Table 2). The occurrence of arsenic in coal is very frequent [43], although the occurrence of arsenic in soil more frequently results from the use of pesticides in agriculture [35].

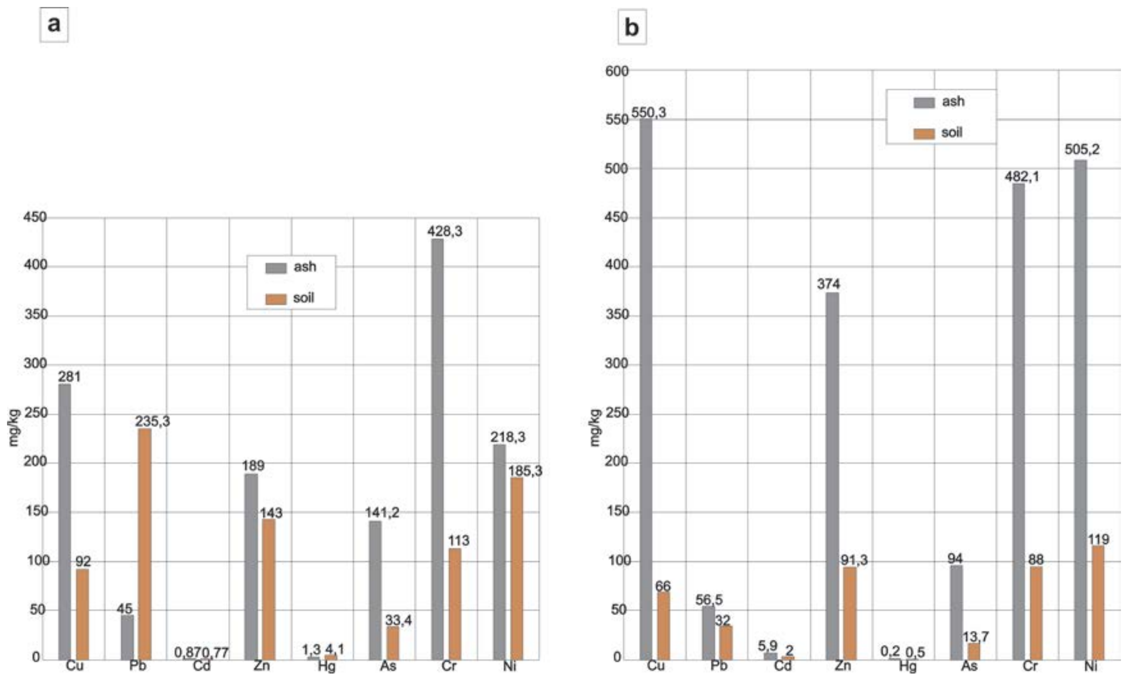

Figure 5. Comparative bar graph of maximum concentrations of elements analyzed in the ash and soil: (**a**) in the area surrounding the Kostolac coal basin; (**b**) in the area surrounding the Gacko coal basin.

Its occurrence in nature is conditioned by many factors, such as the origin of coal and epigenetic processes [44]. The same applies to zinc. Since the presence of arsenic was detected in only one of the 30 analyzed samples, it is safe to say that the contamination of soil by arsenic is only local.

The soil samples collected in the Gacko area showed that the concentrations of Pb, Hg, As and Zn are within permissible values. A cluster composed of only Hg, (Figure 4b), indicates lower contamination with mercury compared to the other metals. Lack of correlation between Hg and other heavy metals, and negative correlations of Pb-Ni, Pb-Cr and Pb-Cd pairs confirm again different sources of Pb and Hg.

The chemical element that does not exceed permissible values in any of the analyzed soil samples from Kostolac area is cadmium. Cadmium is in the same cluster as mercury (Figure 4a). Their values are very strongly associated and significantly differ from other heavy metal values.

This is not the case with Gacko soil. Cadmium, as with nickel, belongs to the group of heavy metals that are characteristically emitted during coal combustion [45]. The values of this element most frequently range from 0.1 to 1 mg/kg [34]. The exceeding of these limits was recorded in six out of eight samples collected in Gacko soil, which is evidently explained by the influence of Gacko coal ash.

The prevailing winds in Gacko coal basin are northwest, northeastern and southeastern. It can be concluded that ash landfill could be responsible for higher concentration of Ni and Cd in the soil, since it is on the blowing route of southeastern and northeastern winds.

A cluster composed of Ni, Cr and Zn showed that these elements have very similar values in analyzed soil samples from both basins.

5. Conclusions

Heavy metals are accumulated in the soil due to natural lithogenic and pedogenetic processes, but also due to anthropogenic factors [37]. It is a well-known fact that due to their stability, heavy metals pose a particular risk to the agroecosystem [46].

Bearing in mind that the remediation of land contaminated by heavy metals is very expensive and complex, it is essential to develop and establish a contamination prevention system. Heavy metals found in a stationary medium such as soil remain there because they cannot be degraded into less harmful products, which is the case with organic matter [42,47].

In this paper, we reached the conclusion that the ash from the Kostolac landfill affects only partially the quality of surrounding soil in terms of contamination by nickel (Ni), copper (Cu) and chromium (Cr), whose concentrations in the analyzed samples are above the prescribed limit values (k = 0.71), whereas their mutual correlation indicates their common origin. There is a moderately strong correlation of the Ni-Cu pair (k = 0.71), which is also the case with the Cu-Cr pair (k = 0.73) and a strong correlation of the Ni-Cr pair (k = 0.82). The assumption is that increased concentrations of Ni, Cu and Cr in the soil are due to west wind, on whose path is the SKO landfill.

As for heavy metals such as lead (Pb) and mercury (Hg), whose concentrations exceeded the limit values in several Kostolac soil samples, the investigations suggest that apart from ash, other sources may be responsible for this contamination, such as motor vehicle traffic on the roads in the surroundings of the subject area, which particularly applies to lead. Also, the investigations have identified agricultural activities as another significant source of contamination, which is due to the use of fertilizers and heavy-metal pesticides that takes place in the farmstead of Hrastovaca.

The lack of significant correlation between Hg and the other heavy elements for both basins confirms that its sources were quite different from those of the others.

In the case of arsenic (As) and zinc (Zn), only local contamination has been detected, since the concentration limit of these metals is exceeded in just one sample.

Based on the analyzed soil samples from the Gacko coal basin, the recorded heavy metals whose concentrations are above the limit values are nickel (Ni), cadmium (Cd) and chromium (Cr), whereas for cadmium the contamination can be considered as local since only two samples showed critical concentrations. In the case of nickel and cadmium, undoubtedly the impact can be attributed to Gacko ash, as evidenced by an extremely strong correlation between this pair of elements with the coefficient k = 0.82, indicating their common origin. The prevailing southeastern and northeastern winds are responsible for that, since the ash landfill is along their airflow pathway. The negative correlations of Pb-Ni, Pb-Cr, and Pb-Cd pairs confirm different source of lead, in the case of Gacko.

The results presented here indicate greater impact of Kostolac landfill ash on the quality of the surrounding soil, compared to Gacko ash, if judged by the larger number of samples in which the maximum permissible concentrations of heavy metals were exceeded (Table 2). It should be taken into account that the recorded concentrations in Kostolac soil are only slightly above the limit values, and far below the remediation values prescribed by regulations. This means that with the application of remediation measures, the disturbed soil functions could be restored to their normal state.

Certainly, it is possible to conclude that the results presented herewith are not alarming and should be observed within the framework of the regular overall environmental protection activities implemented by CFPP Kostolac and Gacko. Besides, the feasibility analysis for the exploitation of remaining coal reserves of the Kostolac and Gacko coal basins, by underground mining, opens the possibility for the disposal of fly and bottom ash from the power plants in this excavated area, which would reduce the associated negative environmental impacts.

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