EXPOSURE RISK ASSESSMENT FOR HEAVY METALS WITH TOXIC POTENTIAL DISPERSED FROM THE COAL MATRIX INTO THE SOIL

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Abstract. *The paper assesses the risk potential determined by the level of exposure to traces of heavy metals with toxic potential (Pb, Ni, Cd) from the soil, vegetation and grains adjacent to the area of exploitation and thermal energy processing of lignite. Average concentrations determined ($mg.Kg^{-1}$): exceed normal values for soil for Pb (43.71) and Ni (64.14), do not show phytotoxic values for spontaneous vegetation and exceed the reference level for Pb and Cd in cereals according to current norms at European and World level. Taking into account exposure routes, exposure assessment parameters and average concentrations in soil and plants, have been estimated the individual risk for Ni, Cd and Pb. These individual risk index values in relation to the limit value WHO (10^{-6}) demonstrated moderate potential impact on food safety and quality of life in this area.*

Keyword: risk assessment, soil contamination, heavy metals, coal combustion

1. Introduction

In Romania, over 80% of the country's primary energy supply is covered by indigenous energy resources, and coal and lignite account for 17.8%, slightly above the EU average [1].The surface carboniferous area of the Middle Jiu basin and the location of the thermoelectric power plants in this area have been subjected in the last decades to a major anthropogenic action: soil decay for the exploitation of the lignite on the surface and the destruction of the fertile soil layer, the bringing to the surface of large quantities underground rocks and environmental pollution with various radionuclides and heavy metals, tailings, ash and slag formation.

Combustion of coal is a potential source for the emission of trace elements, including heavy metals. According to the level of concern based on negative health effects or their abundance in coal, trace elements are part of three categories: Major concern (As, B, Cd, Pb, Hg, Mo, Se); Moderate concern (Cr, V, Cu, Zn, Ni, F); Minor concern (Ba, Sr, Na, Mn, Co, Sb, Li, Cl, Br, Ge); Negligible concern (Be, Be, Ta, Ag, Te). The impact of heavy metals (Zn, Cu, Mn, Pb, Ni, Co, Cd) on the soil and plants near the exploitation and combustion of lignite thermal power plant was the subject of research projects, finalized with reports and scientific communications [2-7].

The property of heavy metals that accumulate in plant and animal organisms, together with the pathology it determines, justifies the rate of interest and concern for such pollutants.

This study seeks to assess the risk of exposure to various concentrations of heavy metals (Pb, Ni, Cd) from the agricultural and technogenic soil considered as a potential hazard to the health of the population of the surrounding areas.

2. The occurrence of heavy metals in the soil and the impact on the quality of life

In the modern concept, soil pollution is any action that causes disturbance of normal soil functioning, manifested by physical, chemical or biological degradation of the soil. The degree of pollution of soils with heavy metals is dependent on several factors: industrialization degree, geographical area, size of human collectives, type of soil, type of source of pollution, distance from source of pollution [8, 9]. Anthropogenic sources of heavy metals are major factors of soil with materials containing heavy metal particles, causing soil pollution both in surface and in depth. Thus, it has been demonstrated that the presence of heavy metals in soil is associated with the quality of agricultural products in rural areas, pose a risk to those who live or consume the products of the crops grown on it [10, 11].The study of soil and human health is a complicated effort: traditional scientific approaches that isolate a single variable, such as a particular contaminant, is not effective because many of the problems affecting human health involve synergistic relationships.

Toxic pollutants such as heavy metals, exert their effects on the various organs and systems of the human body, the effect being specific to the substance in question. It is very important that it accumulates in the environment and in the human body with the possibility of insidious production of serious pathological alterations.The effects of chronic toxicity are manifested as conditions that develop over long periods of chronic exposure to relatively low concentrations [11]. Inside the body, heavy metals act as free radicals, causing cellular damage, rapid aging, exhausting the body's natural abilities to heal, aggravating disease. Heavy metals accumulate slowly in the kidneys, liver, pancreas, bones, central nervous system and brain where they degrade health without being observed or diagnosed. Chronic exposure to heavy metals has been implicated in several degenerative diseases of the same systems and may increase the risk of cancer [12].

3. Research methodology risk assessement

The first methodology for assessing human risks due to exposure to contaminated soils has been developed by the United States Environmental Protection Agency since 1980 [13]. Based on the principles of the USEPA methodology, as a result of increasing concern about soil contamination, a number of countries in Europe have developed their own methodologies. Because heavy metals are a category of indestructible persistent pollutants and toxic effects on living organisms when they exceed a certain concentration, monitoring of these metals is important for assessing environmental safety and human health in particular.

In the present paper the human health risk assessment refers to heavy metals with recognized toxic potential (Pb, Ni, Cd) that are transferred from the lower coal (lignite) matrix into the soil. Exposure routes considered, taking into account land use and metal properties are: dermal contact, ingestion of soil and local agrovegetale products. The assessment of the risk potential of heavy metals for human health in the investigated area takes into account the concentration levels determined for each exposure path by applying calculation formulas (1, 2, 3, 4) [14, 15, 16].

- Exposure calculation by dermal contact I1, (1):

$$I1 = [CS \times CF \times SA \times AF \times ABS \times EF \times ED] / [BW \times AT] \quad (1)$$

- Calculation of exposure to soil ingestion I2, (2):

$$I2 = [CS \times CF \times IR \times FI / BW] \times [EF \times ED / AT] \quad (2)$$

- Food intake exposure I3, (3):

$$I3 = [CF \times IR \times FI \times EF \times ED] / [BW \times AT] \quad (3)$$

$$CF = (C\ dep) \times (GRAF) + Ctrans \quad (3.1)$$

$$C\ dep = 0 \text{ in our case; } C\ trans = Cs \times UF \quad (3.2)$$

Significant notations: (SA), Absorption Factor (ABS), Exposure Frequency (EF), Exposure Time (ED), Body Weight (BW), Average age (AT), ingestion rate (IR), ingested fraction from contaminated source (FI), uptake factor (UF).

To characterize the potential carcinogenic effects defined as the likelihood of developing cancer during the exposure period using the daily dose or the calculated dose according to Formulas 1- 3 and dosage information for each chemical element, the relationship (4) is used:

$$Risk = I \times SF \quad (4)$$

where, I= chronic daily intake (mg/kg-day) and SF=slope factor (mg/kg/day)
The parameters used for the evaluation of dose exposure are listed in Table 1, [15,16].

Table 1. Parameters used in the mathematical model for exposure assessment.

Exposure pathway	**Parameter**	**Value**	**UM**
Site specific	Exposure frequency	120	d/y
Site specific	Total exposure time	30	y
Site specific	Adults exposure time	21	y
Site specific	Children exposure time	9	y
Site specific	Total days of exposure period	2550	d
Site specific	Adults body weight	70	Kg
Site specific	Children body weight	30	kg
Soil ingestion	Soil ingestion rate	100	mg/d
Soil ingestion	Fraction ingested contaminated source	0.2	a
Dermal abortion	Skin surface area available for contact	4700	cm^2/event
Dermal abortion	Soil to skin adherence factor	1.45	
Vegetable ingestion	Corn daily consumption	0.17	kg/meal
Vegetable ingestion	Root uptake factor	Metal sp.	adim
Vegetable ingestion	Corn ingested from the contaminated area	15	%

d-day; y-year, a-adim.

4. Exposure analysis and risk estimation

The area of interest for soil heavy metals analysis used in this study is located on the NW-SE direction on one side and the other of the Jiu River, comprising three fixed points with potential synergic emission of pollutants in the environment: exploitation of lignite - Jilţ quarry, Turceni thermal power plant, central warehouse Ceplea ash and slag. Samples collected and prepared were analyzed by atomic absorption spectrometry, the method recommended in multicomponent analysis of heavy metals in solid medium samples [17,18, 3], using a Thermo Electron Model S Series AA SOLAAR spectrometer, platform software.

The content of heavy metals in the soil of the area surveyed (Table 2) is slightly above the upper limit of the nationally validated range [9] for the content of potentially polluting elements and substances (PPES) in the soil of the agricultural parcels monitoring ground level I (16 x 16 km): Pb (4.9 - 335 $mg.kg^{-1}$, mean values 21.3 ± 18.6), Ni (4.2 - 171 $mg.Kg^{-1}$, mean values 34.49 ± 14. 5); Cd (0.02-1.68 $mg.Kg^{-1}$, mean values: 0.43 ± 0.27). The concentration level of heavy metals in the area of the studied area according to national rules

[17] exceeds the normal values for lead and nickel (mean values, mg, Kg^{-1}): Pb (43.71) and Ni (64.14) being close to normal.

Table 2. Heavy metal concentrations in soil and plant (mean values, total forms)

Sample	**Pb (mg. Kg^{-1})**		**Ni (mg. Kg^{-1})**		**Cd (mg. Kg^{-1})**	
	c	SD	c	SD	c	SD
Soil field blanks	42.3	0.62	63.5	0.71	0.72	0.67
Soil adjacent area	43.71	3.69	64.14	11.24	0.85	0.12
NV (soil)	20		20		1	
AT (soil)[a]	100		100		3	
Herbaceous vegetation.	7.58	1.06	7.28	2.34	0.19	0.027
MPL[b]	3-10		30		0.4	
Wheat	7.51	0.78	6.58	1.97	0.175	0.03
Barley	8,75	0.82	8.00	1.98	0.170	0.03

[a] Sensitive soils, Source: Order nr.756/1997; [b] Order nr.756/1997

Regarding the permitted limits and standards for heavy metals in grain cereals, leaf vegetables and fresh herbs, specified by FAO / WHO, (2011) and EC1881 (2006) [19,20], the analyzed products (wheat and barley) the limits for Pb (mean value, $mg.Kg^{-1}$): 7.51 and 8.75 respectively) than the maximum admissible level of 0.2 mg. Kg^{-1} and Cd (mean value, $mg.Kg^{-1}$) with average values obtained (0.175, respectively, 0.170) against the average reference level of 0.1 $mg.Kg^{-1}$ set by (EC) [20].

Based on the calculation formulas, the exposure assessment parameters and the average concentrations determined in soil and plants, the individual risk for Ni, Cd, Pb can be estimated. The results are valid taking into account the following: the concentration due to the direct deposition of contaminants is zero and the concentration due to the grain transfer is based on the absorption factor (UF) and the soil metal concentration (Cs); it is considered that 100% of the territory is devoted to the cultivation of crops (wheat); 10% of wheat is used in the contaminated area [14]. The general data needed to calculate the individual risk factor for the three heavy metals with toxic potential Pb, Ni, Cd are shown in Table 3.

Table 3 Evaluation of estimated individual risk for heavy metal

Heavy metal	**Comcentration in soil (mg/kg d.w)** average concentration	**Slope factor (mg/kg/day)[a]**	**Individual risk level**
Pb	43.73	8.50×10^{-3}	10^{-7}
Ni	64.14	9.10×10^{-1}	10^{-6}
Cd	0.85	4.20 x 10-1	10^{-5}

[a] Cocârță et al (2016)

Although the determined Pb and Ni concentrations exceed the cadmium values in the soil of approx. 50 and 60 times, and the excess of normal content (Cn) being double to Cd, the highest individual risk index was obtained for Cd (10^{-5}). This is highlighted in two recent researches: Cocârtă et al. (2016), which highlights the high level of Cd (10-4) against Pb (10-6 and Ni (10^{-5})) and by Ye et al. (2015) that highlights the high environmental risk of Cd relative to the other evaluated metals [21]. The reference limit for WHO individual risk index level 10^{-6} set by WHO quoted by Dumitrescu et al (2012) estimates a cancer case in over one million exposed persons [16].

5. Conclusions

- Energy installations, especially coal-fired power plants, can influence the environment, sometimes even affecting the ecological balance in 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 passenger compartments).
- Combustion products dispersed from the lignite matrix, fly ash discharged through the chimneys, ash and slag from the waste deposits, coal dust from the coal deposits or its transport and preparation together constitute a source of traces of heavy metals with potentially toxic for the area of the site.
- Soil polluted by the three synergic sources (thermo-center, ash and slag deposit and lignite quarry) is a soil with a heavy anthropogenic load of heavy metals.
- The physicochemical parameters of this soil maintain these metals at moderate levels, less accessible to plants. This state of affairs is temporary because the impact of emissions with the soil of this area over a longer period determines the concentration of heavy metals in soil and plants.
- As persistent, indestructible pollutants and toxic effects on living organisms when they exceed a certain concentration, monitoring of these metals is important for assessing environmental safety and human health in particular.

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