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ANTHROPOGENIC POLLUTION DUE TO EMISSION OF HEAVY METALS GENERATED FROM A LIGNITE THERMAL POWER PLANT IN ROMANIA

ΒY

DELIA NICA-BADEA¹, LILIANA LAZĂR², BRÎNDUŞA MIHAELA SLUŞER^{2,*} and IGOR CREŢESCU²

 ¹"Constantin Brâncuşi" University of Târgu-Jiu, Romania, Faculty of Technical, Medical and Behavioral Sciences
 ²"Gheorghe Asachi" Technical University of Iaşi, Romania,
 "Cristofor Simionescu" Faculty of Chemical Engineering and Environmental Protection

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Abstract. This experimental study addresses to the distribution of heavy metals in the area of Turceni, as a result of anthropogenic pollution produced by one of the biggest Romanian coal combustion thermal power plant. The concentrations of various heavy metals (Zn, Cu, Mn, Pb, Ni, Co, Cd, and Hg) in soil, vegetation and agricultural products was carried out by using a high resolution analytical technique (Atomic Absorption Spectroscopy). The monitoring area was located around the anthropogenic pollution sources *i.e.* inside the power plant, around the ash deposit, and in some rural communities located in the direction of current propagation where particles generated by the exhaust stacks combustion are predominant distributed. The concentration of heavy metals in plants is dependent on metal type, plant genotype, soil and environmental conditions, decreasing as a result of measures for limitation of emissions. The annual average concentrations do not exceed the maximum allowed concentration, but the enclosure of power plant and the deposit of slag and ash, which was not proved to affect the human health.

^{*}Corresponding author; e-mail: brobu@ch.tuiasi.ro, icre@ch.tuiasi.ro

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1. Introduction

Heavy metals are distributed in different concentrations in soil, water, and air, vegetable or animal food, depending on various factors that determine their pollution. The air can be a contamination source due to the fact there is a vehicular road and accumulation of metals in soil and vegetation. The heavy metal pollution is mainly generated by the following sources: geochemical, anthropogenic, biotic environment (Alloway, 1990; Ross, 1994; Luca *et al.*, 2006). Heavy metal contamination of air is the result of anthropogenic developed activities like: combustion of coal, oil, ferrous metal production, iron and steel production, cement production, gas treatment plants for waste accumulation and waste incineration, etc. Quantitative estimation of heavy metals released into the atmosphere from natural and anthropogenic sources is presented in Table 1.

 Table 1

 Evaluation of the Quantities of Heavy Metals Released into the Atmosphere of Anthropogenic Origin Compared to Natural Sources (Ross, 1994)

Emission	Heavy metals (10^3 tons)						
EIIIISSIOII	Cd	Cu	Ni	Zn			
Natural	0.83	18	26	44			
Anthropogenic	316	2160	1000	14.000			

The thermo-energetic installations, particularly the power plants using coal as fuel, can affect the environmental quality, sometimes having strong influences on the ecological balance in areas where they are located. They generate a complex impact on all environmental factors, not only in their surrounding area (air, water, soil, flora and fauna, food and indoor spaces), thus the energy production based on burning coal is considered as the main source of pollution (Nica-Badea, 2015; Florescu *et al.*, 2011; Corneanu *et al.*, 2013; Radu *et al.*, 2013).

A particular attention in the monitoring area was given to air quality, water, soil, human health, the shortage of plant and animal species recorded. Each of these factors can be qualitatively characterized by indicators clearly defined by the environmental standards and used to assessing pollution level and for which there are set maximum allowed limits (Horaicu *et al.*, 2010; Ştefănescu *et al.*, 2013). The main pollution around the thermal power plant is due to the huge quantity of ashes generated as a result of coal combustion. The fly ash removed by chimneys, together with the dust and wind-blown fine ash from the ash and slag heaps of coal dust deposits, resulted from coal

transportation and its preparation before burning, represent a hazardous source of particulate pollutants. If the generate dash from burning coal has a low concentration of heavy metals, the aerosols exhausted from thermal power plant are less toxic. In terms of toxicity, the heavy metals become dangerous for human health and ecosystems, in case of reaching high concentration, only.

The main polluted systems with heavy metals generated by thermal power plants are: flue gases, ash in landfills and systems of operating, transportation and storage of coal. The impact of heavy metals on the environment is investigated to reveal the levels, effects on biotic components in relation to the environmental regulations. Given the importance of plants in most recipes of food preparation, more studies were focused on investigation of heavy metal accumulation in soil and plants in order to find the measures to diminish their impact on the living environment (Măruțoiu *et al.*, 2006; Lăcătuşu *et al.*, 2009; Nica-Badea, 2017a; Nica-Badea *et al.*, 2017b). Accessibility of the metals from the soil to the plants was described by the transfer factor (TF); heavy metal transfer coefficient indicates the level of bioaccumulation, toxicity and tolerance of the metal for different plants (Kabata-Pendias, 2011).

The distribution of heavy metals in different foliar segments of the vegetation is depending on several factors (Báthory *et al.*, 2003; Greger, 2004): humidity (high humidity favours the foliar absorption); type of metal (Zn and Cu are absorbed faster than Pb, and this is predominant adsorbed on the surface of the leaves); pH of interface; the oxidation state and environmental conditions. Accumulation of heavy metals transferred by air to forest vegetation and tolerance depends on the plant species, vegetative body age, and type of metal. Uptake and accumulation of toxic metals in plants is strong corelated with their bioavailability which in the majority of cases respect the following order: Zn > Cu > Pb, but some exceptions were found depending on the above mentioned factors.

All heavy metals exhibit a toxic potential if their concentrations are high enough. The following heavy metals: Hg, Cu, Pb, Zn and Cd, belong to the category of heavy metals with high toxicity for living organisms, even in trace concentration. The toxic effect is manifested when overcoming the threshold level. On the other hand, some elements such: Co, Cu, Fe, Ni, Zn are essential components of proteins involved in different metabolic pathways. Thus, if the food would be totally free of metals, it would appear nutritional deficiencies (Susan, 1990).

The occurrence of toxic effects on plant metabolism is subject to atmospheric and tolerance vegetation limit. Toxicity of heavy metals accumulated in the plant from dust deposition depends on: metal concentrations in the environment, vector-type of exposure (ingestion, absorption through the roots after the deposit of metals in the atmosphere on the ground), the distribution of dose/exposure time, type and severity of the effect, during necessary for the manifestation of the effect (Ross, 1994). Monitoring of these metals is important for assessing the environmental safety and human health (EC 1881, 2006; Batayneh 2012; Cocârtă *et al.*, 2016).

2. The Mechanism of Interaction Metal – Plants

The mechanisms by which heavy metals toxicity is occurred are: a) blocking functional groups of molecules with important biological role (enzymes, polynucleotide or conveyor systems for nutrients), b) substitution of metal ions or other biomolecules essential cellular function, c) distortion and inactivation of biomolecules in particular enzymes, d) destroying the integrity of cell membranes by the direct effect on sulfhydryl groups and, e) inducing membrane constituents directly or indirectly through lipid peroxidation of membranes and organelles toxic free radical cellular oxidative stress (Onac, 2005). Through there mechanisms of action, heavy metals are likely to become toxic due to the fact that metal ions strongly bind to oxygen atoms, nitrogen, sulphur, which is in large quantities in biological systems and can serve as ligands to ions of all essential metals (Ross, 1994). Effects of heavy metal toxicity are manifested at the cellular level by altering plasma membrane permeability, cell organelles and ultra-structural changes influence metabolic processes in the cytosol.

Physiological effects of heavy metal toxicity are manifested by its influence on plant nutrition with impaired plant growth, photosynthesis and transpiration intensity and increased respiration in the dark, disturbing hydric regime of the plants - one of the first and most important effects that heavy metals have on plant metabolism, the main cause of disturbance to other physiological and metabolic processes (Onac, 2005).

When entering the plant, these pollutants must first penetrate the cell membranes barrier, where a series of processes described in the literature (Farago, 1994) take place. This has shown that some metals may cause changes in membrane permeability, loss of potassium ions (*e.g.* the plant from fam. *Caryophyllaceae*, *Silenecucubalus*), and membrane permeability is immediately lost by the addition of copper. Heavy metals have a high affinity for carboxyl groups and sulfhydryl, depending on their physicochemical properties. Thus, oxidation and formation of disulphide bridges to sulfhydryl groups of erythrocyte membrane proteins play an important role in the mechanism of destruction cell and subsequent hemolysis caused by copper. Heavy metals lead to a higher formation speed of reactive oxygen species (hydrogen peroxide H_2O_2 , superoxide anion O_2^{--} and hydroxyl free radical 'OH) which will initialize the process of lipid peroxidation, resulting an impaired functioning of biomembranes.

Enzyme inhibition is also one of the heavy metals effects, mainly operated by the same mechanism of affinity for sulfhydryl groups necessary for catalytic activity, oxidation, or by substitution of divalent cations in the composition of the enzyme. Demonstrated that the application "in vivo" of cadmium and lead in soybeans produced stimulation intensity of breath, due to the need for ATP production through oxidative phosphorylation, because the rate of phosphorylation was reduced. We established two main mechanisms of inhibition of enzymatic activity under the action of metals: metal binding to functional groups (–SH) important for catalytic activity and ion substitution in the enzyme structure with a toxic ion deficiency determination needed to metal-enzyme.

Effects of metals applied "in vivo" may often be different from those produced "in vivo". For metal to generate an inhibitory effect must be kept in an active form and an inhibitory concentration to interact, or to compete with the metal structure of the enzyme. At various high concentrations, some metals may, however, cause an effect of enzyme induction. This is only one side and appears as a consequence of "in vivo" metals. For example, peroxidase induction was observed in different plant species, the leaves and roots after application of toxic amounts of cadmium, copper, nickel, lead, mercury (peroxidase induction may be induced by another factors: pathogenic infections, air pollution with SO₂). Increased catalase activity was observed following application of toxic doses of lead in *Zea mays* and *Allium cepa* to the action of mercury. In a similar way, the enzymes involved in intermediary metabolism (Krebs cycle) izocitrat-dehydrogenase, malate dehydrogenase, glutamate dehydrogenase undergoes induction.

Effects of metals on enzymes involved in nucleic acid metabolism can cause indirect alterations in replication fidelity, an increased activity of hydrolytic enzymes like ribonuclease and deoxyribonuclease after application "in vivo" cadmium in seedlings of Glycine max (Farago, 1994).

Plants have developed various defence mechanisms against stress effect caused by the presence of toxic metals. Mechanisms can be classified into two categories: preventing the interaction of metal-site and which counteracts the effects of metals. The mechanisms of the first category in the plant may act by altering cell membrane permeability, the roots, mycorrhizal fungal filaments that of cells or cellular level. Mechanisms that neutralize the negative ions in the presence of molecules consisting of glutathione, ascorbic acid, tocopherol, β -carotene and flavonoids that function as important reducers (reduced reactive free radicals resulting from the action of metals) (Farago, 1994).

Heavy metal contamination of food (plant origin) is carried mainly from the soil and atmosphere, especially when the crops are in the vicinity of potential sources of pollution. Heavy metal toxicity is in direct correlation with metal solubility, chemical form of metal, structure of a metal compound and bioavailability, etc. On the other hand, it has been shown in the frame of interaction mechanism a synergism effect between traces of Cu and Zn on potentiation, Cu and As, Cu and Sn, Zn and As, but an antagonism effect between these elements and Pb (Catană, 2002).

3. General Information about Thermal Power Plant of Turceni

Thermal power plant is located in Meadow Jiu, bordering at South with a brook, in East with the Jiu River and in North with Turceni city, located at about 1.5 km far (Fig. 1).

Monitoring area of Turceni Power Plant, from geomorphologic point of view, belongs to the Getic Piemont, presenting transition characters between mountain and plain, with geomorphologic conditions and resources capitalization in dynamics of settlements and landscapes. The study area is characterized by increased fragmentation of the landscape, which favoured the loose rocks marmo-clay, clays, sand, and gravel. The hydrographical network is continuously deepened and broadened the action of tectonic factors, climatic and anthropogenic. In terms of climate, this is influenced mainly by Mediterranean climate, with southern and western part of circulation, interfering with air traffic corridor of Jiu River, the NW-SE. Temperature and rainfall regime is influenced by oceanic air masses from the West, Mediterranean climate combined with the SV. Natural forest vegetation represented narrowed gradually giving way to grasslands and crops.



Fig. 1 – Monitoring area of Turceni Thermal Power Plant, Romania (Satellite map: http://satellite world map.com).

Water cooling is provided by the Jiu River power plant being processed seven natural draft cooling towers in counter: closed circuit - 0.75 intake flow $m^3/s/block$, open circuit - need 12 $m^3/s/block$. Ash and slag are discharged hydraulic: a deposit Ceplea Valley (2 million m^3), two backup storage (6 million m^3). Fuels: oil (for start); gas probe (medium flame); lignite (central storage capacity 500,000 tons); consumption (70% own production:

North Jilţ, South Jilţ quarries, Dragoteşti mine and 30% SNLO supply). Boilers equipped with steam boilers, hot water boilers and hot water present an environmental pollution risk. By burning fuel in boilers outbreaks develop combustion gases that are discharged into the atmosphere through the chimney. These include CO_2 , CO, SO_2 , NO_x and particulate matter (ash etc.). Fly ash is harmful, especially by heavy metals content.

The main pollutants generated into atmosphere by combustion gas fluxes are: SO_2 , NO_x , CO_2 , CO, particulates and unburned particles, traces of heavy metals (Hg, Sb, As, Pb, Cr, Co, Cu, Mn, Ni, V). The main possible sources of soil pollution are the deposit of coal, oil storage, petroleum, chemical storage, chemical water treatment plant and inner channels, slag and ash depot. Due to the wet ash transport to the landfill, the solids emissions in water are possible. Measures to prevent pollution of soil and vegetation are: installation of wetting heaps of slag and ash to prevent the wind dispersion; maintenance protection curtains made of resistant trees and shrubs; landfills comply temporary technology.

4. Objectives of this Study

The overall impact of air pollutants on environmental degradation increased recently the focus on environmental monitoring and control. It has to obtain direct information about the concentration of environmental pollutants in order to establish the interdependencies between pollutants and environmental conditions. Sampling and methodology of environmental pollution investigation, the level of pollution near the sources are achieved by identifying the potential sources of pollutants, the concentration of pollutants and their longer-term monitoring and its rate and effects.

Some plants, such as herbaceous vegetation, vegetables, and fruit can be used as bio-monitors of pollution, in general, heavy metals, in particular, by chemical analysis of components generated from additional sources of pollution, like that produced by combustion of coal.

In order to assess the degree of heavy metal pollution in area of Thermo-energetic Complex of Turceni with largest power plant based on solid fuel (lignite), it was aimed to investigating the concentration of heavy metals in primary ash (the filter), ash deposited into the landfill, soil, vegetation, food plant products.

5. Sampling and Analytical Methods

Given the objectives and the level of funding, it was chosen the area and the sampling to assess the concentration of heavy metals in relation to the rules on three levels of interest: - solid fuel, the primary filter ashes, ashes deposited in the landfill – land adjacent power plant and dump –in the area of power plant vegetation (*i.e.* plants and berries, food products in surround area). Sampling was done along the Jiu Valley, taking into account dominant winds and the eight cardinal directions consisting of: 3 coal samples (lignite), 3 samples from the filter ash, 3 samples of ash and slag dump, 8 soil samples, 9 vegetation samples, 15 plants and agro-food samples.

Quantitative analysis of metals in ash, soil and plant products was carried out by using the atomic absorption spectroscopy. Determination of heavy metals in soil was done according to MA079 Re.0/2006 microwave operation procedure.

Determination of heavy metals in soil by mineralization in concentrated strong acids and wet with hydrogen peroxide. Wet mineralization HNO₃, HCl and H₂O₂ using a microwave digestion system from Milestone: weigh 1 g soil mineralization vials of digestion system; oxidant mixture is added: 6 mL 65% HNO₃ + 3 mL HCl + 0.25 mL 35% H₂O₂ 30%; sealed ampoules and starts the mineralization (Table 2). Cool samples: 30 min ventilation; to keep the samples in digestion vessels at least 12 h (overnight) covered with filter paper to avoid contamination, filter samples in flasks of 50 mL (washing with distilled water filter).

Mineralization Steps Program							
Stage	Time, [min]	Power, [W]	Temperature, [°C]				
1	15	850	150				
2	15	850	210				
3	15	850	210				

Table 2

 Table 3

 Detection Limits and Sensitivity of Atomic Absorption Spectrometer

Metal	Detection limits, $[mg^{-1}]$	Sensitivity, $[mg^{-1}]$
Zn	0.005	0.02
Cu	0.02	0.1
Mn	0.01	0.05
Pb	0.1	0.5
Ni	0.04	0.15
Со	0.05	0.2
Cd	0.005	0.025
Hg	0.0002	_

Determination of trace elements in plant analysis was done according to the methodology for assessment of plant mineral nutrition by dry mineralization (mineralization ignition). Mineralization of plant material: weigh 1 g dried herb in a porcelain or platinum crucible, burn the plant material to a gas burner flame, ash in the oven at 450°C, leave evidence in the oven until a white-gray. Colour can vary depending on the nature of plant material between gray and white with shades of yellow or red, if the colour is too dark, ash is treated with a few drops of concentrated HNO₃, then sits on a sand bath and allow to evaporate again be placed in the oven at the same temperature of 450°C ashes are treated with 1 mL of HCl 6 N, HCl evaporation in a sand bath, repeat the treatment with HCl, samples are put in flasks of 25 mL 0.5 N HCl, filtered in 50 mL Erlenmeyer glasses, distribute extracts obtained by atomic absorption spectrometry to determine trace elements in soil and plants. The detection limits and sensitivity of the atomic absorption spectrophotometer are presented in Table 3.

6. Results and Discussions

The results of quantitative analytical measurements in the target area revealed that the concentrations of heavy metals in ash from the filter basket of gases, ash and slag transported to the landfill, vegetation and agri-food plant products are much lower than maximum limits, as given in Table 4. Heavy metals generated in solid fuel combustion, lignite career stall can be found in all the ash taken from the filters, the ashes and slag from the dump and the area of influence of power plant soil adjacent. The concentrations of heavy metals in soil adjacent power plant is in the normal range with the exception of Cu, Pb, Ni whose averages exceed the maximum limits and alert thresholds in case of agricultural soils standards (OMAPPM756/1997).

	and Coal from Power Plant Area							
Succification	Heavy metal concentration (mg \cdot kg ⁻¹ – average concentration)							
Specification	Zn	Cu	Mn	Pb	Ni	Co	Cd	Hg
Filter ash	12.10	65.40	502	47.90	79.00	13.80	1.024	0.037
Ash dump	55.60	56.90	263	31.80	78.00	11.60	0.139	0.020
Soil sample $(0 - 25 \text{ cm})$	86.20	26.42	501	55.25	43.25	12.12	0.270	0.064
Coal sample	56.50	21.60	132	31.40	30.30	5.79	0.331	0.019
Maximum allowed concentration soil	300	100	1500	100	100	50	3	1

 Table 4

 The Concentration of Heavy Metals in Ash, Slag, Soil

 and Coal from Power Plant Area

Distribution of heavy metals studied in vegetation of the assessed area (Table 5) showed that some metals are measured within permissible limits (C_{ma1} – C_{ma2}) as follows: Mn and Pb in heap ash, Cu, Mn, Pb to the dump, Mn on the

west and Pb for all cardinal directions (North - N, South - S, East - E, West - W) and intercardinale (NE, NW, SE).

Distribution of Heavy Metals in Vegetation in Fowerplant Area								
Specification	Heavy metal concentration, $[mg \cdot kg^{-1}]$							
Specification	Zn	Cu	Mn	Pb	Ni	Co	Cd	Hg
Vegetation in ash dump	48.50	14.20	193	3.11	14.6	1.80	0.250	0.014
Around vegetation ash dump	41.60	15.10	69	5.37	3.91	0.703	0.118	0.012
Vegetation W	35.20	5.75	51.20	8.24	12.20	2.51	0.20	0.014
Vegetation NW	22.20	6.50	23.00	9.03	7.50	2.20	0.17	0.012
Vegetation N	26.50	4.00	23.75	6.04	7.70	2.10	0.20	0.012
Vegetation NE	27.50	5.75	24.50	6.50	5.50	2.20	0.22	0.010
Vegetation E	21.50	5.00	24.30	8.20	6.20	2.00	0.15	0.005
Vegetation SE	23.70	5.50	22.50	7.23	6.20	2.20	0.22	0.004
Vegetation S	24.20	4.01	23.75	8.12	5.70	1.70	0.17	0.017
Maximum allowed concentration $(C_{ma1} - C_{ma2})$	50 - 100	15 – 20	50 - 200	3 - 10	30	5 - 9	0.4	0.050

 Table 5

 Distribution of Heavy Metals in Vegetation in Powerplant Area

The concentrations of other measured metals were below maximum limits, according to national environmental standards. Concentrations of heavy metals measured in food crop in the area of influence of Thermal Power Plant of Turceni (Table 6) are concordant with literature and official reports, so that the heavy metals concentrations are in accepted limits in case of product categories or outside (Ćujić *et al.*, 2016; Emurotu and Onianwa, 2017; Horaicu *et al.*, 2010; Noli *et al.*, 2016).

Evolution of metal concentrations in soil, in period 1997 - 2010 as presented in Table 7, maintains the same level reflects or a slight decrease, something which we believe is due to technical measures taken in lately the line of diminishing pollutants.

Reporting the measured concentration values to environmental standards (Order 756, 1997), all analysed plants are within maximum admissible limits, but compared to literature values, the assessed situation exceeds the allowed limit such as: *a*) berries (Zn, Cu, Pb, Cd), (Gherghi, 2001), leaf vegetables, carrots without (Cd, Pb, Cu), herbs (Cd, Pb), cereals (Pb); *b*) on all products (Ni, Cd), (Kabata-Pendias and Pendias, 2001; Horaicu *et al.*, 2010; Ştefănescu *et al.*, 2013).

Table 6 Distribution of Heavy Metals in Agro-Food of Plant Products in Power Plant Area								nt Area
Samples of								
products	Zn	Cu	Mn	Pb	Ni	Co	Cd	Hg
Berries	48.50	14.20	193.00	3.11	14.60	1.800	0.250	0.014
Carrot	41.60	15.10	69.00	5.37	3.91	0.703	0.118	0.012
Celandine	35.20	5.75	51.20	8.24	12.20	2.510	0.200	0.014
Wormwood	22.20	6.50	23.00	9.03	7.50	2.200	0.170	0.012
Wheat 1	23.75	5.00	32.25	7.25	6.25	2.250	0.170	0.004
Wheat 2	21.50	5.00	24.50	8.25	6.25	2.000	0.150	0.003
Wheat 3	22.25	6.50	26.75	9.00	7.50	2.250	0.170	0.005
Wheat 4	35.25	5.75	22.00	8.25	12.25	2.500	0.220	0.004
Wheat 5	19.00	5.25	24.00	8.50	5.25	1.750	0.170	0.018
Wheat 6	19.00	5.00	23.75	7.75	5.25	1.750	0.150	0.017
Wheat 6	23.25	5.50	23.25	7.25	5.25	2.000	0.200	0.016
Wheat 7	17.25	3.75	14.50	7.25	6.25	2.000	0.220	0.012
Wheat 8	27.50	5.75	25.00	6.50	5.50	2.250	0.220	0.004
Wheat 9	20.25	4.50	26.50	6.50	8.75	2.000	0.120	0.005
Barley	24.25	4.00	17.25	8.00	5.75	1.750	0.170	0.006

Table 7

Heavy Metals Concentration in the Soil of Power Plant Area Between 1997–2010							
Metal	Concentration, $[mg kg^{-1}]$						
Ivicial	1997	2000	2010				
Cu	23 - 43.50	24 - 42	24.20 - 29.20				
Zn	63 - 123	58 - 224	91 - 100				
Pb	38 - 48	25 - 45	40 - 70.20				
Со	16 - 18.50	16 - 19.50	11.60 - 12.60				
Ni	49 - 78	35 - 39	40.80 - 45.20				
Mn	331 - 638	464 - 639	473 - 525				
Cd	0.80 - 0.90	0.70 - 1.80	0.254 - 0.302				

High concentrations of heavy metals as a specific feature of anthropogenic proto soil in power plant zone of influence are caused by the stack emissions, coal dust, ash from coal storage and collection, and landfill dumping shattered, even if the dump is done wet. Plants can be used as bioindicators providing information on the environmental quality or environmental changes as biomonitors, when providing information on the amount of pollutant.

7. Conclusions

Climatic parameters in Turceni power plant area have no significant influence on the accumulation of heavy metals in soil or plants. Given that the ash dump is located west from the Turceni city, is expected that dry winds can contribute to the ash migration and create additional pollution phenomena. This study certified that the higher concentrations of heavy metals, measured around the power plant, located at west of the ash deposit, are found in vegetation situated W or NW.

The soil in Turceni power plant area has an additional anthropogenic load of heavy metals, in particular, copper, nickel, lead and even zinc. Soil physic-chemical parameters increase in this case the inaccessibility for some plants. However, this situation is temporary, and the environmental impact on long time is directly determined by the concentration of heavy metals in soil or plants. The pH and heavy metal content in surface water samples area showed that the dump area has a significant contribution to plant contamination.

Concentration of microelements in plant tissues is conditioned by certain characteristics of plants, such as plant species, vegetative organ development with the greatest capacity to accumulate heavy metal compounds, age, presence in the soil solution of other elements (Fe, Mn, Al), pH and redox potential of the soil.

The experimental results obtained in case of determination of heavy metals in vegetation near the power plant and ash landfill reveal that some of their concentrations constantly increased, although some heavy metals were found in concentrations that are within acceptable limits. Concentrations of heavy metals determined in food crop in Turceni power plant area of influence are depending on product category. This fact shows that pollution is still recent and therefore cannot describe the clear process of heavy metal pollution. The phenomenon is amplified if the human activities are extended, without taking into account specific protection measures for agro-pedological-improvement.

Heavy metals pollution monitoring (Cu, Cd, Pb, Ni, Zn, Co, Mn, and Hg) in the influence area of lignite power plant can be properly achieved by instrumental analysis as atomic absorption spectroscopy which offer high analytical performances in terms of sensitivity and selectivity.

In both types of soil and vegetation analysis, the maximum allowed concentration in case of heavy metal with high toxicity in food products were not significantly exceeded, and it couldn't be proved yet that is affecting the human health, vegetation in the immediate vicinity.

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REFERENCES

- Alloway B.J., *The Origin of Heavy Metals in Soil, in: Alloway, BJ(Ed) Heavy Metals in Soil, Blackie*, Wiley, New York, 29-39 (1990).
- Batayneh A.T., Toxic (Aluminum, Beryllium, Boron, Chromium and Zinc) in Ground Water: Health Risk Assessment, Int. J. Environ. Sci. Technol., 9, 153-162 (2012).
- Báthory D., Nicoară A., Bercea V., Conținutul în metale grele la lăstarii de fag (Fagussylvatica L.) și carpen (Carpinusbetulus L.) din ecosisteme forestiere poluate, in: Environment-Research, Protection and Management (in Romanian), Presa Univ. Clujeană, Cluj-Napoca, 35-38 (2003).
- Catană L., Posibilități de reducere a conținutului de metale grele din produsele horticole industrializate, Hortinform, 7, 119 (2002).
- Cocârtă D.M., Neamţu S., Reşetar, Deac A.M., Carcinogenic Risk Evaluation for Human Health Risk Assessment from Soils Contaminated with Heavy Metals, J. Environ. Sci. Technol., 13, 2025-2036 (2016).
- Corneanu M., Corneanu G., Lăcătuşu A.R., Cojocaru L., Butnariu M., Concentration and Distribution of Heavy Metals and Radionuclides in Topsoils from Middle Jiu Valley Surface Coal Exploitations Surrounding Area (Gorj County, Romania), Geophysical Research Abstracts, **15**, EGU2013-8818 (2013).
- Ćujić M., Dragović S., Dordević M., Dragović R., Gajić B., Environmental Assessment of Heavy Metals Around the Largest Coal Fired Powerplant in Serbia, Catena, 139, 44-52 (2016).
- Emurotu J.E., Onianwa P.C., *Bioaccumulation of Heavy Metals in Soil and Selected Food Crops Cultivated in Kogi State, North Central Nigeria*, Environmental Systems Research (2017) 6:21 DOI 10.1186/s40068-017-0098-1.
- Farago M.E., *Plants and the Chemical Elements: Biochemistry, Uptake, Tolerance and Toxicity*, Margaret E. Farago–Weinheim (Ed.), VCH, 31, 67, 107 (1994).
- Florescu D., Iordache A., Piciorea I., Ionete R.E., Assessment of Heavy Metals Contents in Soil from an Industrial Plant of Southern Part of Romania, AES Bioflux, 3, 2, 206-210 (2011).
- Gherghi A., Burzo I., Bibicu M., Margineanu L., Badulescu L., *Biochimia şi fiziologia legumelor şi fructelor*, Second Edition, Editura Academiei Române, Bucureşti, 253 (2001).
- Greger M., Metal Availability, Uptake, Transport and Accumulation in Plants, in: Heavy Metals Stress on Plants. From Biomolecules to Ecosystems, Prasad MNV (Ed.), Springer Verlag, 1-27 (2004).
- Horaicu C., Robu B., Florea F., Horaicu M.A., Influence on Environment of Heavy Metals Generated by Mining Industry: Influence on Soil Quality of Copper, Zinc, Lead, Mangan and Silver, Generated in Mestecanis Area, Carpathian Journal of Earth and Environmental Sciences, 5, 2 (2010).
- Kabata-Pendias A., Pendias H., *Trace Elements in Soils*, 3rdEdition, CRC Press, 413, (2001).
- Kabata-Pendias A., *Trace Elements in Soils and Plants*, Fourth Edition, CRC Press (2011).

- Lăcătuşu A.R., *Heavy Metals Soil Pollution State in Relation to Potential Future Mining Activities in the Roşia Montană Area*, Carpthian Journal Earth and Environmental Sciences, **4**, 2, 39-50 (2009).
- Luca E., Roman C., Chintoanu M., Luca L., Puşcaş A., Hoban A., *Identificarea* principalelor surse de poluare din Bazinul Arieşului, Agricultura – Ştiinţă şi Practică, **59-60**, *3-4*, 84-90 (2006).
- Măruţoiu C., Gogoaşă I., Măruţoiu O.F., Soran M.L., Nica-Badea D., Separation, Identification and Determination of Some Hard Metals from Silybummarianum L., in: Metal Elements in Environment, Medicine and Biology, Garban Zeno, Dragan Petru (Eds.), Publishing House Eurobit Timişoara, vol.**VII**, 241, (2006).
- Nica-Badea D., Assessing the Degree of Dispersion and Distribution of Heavy Metals in Soil and Plants Associated with Area of Influence of a Coal Power Plant, Journal of Environmental Protection and Ecology, **16**, 2 (Part 1), 453-460 (2015).
- Nica-Badea D., Determination of Traces Heavy Metals from Solid Residues Formed by Combustion of Lignite in Relation to Degree of Accessibility in Soil and Plants, Revista de Chimie București, **68**, 10, 2363-2366 (2017).
- Nica-Badea D., Dumitru M.G., Cretescu I., Monitoring of Mercury Content in the Main Environmental Components Caused by Lignite Combustion, Materiale Plastice, 54, 4, 781-784 (2017).
- Noli F., Tsamos P., Concentration of Heavy Metals and Trace Elements in Soils, Waters and Vegetables and Assessment of Healt Hrisk in the Vicinity of a Lignite-Fired Power Plant, Scienice Total Environmental, **563-564**, 377-385 (2016).
- Onac S., Cercetări privind influența unor metale grele din haldele de steril din zona Cavnic asupra unor procese fiziologice la plante, Doctoral Thesis, Babeş Bolyai Univiversity of Cluj-Napoca, Faculty of Biology and Geology, 24-45, 2005.
- Radu C., Nedeff V., Chitimu A.D., *Theoretical Studies Concerning Residual Soil Pollution by Heavy Metals*, Journal of Engineering Studies and Research, 19, 2, 89-97 (2013).
- Ross S., Sources and Forms of Potentially Toxic Metals in Soil-Plant System, in Toxic Metals in Soil–Plant Systems, John Wiley & Sons, 3-2 (1994).
- Susan L.M., *Metals in Foods. A Literature Survey*, The British Food Manufacturing Industries Research Association, No. 12, Surrey, UK (1990).
- Ştefănescu L., Robu B.M, Ozunu Al., Integrated Approach of Environmental Impact and Risk Assessment of Rosia Montana Mining Area, Romania, Journal of Environmental Science and Pollution Ressearch, 20, 11, 7719-7727 (2013), DOI 10.1007/s11356-013-1528-x.
- *** EC 1881, Commission Regulation (EC) no 1881/2006: Setting Maximum Levels for Certain Contaminants in Food Stuffs, Official Journal of the European Union, L 364, 5-24 (2006).
- *** OMAPPM 756, Order of Romanian Ministry No756/1997 for Approval of Regulation Concerning the Environmental Pollution Assessment, Official Gazette of Romania, First Part, No. 303, Bucharest, 1997 (in Romanian).

POLUAREA ANTROPICĂ DETERMINATĂ DE EMISIA METALELOR GRELE GENERATĂ DE O TERMOCENTRALĂ PE BAZĂ DE LIGNIT DIN ROMÂNIA

(Rezumat)

Acest studiu experimental abordează distribuția metalelor grele în zona Complexului Termo-Energetic Turceni (România) ca urmare a poluării antropice produsă de una dintre cele mai mari termocentrale bazată pe combustia cărbunelui. Concentrațiile diferitelor metale grele, cum ar fi: Zn, Cu, Mn, Pb, Ni, Co, Cd, Hg în sol, vegetație și produse agricole, s-au determinat utilizând o tehnică analitică de înaltă rezoluție: spectroscopia de absorbție atomică. Zona de monitorizare a fost localizată în jurul surselor de poluare antropică, adică în interiorul centralei termo-electrice, în jurul depozitului de cenuşă și în unele comunități rurale situate în direcția propagării curenților de aer, unde ajung preponderant particulele emise de gazele de ardere emise de coşurile de evacuare. Concentrația metalelor grele în plante depinde de tipul de metal, de genotipul plantei, de condițiile de sol și de mediu, fiind în scădere ca urmare a măsurilor de limitare a emisiilor. Concentrațiile medii nu depășesc concentrația maximă admisă, cu excepția incintei centralei electrice și a depozitelor de zgură și cenuşă, care nu afectează încă sănătatea populației.