

ORIGINAL ARTICLE



Bioconcentration of Heavy Metals with Toxic Potential in Soil and Plants in Residential Areas

Delia Nica-Badea

Faculty of Medicinal and Behavioral Sciences, Constantin Brancusi University, Târgu – Jiu, Romania

Corresponding Author: Delia Nica-Badea

Résumé

This paper presents the evaluation of the level of translocation of traces of some metals Hg, Pb, Ni, Cd from the coal matrix (lignite) into slag, ash. Stored in heaps in the soil and plants from the local residential environment, near the power plant. Analysis of trace metals in the multicomponent sample was carried out by AAS. Heavy metals were found in the composition of coal, ash and slag samples, in the soil and vegetation related to the area of influence of the power plant. The enriched metal content in the residues is characterized by RE Meiji < 1 (Pb and Hg) and RE Meiji ≈ 1 (Ni and Cd) for filter ash. The content of Pb and Ni in the soil exceeds the normal values, and Pb also exceeds the alert value for sensitive soils around the waste deposit (70.20 mg.Kg⁻¹). Availability of heavy metals in soil and plants, reflected and by the translocation factor TF, places Cd and Hg above the reference value (Khan) of bioaccumulation (0.5), and individual carcinogenic risk for Pb Ni Cd estimated at levels of: 10^{-7} ; 10^{-6} ; 10^{-5} relative to the WHO reference limit of 10^{-6} : it estimates a potential food safety risk.

Keywords: AAS, heavy metals, translocation, bioconcentration, lignite combust, soil-plant accessibility

Introduction

Thermal power plants, in particular, power plants that use coal as fuel, can affect the quality of the environment, sometimes having strong influences on the ecological balance in the areas where they are located. They generate a complex impact on all environmental factors, not only in the surrounding area (air, water, soil, flora and fauna, food and indoor spaces), thus energy production based on burning coal is considered the main source of pollution (Nica-Badea, 2015; Florescu et al., 2011; Che Ket al. 2022; Altikulaç et al, 2022). The area of surface coal mining in the Jiu Middle Basin and the location of thermoelectric power plants in this area, has been subjected in the last decades to a major anthropogenic action: the uncovering of the soil for the surface mining of lignite and the destruction of the fertile soil layer, the bringing to the surface of large quantities of

underground rocks and the pollution of the environment with different radionuclides and heavy metals, the formation of tailings, ash and slag dumps. (Corneanu M. et al., 2013).

The main polluters with heavy metals in the area of action of coal-fired power plants are: combustion gases, ash from dumps, and the system of exploitation, transport and storage of coal. According to the level of concern based on adverse health effects or their abundance in coal, trace elements fall into three categories: major (As, B, Cd, Pb, Hg, Mo, Se); moderate (Cr, V, Cu, Zn, Ni, F); minor (Ba, Sr, Na, Mn, Co, Sb, Li, Cl, Br, Ge); negligible (Be, Be, Ta, Ag, Te) (Nalbadian, 2012). The impact of heavy metals (Zn, Cu, Mn, Pb, Ni, Co, Cd) on the soil and plants in the vicinity of the Turceni thermal power plant, has been the subject of research projects,

completed with reports, with the main objective being the influence of the polluting emissions of the thermal power plants on soil acidity and heavy metal pollution of soil and plants. (ICEMENERG, 2000; Nica-Badea, 2010). The emission of heavy metals from the coal matrix through combustion, the dispersion and transfer of some heavy metals in the soil, in cultivated plants and in medicinal plants from the spontaneous flora adjacent to the power plant, highlighted the fact that the metals detected in the coal samples are found in ash, slag, soil-plant distribution chain, in concentrations that do not exceed normal values or bioaccumulation limit values or that exceed the limits imposed by national regulations or literature reports. (Bălăceanu et al., 2011; Turhanet al. 2020). The content of heavy metals analyzed (total forms) from the population gardens, the crop fields around the thermoelectric power plant, the raw sterile dumps, the cultivated sterile dumps and the ash dumps exceeded the normal limits in most of the samples, in some cases they had values close to the limit alert or even intervention at a distance of 15-20 km north of the power plant in the public gardens (Corneanu M. et al., 2013; Mandal et al. 2022). The trace elements present in the carbon matrix through combustion are dispersed into the environment becoming hazardous trace elements that cause actual damage to human health and the environment (Wang et al. 2019). Trace elements from coal use, although less than 1% (EPRI, 2010), are considered to be of health concern: As, Cd, Cr, Hg, Mn, Ni and Pb. In this context, this

paper presents the assessment of the level of translocation of trace metals Hg, Pb, Ni, Cd in the matrix of lignite in slag, ash deposited in dumps in the soil and plants from the local environment, reporting the concentrations determined at the data from the specialized literature, national and international standards.

Material and methods

Study Site

The Turceni thermal power plant is located in Lunca Jiului, GORJ county, Romania, south of the Jił stream, near it with Jiu River, approximately 1.5 km - E of the Turceni de Sus locality (Figure 1). Geomorphologically, the area of influence of the thermal power plant belongs to the Getic Piedmont, presenting transitional characters between mountains and plains, both geomorphologically and in terms of conditions and resources, their exploitation, the dynamics of settlements and landscapes. From a climatic point of view, it is under the influence of the predominantly Mediterranean climate, with southern and western component circulation, interfering with the air circulation on the Jiu corridor in the NW-SE direction. The temperature and precipitation regime is influenced by the oceanic air masses from the west, combined with the Mediterranean climate from the N-W. The natural vegetation represented by forests has gradually shrunk, giving way to meadows and agricultural crops.

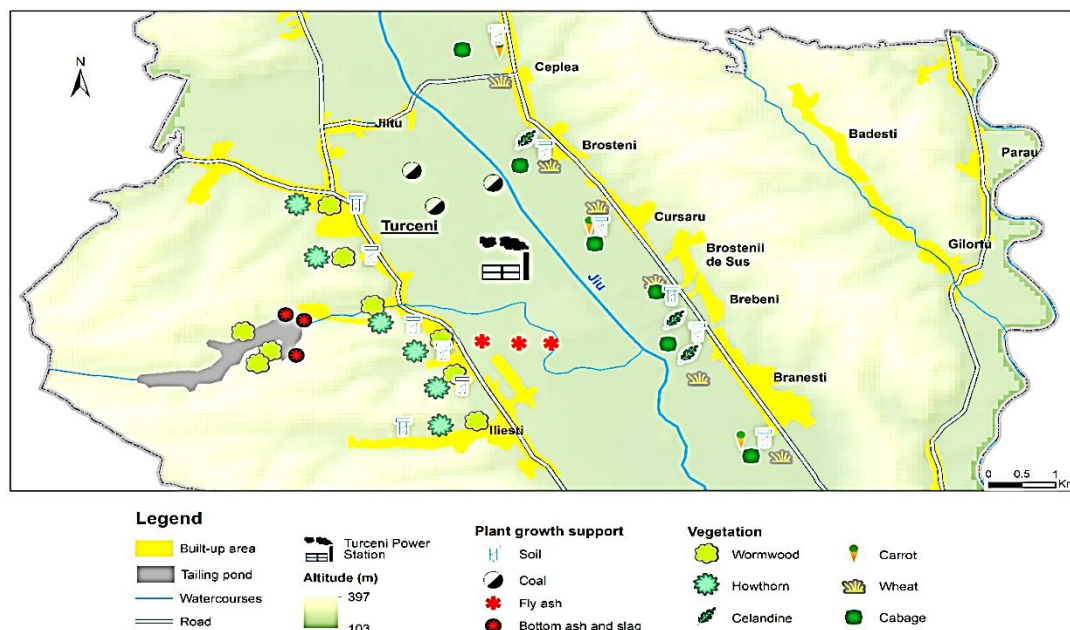


Figure 1 Map of sampling areas. Legend: Scale: 1:20,000

Turceni thermal power plant that is equipped with hot water and steam boilers represent an environmental pollutant. The main pollutants emitted into the atmosphere, contained in the gases resulting from the combustion of fuel together with the combustion air, in the hearths of the boilers, are: SO₂, NO_x, CO₂, CO, unburned powders and particles, traces of heavy metals. The main possible sources of soil and subsoil pollution are: coal storage area, storage of oils, petroleum products, chemical storage, chemical water treatment plant and internal canals, slag and ash storage. Due to the wet ash transport system emissions to water are also possible at the landfill. Preventive measures of soil and vegetation pollution consist of: wetting installation of slag and ash heaps, to prevent scattering by the wind; maintenance of protective curtains built from resistant trees and shrubs; compliant temporary technological waste depots.

Sampling and method of analysis

Samples of soil and plant were collected carried out along the Jiu river corridor, between the towns of Țintăreni and Valea Văi, in the NW-SE direction, (Figure 1) considering the relief of the area and the prevailing directions of the atmospheric circulation adjacent to the pollution sources (quarry, thermal power plant, solid waste). Soil samples (h = 20 cm), plant samples of which cereal samples were collected simultaneously. The methodology used in this research was based on the characteristics of the fossil fuel, the mode and the type of solid residues resulting from the technological process of burning coal (lignite) in the boilers of the thermal power plant Turceni, Gorj. Coal samples were prepared for quantitative analysis of trace metals according to ISO 11466: 1999, analyzed by

atomic absorption spectrometry according to international methodology and standards, using a Thermo Electron Spectrometer Model S Series AA SOLAAR, Flame Furnace and Graphite ICPA Bucharest, fully automated, software platform. For the determination of Hg in soil and plant samples using the VP Vapor 100 Kit generator, the assay is done directly by atomic absorption spectrometry without thermal atomization, the cold vapor technique (CVAAS). The sampling and analysis method used, AAS, is characterized by a series of superior qualitative analytical parameters for multicomponent samples. The method recommended in the analysis of multicomponent samples of heavy metals from solid environmental samples (MO, 1997; Csuros and Csuros, 2002). Detection limits (mg·L⁻¹): 0.005 Zn and Cd; 0.04 Ni; 0.5 Pb and the sensitivity in the range 0.02-0.5 mg·L⁻¹.

Results and Discussion

The global impact of pollutants on environmental degradation determines increased attention paid lately to monitoring and controlling the state of the surrounding environment. A series of plants, in this case, herbaceous vegetation, vegetables, fruits can be used as biomonitors of the degree of pollution, in general, with heavy metals in particular, through the chemical analysis of the components in the areas adjacent to the sources of pollution with combustion products of power plants coal-fired. Starting from the data from the literature to evaluate the degree of heavy metal pollution, we set out to investigate the level of concentration of heavy metals in primary ash (at the level of filters), ash stored in the dump, soil, vegetation, vegetable products of agro-food interest from the area of a thermal power plant based on solid fuel, coal (Tables 1).

Table 1. Heavy metal concentrations in the analyzed samples (total forms) c- average concentration; sd-standard deviation; a Soil sensitivity (Source: OM no. 756/1997)

Samples collected	Hg (mg·Kg ⁻¹)		Pb (mg·Kg ⁻¹)		Ni (mg·Kg ⁻¹)		Cd (mg·Kg ⁻¹)	
	c	sd	c	sd	c	sd	c	sd
Coal (lignite) n=3	0,020	0,012	31,40	0,87	30,30	0,98	0,331	0,32
Ash filters n=3	0,037	0,014	47,63	0,64	79,00	0,39	1,024	0,42
Ash, deposit slagn = 4	0,022	0,010	31,80	0,75	78,00	0,43	0,139	0,54
Soil bordering the warehouse n = 6	0,102	0,02	70,20	3,69	45,2	11,24	0,302	0,12
Thermal boundary soiln = 6	0,049	0,022	40,00	2,23	40,8	12,0	0,254	0,12

Normal soil values	0,1		20		20		1	
Ground alert level ^a	1		50		75		3	
Warehouse vegetation ⁿ = 4	0,014	0,004	3,11	0,16	14,6	2,34	0,250	0.04
Vegetation bordering the warehouse n = 6	0,005	0,001	5,37	0,28	3,91	1,17	0,118	0.03
Bordering vegetation Termo n = 6	0,004	0,002	3.64	0,17	2,94	1,12	0,050	0.01
Permitted limits, vegetation ^a	-		3-10		30		0,4	

The average values of trace metals in coal (Romanian lignite) obtained in this experiment (Table 2), were compared with the values reported at the international level, according to: International Energy Agency IEA, Clean Coal Centers (Nalbandian, 2012), Australia (Swaine, 1994) and China (Zhang et al. 2004). The experimental data (Table 2) place the concentrations of heavy metals in Romanian lignite compared to the levels reported in the literature: in the world value range, Hg (Swaine, 1994) and (Nalbandian, 2012), Pb and Ni

(Swaine, 1994) with values below the international level Hg and Cd (Zhang et al., 2004) at values above the international level Pb and Ni (Nalbandian, 2012; Zhang et al. 2004). The concentration of trace elements can vary depending on the type of coal, the coal basin and even between coals from the same basin, for example, the lignite from the Jilț-Gorj quarry contains twice as much lead (31, 40 ppm) as that of the Schitu - Golești quarry (15 ppm) (Bugaru Rujoi et al., 2014).

Table 2. Heavy metal concentrations in Romanian lignite compared to other international reports

Heavy metals	Experimental Medium values România(ppm)	Nalbandian Medium values IEA (ppm)	Swaine Global Average Australia (ppm)	Zhang et al. Global average China (ppm)
Hg	0,020	0,03–0,19	0,02 – 1	0,12
Pb	31,40	1–22	2 – 80	25
Ni	30,30	1,5–21	0,5 – 50	15
Cd	0,331	0,01–0,19	0,1 – 3	0,6

Residues generated by burning coal in power plants are major wastes generated in enormous quantities around the world. The main concern about the use of coal in electricity production is the generation and storage of large amounts of coal ash with an impact on the environment and the quality of human life, for example, a 330 MW thermal power plant consumes around 1000 tons / h of coal and generates at the same time 400 tons of ash and slag (Cruceru et al. 2017). In this context, the Turceni Energy Complex, Gorj County, produces approximately 7400 m³ of ash per day using lignite as the main fuel. The level of heavy metal concentrations, determined in the bottom ash obtained for the metals selected in this study (Table 1), is (mg·Kg⁻¹): Hg (0.037), Pb (47.63) and Ni (79.00). Experimental concentrations are at a lower level for Ni, Hg, Cd and slightly elevated for Pb compared to EU lignite fly ash concentrations (Moreno et al.

2005), (mg·Kg⁻¹): Hg (0.05), Pb (44), Ni (220), Cd (2). A series of research shows that traces of heavy metals are subject to an enrichment process in the solid products resulting from coal combustion plants (Bhangare et al. 2011; Vuet al. 2019), and the level of enrichment depends on the type of ash and the particularities of each element (Meij, 1994; Meij et al. 2009). This process is defined and quantified by the term relative enrichment (RE) according to equation (1).

$$RE = [(Ash Conc. / Coal Conc.) \times Crude Coal Ash Content \%] / 100 \quad (1)$$

Using this equation (1), considering the ash concentration in the Romanian crude lignite (36%), the RE Meij enrichment factor values for the ash collected at the bottom of the power plant filters are shown in figure 2, compared to other values reported in the literature: China (Li et al. 2012); India, (Bhangare et al. 2011) Canada, (Goodarzi et al. 2006). The ash enrichment factors

retained (Figure 2) at the base of electrostatic precipitators, compared to the classification made by Meij (Meji, 1997), place the metals analyzed in our research as follows: nickel (0.94) and cadmium (1.1) in groups I and II (non-volatile, respectively volatile and condensation occurs, $RE \approx 1$); lead (0.54) and mercury (0.7) in group III

(highly volatile, limited condensation, $RE < 1$). The level of trace metal concentrations determined in the fly ash, bottom ash and slag that are hydraulically transported to the deposit, is at slightly lower levels than the fly ash collected by the filters ($mg \cdot Kg^{-1}$): 0.022 (Hg); 31.80 (Pb); 78.00 (Ni); 0.139 (Cd).

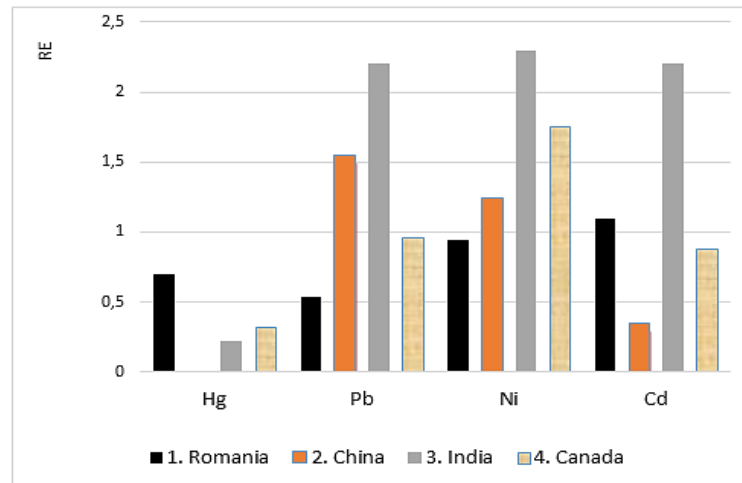


Figure 2 Enrichment factors (RE Meij) in electrostatic fly ash filter

The two entities, the power plant and the ash deposit, located at a distance of approximately 1.5 km from the NW-SE direction, through the related technological processes and the pedo-climatic characteristics of the area, are synergistic sources of dispersion of trace metals for the soil, vegetation and agricultural crops, from rural and urban areas. The average values of Pb and Ni concentrations exceed the normal values both for the soil at the base of the ash deposit ($mg \cdot Kg^{-1}$): 70.20 and 45.2, respectively, and for the soil surrounding the thermal plant ($mg \cdot Kg^{-1}$): 40.00 and 40.8 respectively, but they are below the alert level for sensitive soils (Table 1). To assess the degree of loading and to compare the intensities of soil accumulation and contamination with traces of heavy metals, a coefficient (Cn) is used, defined as the ratio between the experimentally

determined concentration and the normal soil concentration established by MO 756/1997. Cn values have three meanings: greater than 1 indicates a high level of pollution; values equal to 1 indicate a normal level; subunit values indicate the absence of these elements. The transfer capacity of heavy metals from soil to plants has generally been described using the translocation factor (TF), calculated as the ratio of the metal concentration in plants to the concentration of the same metal in the plant's own soil (Khan et al. 2009; Tanase et al. 2014). TF values around 0.1 do not indicate bioaccumulation of metals; values around 0.5 indicate an accumulation that should be considered for food safety (the reference value in this study). The calculation of Cn and TF values for the impact zone of the power plant and the ash deposit are presented in Table 3.

Table 3. Availability of heavy metals in soil (Cn) and in plants (vegetation) (TF)

	Cn Ash storage area	Cn Power plant area	TF Ash storage interior	TF Limitrof ash deposit	TF Limitrof the thermal power plant
Hg	1,0	0,49	0,6	0,05	0,80
Pb	3,5	2,0	0,1	0,07	0,09
Ni	2,2	2,0	0,2	0,08	0,06
Cd	0,36	0,25	1,9	0,39	0,19

Experimentally, it is found that there is a high level of soil transfer (Cn) for Pb (3.5, 2.0) followed by Ni (2.2, 2.0). The high rate of transfer, reflected by the values of excessive normal content (Cn) for lead (3.5) and even nickel (2.2), is also confirmed by the level of concentrations determined and reported according to national norms for reference values of trace elements in soil (MO 756/1997). Thus, the concentration of lead in the soil in the ash storage area (70.20 mg Kg^{-1}) exceeds the threshold established for sensitive soils of 50 mg Kg^{-1} . The maximum TF values obtained for the studied plants (Table 3) are above the reference value: 0.5: Cd (1.9) and Hg (0.6), inside the landfill; Hg (0.8), in the area of the thermal plant and even Cd (0.39) in the area of the ash and slag deposit, indicate a bioaccumulation that must be considered for the impact on the quality of life. The other TF values obtained, between 0.005 and 0.19, are well below the reference values (Khan, 2009), indicating the lack of bioaccumulation of the studied metals.

The main pollutant of the area of influence of coal-fired power plants is ash. Flying ash a road from chimneys, fine wind ash from pile of slag and coal from chimneys, windblown fine fly ash from slag heaps and coal dust from coal storage or coal transport and preparation together constitute a solid contaminant that can be found in aerosol form. Knowledge of the regional content, as well as the variability and values of trace element concentrations in soils and plants, is of critical importance to assess human impact on the

environment based on quality standards (Inigo et al. 2013). The distribution of a metal species in its various forms to migrate from the soil through plant parts represented by the transfer factor (TF) which is a function of various chemical and physical parameters indicates the level of accumulation of that metal for different plants, toxicity and tolerance (Khan et al. 2009; Kabata Pendias, 2011). In this context, we analyze the specific characteristics of the spatial distribution of heavy metals in the soil, the spontaneous vegetation in the same area as the grain crops (wheat and barley) in the area of the thermal power plant as a potential anthropogenic pollutant. Heavy metals found in the composition of coal used as fuel were found in the composition of ash samples at the bottom of the plant's filters, in ash samples, in the soil and vegetation deposit and in the influence area of the power plant. All soil samples were within the range of maximum permissible limits (MPLs) for sensitive soils, according to national standards (MO, 756/1997). The climate of the researched area is predominantly Mediterranean, with southern and western component circulation, interfering with the air circulation on the Jiului corridor, in the NW-SE direction. The temperature and precipitation regime is influenced by the oceanic air masses from the west, combined with the Mediterranean climate from the N-W. The natural vegetation is mainly represented by meadows and agricultural crops. The concentration level of heavy metals in the soil adjacent to the plant and the spatial distribution are shown in Figure 3.

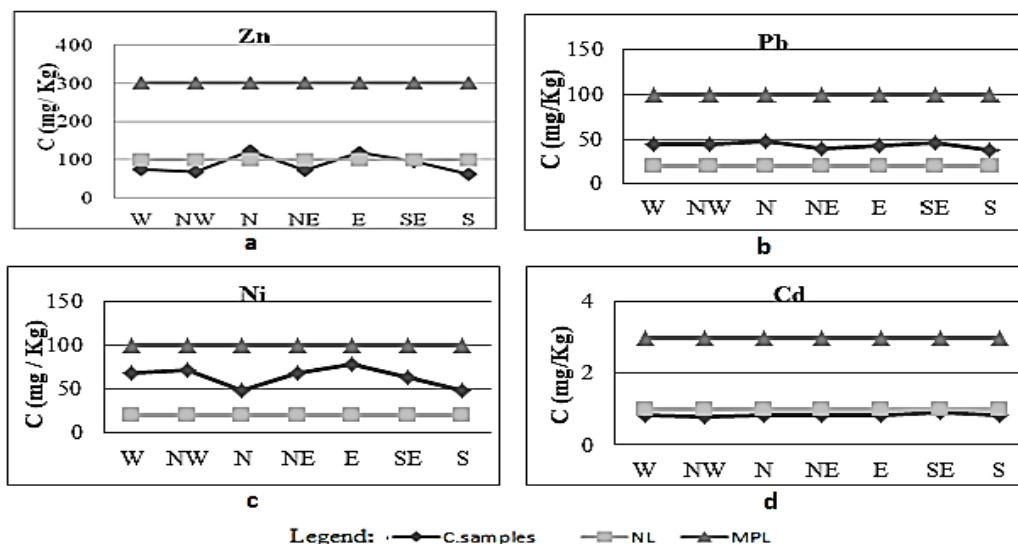


Figure 3 Spatial distribution of metals in vegetation: a) Zn; b) Pb; c) Ni; d) Cd.

It can be found that the levels of heavy metal concentrations in the analyzed soil are placed above the normal levels established at the national level (MO, 756/1997), ($\text{mg}\cdot\text{Kg}^{-1}$):

- The average value of Pb of 43.71 and Ni of 64.14;
- Maximum Zn value (123), profile direction N, characterized by clayey alluvial soils and pH 6.6 (Figure 3.a);
- Maximum Pb value (49.20), N direction profile, characterized by alluvial clayey carbonate soils and pH 7.4 (Figure 3.b);
- The maximum value of Ni (76.22), profile direction E, brown alluvial soils and pH 7.7 (Figure 3.c).

The concentrations of heavy metals determined in

the soil adjacent to the thermal power plant fall within the nationally validated range (Romania) regarding the content of elements and potentially polluting substances (PPES) in agricultural soil, monitoring of level I samples (16 x 16 km) (Dumitru, 2011) ($\text{mg}\cdot\text{Kg}^{-1}$): Zn (24.5 – 974), average values: 87.34 ± 61.4); Pb (4.9-335, mean values: 21.3 ± 18.6); Ni (4.2 – 171, average values 34.49 ± 14.5); Cd (0.02 – 1.68, mean values: 0.43 ± 0.27).

The spatial distribution of the concentrations determined in spontaneous vegetation (Figure 4) shows that lead (Figure 3b) exceeds the lower permissible limit in all cardinal directions, the values being close to the maximum permissible limit (MPL2), similar to the quantitative and spatial variation of lead in soil (Figure 3b).

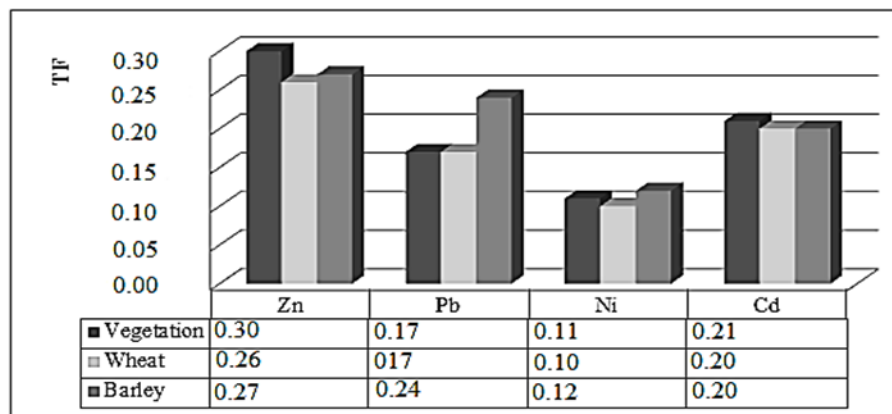


Figure 4. Soil-plant transfer factor of heavy metals in the plant area

Observing the concentrations of heavy metals in the vegetation, in general the maximum permissible limit is not exceeded, except for the slag deposit and its eastern base for Pb which is

above the lower limit of the range with a concentration of $7.58 \text{ mg}\cdot\text{Kg}^{-1}$, relative to national norms (3-10 $\text{mg}\cdot\text{Kg}^{-1}$), Table 4.

Table 4. Metal content in plants (Average values, total forms)

Samples	Zn ($\text{mg}\cdot\text{Kg}^{-1}$)		Pb ($\text{mg}\cdot\text{Kg}^{-1}$)		Ni ($\text{mg}\cdot\text{Kg}^{-1}$)		Cd ($\text{mg}\cdot\text{Kg}^{-1}$)	
	c	SD	c	SD	c	SD	c	SD
Grassy vegetation	24.4	5.80	7.58	1.06	7.28	2.34	0.19	0.027
Standard ^a	50-100		3-10		30		0.4	
Wheat	22.96	4.92	7.51	0.78	6.58	1.97	0.175	0.03
Barley	24.25	4.74	8.75	0.82	8.00	1.98	0.170	0.03

^a Source: MO 756/1997.

SD-standard deviation

The concentrations of heavy metals analyzed in plant products (agri-food) from the areas adjacent

to the plant and the ash deposit are placed within or outside the permitted concentration limits by product category, depending on the reporting source in the literature. According (Pendias and Pendias, 2001) the normal values for heavy metals in plants are ($\text{mg}\cdot\text{Kg}^{-1}$): Zn 20-60; Pb 5-10; Ni 0.1-2.0); Cd 0.0-0.1, the average values that are exceeded by wheat and barley according to the experimental data in Table 4: Ni (6.58, respectively 8.00) and Cd (0.17, respectively 0.170). In accordance with the accepted international norms and standards for cereals, vegetable leaves and fresh herbs (EC 1881/2006; FAO/WHO 2011), the limits allowed for concentrations in wheat and barley ($\text{mg}\cdot\text{Kg}^{-1}$) are exceeded: for Pb with experimental values of 7.51, respectively 8.75, relative to the maximum allowed concentration of 0.2 and for Cd with experimental values of 0.175, respectively 0.170, average concentration, relative to a maximum permitted level of 0.1. The transfer factor (TF) calculated in for spontaneous vegetation in the area of wheat and barley crops analyzed, shows a moderate distribution of the level of heavy metals, ranging from 0.30 to 0.11 and from 0.27 to 0.11 for cereals grown in the same area. The transfer factor (calculated on the basis of average

concentrations) decreases in the order: (a) Zn, Cd, Pb, Ni for spontaneous vegetation and wheat; (b) Zn, Pb, Cd, for barley (Figure 4).

Quantification of individual risk

Due to the fact that heavy metals represent a category of indestructible persistent pollutants with toxic effects on living organisms when they exceed a certain concentration, the monitoring of these metals is important for the assessment of environmental safety and human health, in particular (Batayneh, 2012; Cocârta et al. 2016). Based on average concentrations determined in soil ($h = 0.25\text{m}$) and plants (wheat), the individual risk for Ni, Cd, Pb can be calculated taking into account the following: concentration due to direct deposition of contaminants is zero and concentration due to transfer to grain is based on absorption factor (UF) and soil metal concentration (C_s); it is considered that 100% of the territory is dedicated to the cultivation of crops (wheat); 10% of the wheat is used in the contaminated area. The general data needed to calculate the individual risk factor for the three potentially toxic heavy metals Pb, Ni, Cd are presented in Table 5.

Table 5. Estimating the order of magnitude of individual risk.

Heavy metals	Concentration in soil $\text{mg}/\text{kgd.w}$ Average values	Slope factor ($\text{mg}/\text{kg}/\text{day}$) ^a	Individual risk order I_r
Pb	43.73	8.50×10^{-3}	10^{-7}
Ni	64.14	9.10×10^{-1}	10^{-6}
Cd	0.85	4.20×10^{-1}	10^{-5}

Although the determined concentrations of Pb and Ni exceed normal soil traces of approximate. At 50 and 60 times the excess of normal content (C_n) being double that of Cd (Table 3) the highest individual risk index was obtained for Cd (10^{-5}). This is highlighted in two recent researches (Cocârta et al. 2016), which highlights the high level of Cd (10^{-4}) compared to Pb (10^{-6}) and Ni (10^{-5}) and Ye, which highlights the high risk (Ye et al. 2015). The reference limit for the WHO, the level of the individual risk index 10^{-6} established by the WHO, cited (Dumitrescu et al. 2012) and which means one case of cancer in over one million exposed people. The monitoring of these metals is important for the assessment of

individual risks, environmental safety and especially human health. Based on the average concentrations determined in soil and plants (wheat), the individual risk for Pb, Ni, Cd is estimated at levels of: 10^{-7} ; 10^{-6} ; 10^{-5} compared to the WHO reference limit of 10^{-6} .

Conclusions

Energy installations, especially coal-fired power plants, can influence the environment, sometimes even affecting the ecological balance of the areas where they are located, with a complex impact on all environmental factors in the surrounding area (atmosphere, water, soil, flora and fauna, food and housing). Dispersed combustion products from the lignite matrix, fly ash discharged through

chimneys, ash and slag from landfills, coal dust from coal dumps or its transport and preparation together constitute a potentially toxic trace of heavy metals for the site area. The soil of the Turceni Thermal Power Plant is an anthropogenically loaded soil with heavy metals, especially nickel, lead and even zinc. The physico-chemical parameters of this soil keep these metals at moderate levels, less accessible to plants. This state of affairs is temporary because the impact of ash with the soil of this area over a longer period determines the concentration of heavy metals in the soil and plants. Being persistent, indestructible pollutants and having toxic effects on living organisms when they exceed a certain concentration, the monitoring of these metals is important for the assessment of individual risks, environmental safety and especially human health. The experimental results of this research prove to be relevant because the transfer and accumulation of potentially toxic heavy metals in soils and agricultural plants (spontaneous vegetation, crops) are of increasing concern due to food safety issues and potential health risk for residents of neighboring towns. Thus, the transfer has a role especially if the source of pollution is located near rural socio-economic systems characterized by subsistence agriculture, a case highlighted in this paper.

Analyzing the research results, can be summarized as follows:

The climatic parameters in the Turceni power plant area do not have a significant influence on the accumulation of heavy metals in soil and plants.

The experimental results related to the determination of the content of heavy metals in the vegetation near the power plant and the ash waste dump reveal increased concentrations for some metals.

The loading level of heavy metals and the spatial distribution in the soil-plant system in the studied area are the results of the synergism: pedo-climatic and geomorphological characteristics, mining, transportation and storage of lignite, combustion of lignite in the boiler and ash emission and slag deposit ash as the main sources of pollution.

The studied heavy metal traces transferred from the coal matrix (36% lignite raw ash content) to

the solid combustion products characterized by $REMe_{ij} \leq 1$, are determined by the characteristics of each analyzed heavy metal content, of the ash, but also the technical characteristics of the system of burning brown coal.

The toxic potential and health implications of exposure are reflected by the level of trace concentrations of toxic heavy metals determined in lignite, combustion products, soil and plants adjacent to emission sources. Thus, the level of concentrations observed in the soil of the area exceeds the normal values (Pb and Ni) and the reference values for sensitive soils (Pb), according to national standards (MO 756/1997).

The availability of heavy metals in soil and plants, reflected by the translocation factor TF, places Cd and Hg above the reference value (Khan) of bioaccumulation (0.5), estimating potential food safety risk for Pb, Ni, Cd is at levels of: 10^{-7} ; 10^{-6} ; 10^{-5} compared to the WHO reference limit of 10^{-6} .

References:

1. Altıkulaç A, Turhan Ş, Kurnaz A, Gören E, Duran C, Hançerlioğulları A, Uğur FA (2022) Assessment of the Enrichment of Heavy Metals in Coal and Its Combustion Residues. *ACS Omega*. 7(24): 239-21245. Doi: 10.1021/acsomega.2c02308.
2. Balaceanu CE, Dumitru M, Lacatusu AR, Florea N (2011) Soil pollution in the Rovinari area under the influence of the coal-fired power station. *Scientific Papers UASVM Bucharest. Series A* 14: 89-96.
3. Batayneh AT (2012) Toxic (aluminum, beryllium, boron, chromium and zinc) in groundwater: health risk assessment. *Int. J. Environ. Sci. Technol.* 9: 153–162. Doi:10.1007/s13762-011-00093.
4. Bhangare RC, Ajmal PY, Sahu SK, Pandit GG, Puranik VD(2011)Distribution of trace elements in coal and combustion residues from five thermal power plants in India.*Int.J. Coal Geol.*86,:49-356.
5. Bugaru M, Rujoi BG (2014) Toxic elements in coal and their ashes. *UPB. Sci. Bull. Series B*, 76(1):1 27-130.
6. Che K, Chen CM, Zheng QY, Fan H, Wei ML, Luo P, Yu J (2022) Heavy Metal Emissions from Coal-fired Power Plants and Heavy Metal Pollution Characteristics and Health Risks in Surrounding Soils. *Environ.*

- Sci. 43(10): 4578-4589.
DOI:10.13227/j.hjkx.202201032.
7. Corneanu M, Corneanu G, Lacatușu AR, Cojocaru L and Butnariu M (2013) Concentration and distribution of heavy metals and radionuclides in topsoil's from Middle Jiu Valley surface coal exploitations surrounding area (Gorj County, Romania). *Geophys. Res. Abstracts* Vol. 15, EGU2013-8818.
 8. Cocârță DM, Neamțu S, Reșetar Deac AM (2016) Carcinogenic risk evaluation for human health risk assessment from soils contaminated with heavy metals. *J. Environ. Sci. Technol.* 13, 2025–2036.
 9. Cruceru M, Abagiu TA, Anghelescu L, Diaconu D (2017) Obtaining building materials from coal ash after separation of the residual carbon. *Int. J. Syst. Appl. Eng. Dev.* 11: 45-49.
 10. Csuros M, Csuros C (2002) *Environmental Sampling and Analysis for Metals*. New York, NY: Lewis Publishers.
 11. Dumitrescu C, Cocârță D, Badea A (2012) An integrated modeling approach for risk assessment of heavy metals in soils. *Sci. Bull. Univ. POLITEHNICA Bucharest. Ser. D.* 74(3): 217–228.
 12. Dumitru M (2000) *Monitoring Soil Quality Status in Romania*. SITECH Publishing. Craiova.
 13. EC, European Commission (2006) *Commission Regulation: Setting Maximum Levels for Certain Contaminants in Foodstuffs*. OJEU, L 364: 5-24.
 14. Electric Power Research Institute (EPRI). (2010) *Comparison of Coal Combustion Products to Other Common Materials: Chemical Characteristics*. Electric Power Research Institute, Palo Alto, CA. 1020556: 3-1.
 15. FAO/WHO (2011) *List of Maximum Levels for Contaminants and Toxins in Foods, Part 1*. Joint FAO/WHO Food Standards Programme CODEX committee on contaminants in foods. CF/5 INF/2, Hague, p.13- 15.
 16. Florescu D, Iordache A, Picioarea I, Ionete R. E (2011) Assessment of heavy metals contents in soil from an industrial plant of southern part of Romania. *AES. Bioflux.* 3(2): 206-210.
 17. Goodarzi F (2006) Characteristics and composition of fly ash from Canadian coal-fired power plants. *Fuel.* 85(10-11): 1418-1427.
 18. ICEMERG. (2000) Establishment of the impact of thermal power plants on the ground (return of the Turceni Thermal Power Plant). Document C.4145/2000. (In Romanian).
 19. Inigo V, Andrades MS, Alonso-Martirena JI, Marín A, Jiménez-Ballesta R (2013) Spatial Variability of Cadmium and Lead in Natural Soils of a Humid Mediterranean Environment: La Rioja. Spain. *Arch. Environ. Con. Tox.* 64(4): 594-604.
 20. Jiahua Zhang J, Ren D, Zhu Y, Chou CL, Zeng R, Zheng B (2004) Mineral matter and potentially hazardous trace elements in coals from Qianxi Fault Depression Area in southwestern Guizhou, China. *Int. J. Coal Geol.* 57: 49-61.
 21. Kabata Pendias A (2011) *Trace Elements in Soils and Plants*. 4th ed. CRC Press Boca Raton. London -New York.
 22. Kabata-Pendias A, Pendias H (2001) *Trace Elements in Soil and Plants* (3rd Ed.), CRC Press, p. 65.
 23. Khan S, Farooq R, Shahbaz S, Mohammad Aziz M, Khan MA, Maria Sadique M (2009) Health risk assessment of heavy metals via consumption of spinach vegetable grown in Elall River. *World Appl. Sci. J.* 6(12): 1602-1606.
 24. Li J, Zhuang X, Querol X, Font O, Moreno N, Zhou J (2012) Environmental geochemistry of the feed coals and their combustion by-products from two coal-fired power plants in Xinjiang Province, Northwest China. *Fuel.* 95: 446-456.
 25. Mandal S, Bhattacharya S, Paul S (2022) Assessing the level of contamination of metals in surface soils at thermal power area: Evidence from developing country (India). *Environ. Chem. Ecotoxicol.* 4: 37– 49, DOI: 10.1016/j.enceco.2021.11.003
 26. Meij R (1997) Trace element behavior in coal-fired power plants. *Fuel Process Technol.* 39: 199-207.
 27. Meij R, Winke BH (2009) Trace elements in world steam coal and their behaviour in Dutch coal-fired power stations: a review. *Int. J. Coal Geol.* 77: 289–293.
 28. M.O. Ministry Order No. 756 from November 3, 1997 for approval of Regulation concerning environmental pollution assessment”, Official

- Monitor, No. 303/6, Nov.1997.
29. Moreno N, Quero LX, Andres JM, Stanton K., Towler M, Nugteren H, Janssen-Jurkovicová M, Jones R (2005) Physico-chemical Characteristics of European Pulverized Coal Combustion Fly Ashes. *Fuel*. 84(11): 1351-1363.
 30. Nalbandian H (2012) Report: Trace element emissions from coal CCC/203, ISBN 978-92-9029-523-5, 89 pp Profile No 12/13 In: IEA Clean Coal Centre, London SW15 6AA United Kingdom, www.iea-coal.org.uk/documents/83083/8631/Trace-element-emissions-from-coal,-CCC/203. Accessed 02.08.2017
 31. Nica-Badea D (2015) Assessing the degree of dispersion and distribution of heavy metals in soil and plants associated with area of influence of a coal power plant. *J.E.P.E.*16(2),(Part 1),: 453-460.
 32. Nica Badea D (2010) Scientific research project with the theme: The study regarding the influence of pollutant emissions from the Turceni Thermal Power Plant on heavy metal pollution of soil and vegetation. Research contract 2010, no: 456/21.06.2010: Constantin Brancusi University; Turceni Energy Complex.
 33. Swaine DJ (1994) Trace elements in coal and their dispersal during combustion. *Fuel process, Technol.* 39: 121-137.
 34. Tanase C, Volf I, Popa VI (2014) Enhancing copper and lead bioaccumulation in rapeseed by adding hemp shaves as soil natural amendments. *J. Environ. Eng. Landsc.* 22(4): 245-253.
 35. Turhan Ş, Garad AMK., Hançerlioğulları A, Kurnaz A, Gören E, Duran C, Karataşlı M, Altıkulaç, A, Savacı G, Aydın A (2020) Ecological assessment of heavy metals in soil around a coal-fired thermal power plant in Turkey. *Environ. Earth Sci.* 79:134-139, DOI: 10.1007/s12665-020-8864-1.
 36. Vu DH, Bui HB, Kalantar B, Bui XN, Nguyen DA, Le QT, Do NH, Nguyen H (2019) Composition and Morphology Characteristics of Magnetic Fractions of Coal Fly Ash Wastes Processed in High-Temperature Exposure in Thermal Power Plants. *Appl. Sci.* 9, 1964. <https://doi.org/10.3390/app9091964>
 37. Wang J, Yang Z, Qin S, Panchal B, Sun Y, Niu H (2019) Distribution characteristics and migration patterns of hazardous trace elements in coal combustion products of power plants. *Fuel.*, 258, 116062, DOI: 10.1016/j.fuel.2019.116062.
 38. Ye A, Zang S, Xiao H, Zhang L (2015) Speciation and ecological risk of heavy metals and metalloids in the sediments of Zhalong Wetland in China. *Int. J. Environ. Sci. Technol.* 12: 115–124. doi:10. 1007/s13762-013-0399-5.