Determination of Traces Heavy Metals from Solid Residues Formed by Combustion of Lignite in Relation to Degree of Accessibility in Soil and Plants

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The paper evaluates the presence and content of traces of heavy metals Hg, Pb, Ni, Cd (total forms) from coal and solid combustion products, the degree of transfer and accessibility in the area of influence of a lignite power plant. The content of toxic heavy metals in residues are characterized by $RE_{Meiji} < 1$ (Pb and Hg) and $RE_{Meij} \approx 1$ (Ni and Cd) for the filter ash. Pb and Ni content in the soil exceeds normal values, and Pb exceeds and alert value for sensitive soils around the residue deposit (70.20 $mg.Kg^{1}$). The degree of accessibility of the metals in plants (TF), reported at the Khan reference value (0.5), indicates a significant bioaccumulation level for the metals: Cd (1.9) and Hg (0.6) inside the deposit; Cd (0.39) at the base of the deposit, Hg (0.8) in the area of the thermal power plant. The trace levels of heavy metals analyzed by GFAAS and CVAAS (Hg), indicates a moderate risk potential for food safety and quality of life in the studied area.

Keyword: Toxic heavy metals, lignite combustion, solid waste, soil plant accessibility

Residues generated by coal combustion in power plants are major waste generated in enormous quantities worldwide. In Romania, there are currently 108 ash and slag deposits, covering an area of 2800 hectares, of which the largest area (800 hectares) is located in Gorj country [1]. The major concern about the use of coal in the production of electricity is the generation and storage of large quantities of coal ash with an impact on the environment and human quality of 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 [2]. In this context, Turceni Energetic Complex, Gorj County, produces about 7400 m^3 of ash per day using lignite as the main fuel.

Combustion of coal is a potential source for the emission of trace elements, including heavy metals [3], elements that are enriched 4 to 10 times during the combustion process [4]. Trace elements of coal ash, although representing less than 1% [5], are of interest from the perspective of health: As, Cd, Cr, Hg, Mn, Ni, and Pb. The US National Research Council (NRC) performs a classification of trace elements according to their level of concern based on negative health effects or their abundance in coal (table 1).

Heavy metals are an important category of toxic pollutants that are not biodegradable, persist in storage compartments (soil, sediments) for a long time, are neither created nor destroyed by biological or chemical processes that can only cause the metal to pass different chemical species or the conversion of inorganic and organic forms [7]. The absorption and accumulation of heavy metals in plants are the result of the influence of external factors such as the heavy metal concentration in the soil, the composition and intensity of atmospheric deposition, precipitation and plant growth [8]. It is very important that heavy metals accumulate in the environment and in the human body, with the possibility of insidious production of serious pathological alterations. Practically all metal

Table 1
CLASSIFICATION OF TRACE ELEMENTS ACCORDING TO TOXIC POTENTIAL
(ADAPTATION AFTER NALBANDIAN (2012) [3]

Level of concern	Oligoelements	Health effects
Major concern	As, B, Cd, Pb, Hg, Mo, Se.	As, Cd, Pb, Hg are highly toxic to most biological systems at concentrations above critical levels. Selenium is an essential element but is also toxic above certain levels. High levels of molybdenum and boron in plants are of concern. Molybdenum affects the lactation of cows and boron is phytotoxic.
Moderate concern	Cr,VCu, Zn, Ni, F	These elements are potentially toxic and are present in coal combustion residues at elevated levels. Bio-accumulation is of some concern. Fluorine has an adverse effect on forage.
Minor concern	Ba, Sr, Na, Mn, Co, Sb, Li, Cl, Br, Ge.	These elements are of little environmental concern mainly they are present in residues
Negligible concern	Be, Be, Ta, Ag, Te	These elements have low levels are considered to have negligible impact.for health.

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combinations are toxic chemicals over a specific dose specific to each element [9, 10]. The effects of chronic toxicity are manifested and developed over long periods of chronic exposure to relatively low concentrations [11, 12].

Chronic exposure to heavy metals has been implicated in many degenerative diseases of the same systems and may increase the risk of some cancers [13, 14]. Due to the toxic potential and health implications, a series of research and communications have been carried out on the concentration levels of heavy metal traces in the coal matrix and the solid combustion products generated and emitted by the thermal power plants in the environment [15-20].

In this context, the purpose of this research is to investigate the presence and concentration of heavy metals traces Hg, Pb, Ni, Cd of lignite and solid combustion by-products, assessing the degree of accessibility in the soil and plants in the impact area of the thermal plant and the deposit of residues.

Experimental parts

Materials and method

The methodology used in this research was based on the characteristics of fossil fuel, the mode and the type of solid residues resulting from the technological process of burning coal (lignite) in the boilers of the Turceni Thermal Power Plant, Gorj country. The samples were taken in accordance with the sampling methodology provided by the national sampling standards: coal, fly ash from the filters, ashes and slag of the Ceplea deposit. Soil and plant sampling was adapted to the pedo-climatic and hydrographic conditions of the area investigated, targeting the east base of the slag and ash deposit and thermal power plant, at a distance of 1 to 10 km from emission sources, on the north-west, south-east, on the Jiu River valley.

Coal samples, solid residues and soil were crushed and dried at room temperature for 48 h and passed through a 2 mm sieve. A 2.5 g solids portion was used for mineralization with aqua regia and hydrogen peroxide using the Milestone digester according to ISO 11466: 1999. The obtained solutions were transferred to 50 ml volumetric flasks with ultra-pure water; 1 mL of each solution was diluted 1:10 for chemical analysis. Selected and prepared plant material is calcined using a NABERTHERM oven, L9 / 11 / B170. A portion of 1.0 g of the calcined product was subjected to the aqueous extraction and hydrogen peroxide method according to ISO 11466: 1999. The obtained extracts were analyzed by atomic absorption spectrometry in accordance with international methodology and standards using a Thermo Electron Model S Series AA SOLAAR, a platform software. For this purpose, the atomic absorption spectrometer, fully automated, flame and graphite furnace (ICPA Bucharest). For the determination of Hg in soil and plant samples using the VP Vapor 100 Kit generator, dosing is done directly by atomic absorption spectrometry without atomization to heat, cold vapor technique (CVAAS).

Results and discussions

The analytical technique used, GFAAS and CVAAS (Hg) is recommended for the analysis of solid coal combustion products, the multicomponent samples in the environment are characterized by a series of performant analytical parameters: linear calibration in the range of concentrations (0 - 40 mg. L^{-1}); detection limit expressed in $mg.Kg^{-1}$ (Hg 0.0001- 0.0002; Pb 0.1; Ni 0.04; Cd 0.005), sensitivity (0.025-0.5mg.L^{-1}), standard equipment, software platform (table 2).

The concentrations of heavy metals Hg, Pb, Ni, Cd, total forms, in the analyzed samples are given in table 3.

Trace Heavy metal in coal

The average values of trace metals in the coal (lignite) obtained in this experiment (table 4) were compared with the internationally reported values: IEA Clean Coal Centers [3], Swaine [21], and Zhang et al. [22]. The experimental data (table 4) places the concentrations of heavy metals in the Romanian lignite relative to the levels reported in the literature: in the world value range (Hg - Swaine and IEA CCC, Pb and Ni - Swaine); with values below the international level (Hg and Cd - Zhang); at values above the international level (Pb and Ni, IEA CCC and Zhang). The concentration of trace elements may vary depending on the type of coal, the carbonate basin and even between coals from the same carbon pool [17]. The lead concentration of the Jill-Gorj quarry lignite contains twice as much lead (31.40 ppm) than that of the Schitu - Golesti lignite quarry (15 ppm) [18].

Traces of heavy metals distribution from solid residues

The level of heavy metal concentrations, determined in the ashes obtained at the base of the filters, obtained for the metals selected in this study, is ($mg.Kg^{-1}$): Hg (0.037), Pb (47.63) and Ni (79.00). Experimental concentrations

Characteristics	Hg	Pb	Ni	Cd
Spectometer				
Atomic mass	200.59	207.2	58.71	112.40
Prim.wavelength (nm)	253.7	217.0	232.0	228.8
Emis wavelength (nm)	253.7	405.8	341.5	326.1
[a]FCC (mg.L^{-1})	2.7	0.07	0.05	0.013
[b]FCM (pg)	58 (0.26)[c]	1.8	3.6	0.6
Bandpass (nm)	0.5	0.5	0.2	0.5
Calibration				
Y	0.0067x + 0.0059	0.00357x + 0.0006	0.01960x + 0.0006	0.62225x + 0.0003
Fit	0.9995	0.9973	0.9986	0.9998
Charact. Conc.	0.6486	1.2329	0.2245	0.071
Detect limits (mg.L^{-1})	0.0002	0.1	0.04	0.005
Sensitivity (mg.L^{-1})	0.5	0.5	0.15	0.025

Table 2
THE CHARACTERISTICS OF QUANTITATIVE ANALYSIS (AAS)

[a]FCC flame characteristic concentration; [b]FCM furnace characteristic mass; [c] Vapour characteristic concentration (ug.L^{-1})

Sample	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
Filter ash n=3	0.037	0.014	47.63	0.64	79.00	0.39	1.024	0.42
Ash and slag dump n = 4	0.022	0.010	31.80	0,75	78.00	0.43	0.139	0.54
Soil area ash dump n = 6	0.102	0.02	70.20	3.69	45,2	11.24	0.302	0.12
Soil area termo n = 6	0.049	0.022	40.00	2.23	40,8	12.0	0.254	0.12
NV (soil)	0.1		20		20		1	
AT (soil)[a]	1		50		75		3	
Plants ash dump n = 4	0,014	0.004	3.11	0.16	14.6	2.34	0.250	0.04
Plants area ash dump n = 6	0,005	0.001	5.37	0.28	3.91	1.17	0.118	0.03
Plants area termo n = 6	0.004	0.002	3.64	0.17	2.94	1.12	0.050	0.01
MPL[a] vegetation	-		3-10		30		0.4	

Table 3
STATISTICAL DATA: MEAN VALUES OF THE HEAVY METAL CONCENTRATIONS IN THE ANALYZED SAMPLES (TOTAL FORMS)

c- average concentration; sd: standard deviation; [a] Sensitive soils, Source: Order nr.756/1997; NV: Normal values; AT: Alert thresholds; MPL[b] - Maximum Permissible Limit, Source: Order nr.756/1997

Traces element (ppm)	Experimental Average value Romania	Clean Coal Centre Average range IEA	Swaine Global Average Australia	Zhang et al. Global Average China	Raushaan M Average value South Africa
Hg	0.020	0.03–0.19	0.02 – 1	0.12	0.20
Pb	31.40	1–22	2 – 80	25	13.7
Ni	30.30	1.5–21	0.5 – 50	15	11.2
Cd	0.331	0.01–0.19	0.1 – 3	0.6	0.10

Table 4
TRACE CONCENTRATIONS OF HEAVY METALS IN ROMANIAN LIGNITE COMPARED TO OTHER INTERNATIONAL REPORTS

are at a lower level for Ni, Hg, Cd and slightly increased for Pb relative to EU lignite fly ash concentrations [23] (mg. Kg^{-1}): Hg (0.05), Pb (44), Ni (220), Cd (2). A series of research shows that heavy metal traces are subject to an enrichment process in solid products resulting from coal combustion plants [4,16], and the level of enrichment depends on the type of ash and the particularities of each element [24]. This process is defined and quantified by the relative enrichment term (RE) according to equation (1).

$$RE = [(Conc.\ element\ in\ ash / Conc.\ element\ in\ coal) \times Ash\ content\ rav\ coal\ \%] /100 \quad (1)$$

Using this equation (1), given the ash concentration in the raw lignite (36%), the values of the RE Meij enrichment factor for the ash collected at the base of the filters are shown in figure 1 compared to other values in literature reports: China, Li et al. [15]; India, Bhangare et al. [16]; Canada, Goodarzi [25].

The factors of enrichment in the ash retained at the base of the electrostatic precipitators, compared to the classification made by Meiji (1997), place the metals analyzed in our research as follows: nickel (0.94) and cadmium (1.1) in groups I and II (not volatile, respectively volatile and condensation occurs, RE ≈1); lead (0.54) and mercury (0.7) in group III (very volatile, limited condensation, RE < 1). The level of trace metal concentrations determined in fly ash and bottom slag, hydraulically transported in the deposit, is at slightly lower levels of fly ash collected by the filters (mg.Kg^{-1}): 0.022 (Hg); 31.80 (Pb); 78.00 (Ni); 0.139 (Cd).

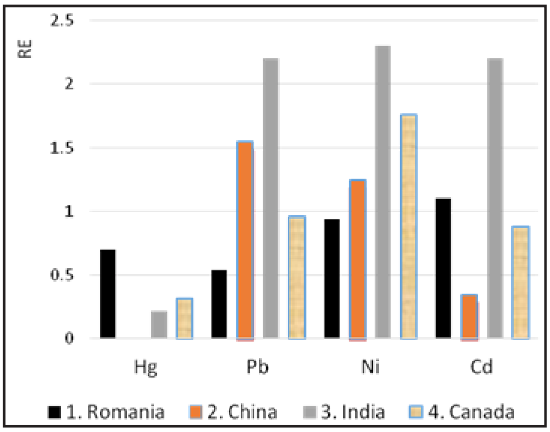

Fig. 1. Experimental enrichment factors (RE Meij) in fly ash electrostatic filter, compare with other research

Accesibility traces metals in soil and plant

The two entities, the power plant and Ceplea ash deposit, located at a distance of approximately 1.5 Km to the NW-SE direction, through the related technological processes and pedo-climatice characteristics of the area, are synergistic point sources of dispersion of trace heavy metals for soil, vegetation and agricultural crops, of the rural and urban areas. The average values of Pb and Ni concentrations exceed the normal values in the soil at the base of the deposit (70.20 mg.Kg^{-1} and 45.2 mg.Kg^{-1}) and for the surrounding soil of the thermal power plant (40.00 mg. Kg $^{-1}$ and 40.8 mg.Kg $^{-1}$), but are below the alert level for sensitive soils (table 3). The average values of Pb and Ni concentrations exceed the normal soil values at the bottom of the ash deposit (70.20 mg Kg^{-1} and 45.2 mg Kg^{-1}) and for the surrounding soil of the boiler (40.00 mg Kg^{-1} and 40.8

	Cn Area ash dump	Cn Area power plant	TF Inner area ash dump	TF Area ash dump	TF Area 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

Table 5
ACCESSIBILITY OF TRACES HEAVY METAL IN SOIL (Cn) AND PLANTS (TF)

$mg.kg^{-1}$), but are below the alert level for sensitive soils (table 3). For the assessment of the degree of loading and to compare the intensities of soil accumulation and contamination with traces of heavy metals, resort to excess coefficient of normal content (Cn), defined as the ratio between the experimentally determined concentration and the normal soil concentration established by Order 756 / 1997 [26]. Cn values have three meanings: greater than 1 indicates a high level of pollution; values equal to 1 indicate normal; the subunit values indicate the absence of these elements. From this point of view, there is a high level of soil transfer for Pb (3.5, 2.0) followed by Ni (2.2, 2.0). The high transfer rate, reflected by the values of the 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 rules for reference values of trace elements in soil [26]. Thus, the lead concentration in soil in the ash deposit area (70.20 mg Kg^{-1}) exceeds the set threshold for susceptible soils of 50 $mg.kg^{-1}$. The transfer capacity of heavy metals from soil to plants was generally described using translocation factor (TF), calculated as the ratio of the metal concentration in the plants and the concentration of the same metal in the plant's own soil [27-29]. 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 (value of reference in this study). The maximum TF values obtained for the studied plants (table 5) are above the reference value (0.5): Cd (1.9) and Hg (0.6) inside the landfill; Hg (0.8) in the area of thermal power plant and Cd (0.39) in the area of ash and slag deposit, indicates a bioaccumulation to be considered for the impact on the quality of life. The other TF values obtained, ranging from 0.005 to 0.19, are well below the Khan reference values, indicating the lack of bioaccumulation of the studied metals.

Conclusions

Quantification of traces of heavy metals with toxic potential generated by thermal power plant was obtained using the analytical technique GFAAS and CVAAS (Hg), characterized by high performance parameters, predictable for trace analysis of heavy metals in coal, solid combustion products and multicomponent samples soil and plants. Traces of heavy metals studied are transferred from the matrix of the coal (lignite crude ash content 36%) in the solid products of combustion characterized by RE_{Meij} ≤, are determined by the characteristics of each analyzed heavy metal content of the raw lignite ash, such as ash, but also the technical characteristics of the brown coal combustion system.

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 observed concentrations 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 (Order 756/1997). The availability of heavy metals in soil and plants, reflected by the TF translocation factor, places Cd and Hg above the bioaccumulation reference value (0.5), estimating the potential for food safety risk.

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Manuscript received: 15.03.2017