Determination of Potentially Toxic Heavy Metals (Pb, Hg, Cd) in Popular Medicinal Herbs in the Coal Power Plant Area

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Medicinal and aromatic plants are of particular interest for human health. The purpose of this research is to determine the concentration and dispersion of heavy metals Pb, Cd, Hg, in medicinal herbs Chelidonium majus L, Crataegus monogyna, Artemisia absinthium L, Hypericum perforatum, from spontaneous flora bordering coal power plants. The method used (AAS) is recommended by high performance parameters in the determination of trace metals in plant samples. Detection Limit (mg.L^{-1}): Pb (0.10), Hg (0.0002), Cd (0.005); sensitivity (mg.L^{-1}): Pb (0.5), Cd (0.025). The metals detected in the coal used as fuel are found in all samples analyzed: ash, slag, soil, vegetation, medicinal plants of spontaneous flora. The concentration in the soil exceeds national normal value for Pb: 55.10 mg. Kg^{-1}. The metal bioaccumulation in medicinal plants is reflected in the values of transfer coefficient (TF): Cd (0.47)> Hg (0.15) > Pb (0.13). The concentration level related to the maximum extent permitted under the force rules for herbs: FAO / WHO (2011), Ph Eur (2008), RC / EC (2006) have been exceeded for lead in Hypericum perforatum (7.21 mg. Kg-1), Artemisia absinthium (5.37 mg. Kg-1). The trophic transfer of toxic heavy metals in plants used as medicines may represent a potential health hazard to consumers, fact which imposes the need for a systematic control.

Keywords: Heavy metals; AAS, medicinal herbs, bioaccumaulation, coal power plant

Energy installations, power plants using coal as fuel can affect the environment, sometimes affecting the ecological balance in areas where they are located [1]. The coal combustion give off significant amounts of nitrogen oxides, sulfur dioxide, dust and heavy metals. Heavy metals represent an important category of establish toxic pollutants. Metals such as Zn, Fe, Cu, Co and Cr are essential nutrients to plants, showing only high concentrations toxic nature. Heavy metals such as lead (Pb), mercury (Hg) and cadmium (Cd) are known as toxic metals, without any functional role in metabolism [2-3]. The accumulation of heavy metals in plants is one of the most serious environmental concerns, also because they transfer heavy metal pollutants from soil into the food chain, causing adverse health effects in humans [4-6].

For many years various plants known as medicinal herbs have been used in therapeutics to cure illness or as dietary supplements [7-8]. Medicinal and aromatic plants are of particular interest for human health, 80% of the population of developing countries still use traditional medicines in plant drug forms [9]. However, environmental pollution especially with heavy metals (Al, As, Be, Cd, Cr, Cu, Hg, Ni, Pb, Se, Sb), poses serious problem on quality of medicinal plants and their products because of their potential for human exposure and increased health risk. It was found that the medicinal plants can accumulate larger amounts of trace elements than any other plants: Ernst, 2002, quoted by Kabata-Pendias [8] report high Hg, Pb, As levels in Asian herbal medicines; Zhang R. et al., (2007) [10] report high trace metal concentrations in tea leaves; 54 samples of Asian remedies from Vietnam, Hong Kong, Florida and New Jersey were analyzed for heavy metal contamination and 49 % presented toxic concentrations [11]. Plants for pharmaceutical products should meet quality control standards regarding allowable concentrations of heavy metals [12-15].

Research studies on heavy metal contamination of plant resources for food and therapeutic properties based on a variety of aspects of approach and various research methodologies and techniques [16-19]. Extensive uses of traditional medicines are of special concern because they are not rigorously regulated, thus the focus of this study was to determine the amount of toxic heavy metals (Pb, Hg, Cd) in: the primary ash (the filters), ash deposited in landfill, soil, vegetation, selected medicinal plants, evaluating the dispersion of these metals (Transfer Factor: TF) [20]. The aim of this work was to determine the content of three important environmental pollutants, cadmium, mercury and lead in wild populations of *Chelidonium majus L, Crataegus monogyna, Artemisia absinthium L, Hypericum perforatum* in the area adjacent lower coal combustion thermal power (lignite), using a high performance technique of atomic absorption spectrometry (AAS). The performance and advantages of the quantitative analysis of heavy metals in multicomponent samples were reported in similar studies [21-24] .

Experimental part

Samples collection and preparation

Soil and plant sampling was conducted on the Jiu river corridor, between the localities, Ţinţăreni and Valea Văii, in the NW-SE direction, considering the relief of the area and the predominant directions of the atmospheric circulation adjacent to the pollution sources (Turceni thermal power plant and cinder deposit). The methodology of sampling, preparation and extraction of heavy metals from soil and plants are in accordance with the requirements of instrumental analysis of multicomponent environmental samples. Soil samples were air dried, crushed, passed through a 2 mm mesh sieve and stored at ambient temperature for analysis. The sample preparation for the

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determination of heavy metals in soil was done according to MA079 Re.0/2006 Microwave Operating Manual, wet mineralization HNO_3, HCl and H_2O_2 using digester Milestone. The digestion solutions were transferred into volumetric flasks of 50 mL (washing with distilled water filter); 1 mL of each solution was diluted 1:10 and analyzed by flame atomic absorption spectrophotometer FAAS. The same protocol was applied to the samples of lignite, the ashes from the bottom of the filter, slag and ash deposits collected.

Samples of herbs were collected and prepared for experiments in a standard way described in the literature for these kinds of materials. All the collected samples of herbs were thoroughly segregated and purified but not washed, then were placed in a ventilated room and were oven dried at 80° C to constant weight. The dried samples were grinded to fine homogeneous powder and stored in plastic bags for metal analysis. Determination of trace elements in plant analysis was done according to the methodology for assessment of plant mineral nutrition by dry mineralization (mineralization by calcination). Mineralization of plant material: weighed samples of 1g dried plant material were placed in a porcelain or platinum crucible, is burned plant material in the flame of a gas burner. It was calcined in the oven at 450° C, and left in the oven until a white-gray. If the color is too dark, the ash was treated with a few drops of concentrated HNO_3, then placed on a sand bath and allowed to evaporate and placed again in the oven at the same temperature of 450° C. The ashes treated with 1 mL HCl 6n, HCl evaporate per sand bath and the treatment is repeated with HCl. Put the samples in flasks with 25 mL 0.5N HCl. Filter 50 mL Erlenmeyer glasses. Calcination plant material is ignited by a furnace NABERTHERM, L9/11/B170. The extracts thus obtained is dosed by atomic absorption spectrometry for determination of trace elements in coal, ash, slag, soil and plants.

Method of analysis

The quantitative analysis of the heavy metals in fuel (lignite), cinder, ash, soil and vegetable plants was accomplished by instrumental techniques, atomic absorption spectrometry (AAS), according to standards international with a spectrometer Thermo Electron Model S Series AA SOLAAR, software platform. To this end was used atomic absorption spectrometer which is fully automatic, single and double the beam, with flame atomization and transverse heated graphite furnace. The device is controlled via external evaluation and control unit (computer) and has the possibility of moving from one technique to another through software preinstalled. For the determination of Hg in soil and plant samples using hydride generator VP Vapour 100 Kit, dosing is made directly by atomic absorption spectrometry without heat atomization: it should be reduced from its compounds to elemental state and transferred to a vapour gas flow, cold vapour technique. Mercury in soil samples is reduced by $NaBH_4$ borohidrura 0.5% in NaOH 0.5% to mercury and dosed with the aid of conventional cold vapour atomic absorption thus determining the total mercury (organic and inorganic). The oven is equipped with multi-layer insulation and high-quality insulating, which helps to save energy. The oven is also equipped with a controller that gives security against most operating errors. The oven temperature is measured and regulated by a thermocouple with long life, the NiCr-Ni ($T_{max.}$<1100°C) or PtRh-Pt ($T_{max.}$>1100°C).

Results and discussions

The sampling and AAS analysis methodology used in this research, is characterized by a series of qualitatively superior analytical parameters multicomponent analysis of environmental samples : calibration, detect limits, sensitivity, standard equipment and software platform. Details of operating parameters, specific data calibration and plotting calibration curves using software connected to high standards spectrometer for analysis of heavy metals in soil and plants are shown in Table 1 and figure 1, 2 ,3. Spectrometric analysis performed is characterized by a high level of precision and accuracy: detection limits ($mg.L^{-1}$): Pb (0.10), Hg (0.0002), Cd (0.005); sensitivity ($mg.L^{-1}$): Pb (0.5), Cd (0.025); flame characteristic concentration ($mg.L^{-1}$): Pb (0.07), Cd (0.013), Hg (2.7); furnaces characteristic mass (pg): Pb (1.8), Cd (0.6), Hg (58); vapour characteristic concentration ($\mu g.\ L^{-1}$): Hg (0.26). The limits of quantification (LOQ) for heavy metals in samples of herbal drugs, fresh and dried: 0.4 mg/kg for Pb, 0.07 mg/kg for Cd and 0.02 mg/kg for Hg are reported using validated methods such as: atomic absorption spectrometry (AAS) according to Ph. Eur. (2.4.27, 2007a) [25], inductively coupled plasma mass spectrometry (ICP-MS) according to Ph. Eur.2.2.58, 2007b [26], other publications (ICP-AES, ICP-OES) and voltametric methods [27-28].

Metals detected in coal used as fuel are found in all samples analyzed: ash, slag waste dump, soil, vegetation,

Table 1
CHARACTERISTICS OF QUANTITATIVE ANALYSIS (AAS)

Characteristics	Pb	Hg	Cd
Spectrometer			
Atomic mass	207.2	200.59	112.40
Prim.wavelength (nm)	217.0	253.7	228.8
Emis wavelength (nm)	405.8	253.7	326.1
[a]FCC ($mg.L^{-1}$)	0.07	2.7	0.013
[b]FCM (pg)	1.8	58(0.26)[c]	0.6
Bandpass (nm)	0.5	0.5	0.5
Detect limits ($mg.L^{-1}$)	0.1	0.0002	0.005
Sensitivity ($mg.L^{-1}$)	0.5	-	0.025
Calibration details			
Charact. Conc.	1.2329	0.6486	0.071
Signal abs. [d]	0.001 0.003 0.008 0.015	0.016 0.038 0.210	0.019 0.032 0.062 0,125
%RDS	7.4 4.4 1.5 1.5	0.9 1.0 1.0	1.8 1.1 0.5 0.5
SD	0.0003 0.0002 0.0001 0.0002	0.0001 0.0004 0.0022	0.0003 0.0003 0.0003 0.0006

[a] Flame Characteristic Concentration (F CC); [b] Furnace Characteristic Mass (FC); [c] Vapour characteristic concentration(ug.L-1); [d] Auto dilution.

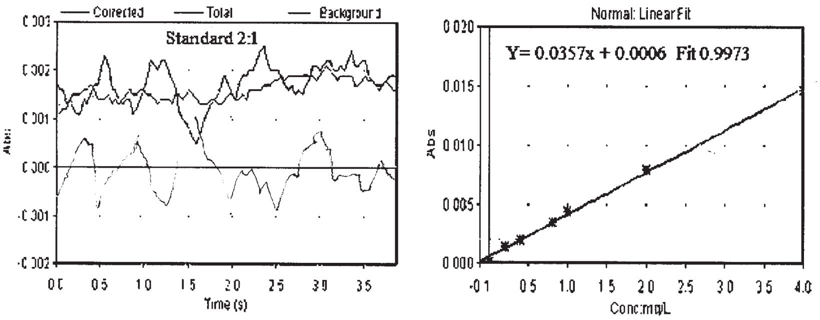

Fig.1. The lead : signal and calibration

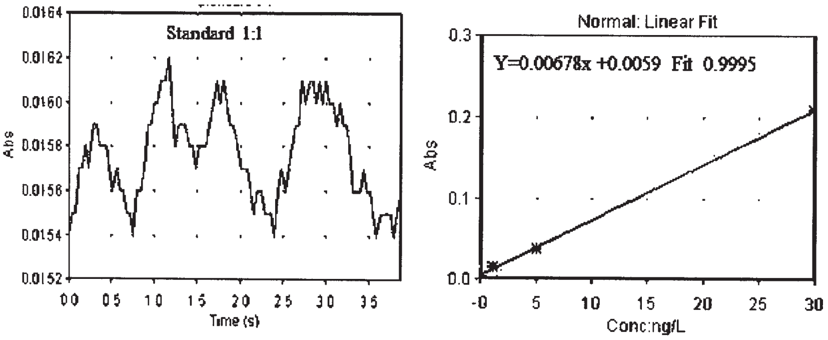

Fig. 2. The mercury: signal and calibration

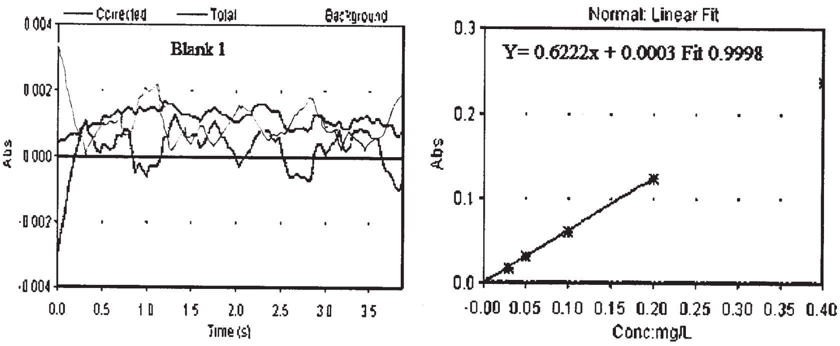

Fig. 3. The cadmium: signal and calibration

medicinal plants in the spontaneous flora. The determined values of heavy metals in soil and medicinal plants have been reported in normal values and maximum permissible limits described in the literature. Such soil samples from the area of influence of the power plant (table 2) do not exceed normal value [29], excepted lead that exceeds normal value Pb (55.10 mg. Kg^{-1}). Experimentally obtained values fall in the concentration range (minimum/ maximum) of potentially toxic elements monitored for upper horizon of soils in Romania by type of use [30].

The transfer capability of heavy metals from soil to the edible part of vegetables was generally described using the translocation factor [31] . Translocation factors (TF) of heavy metals were calculated as follows: metal concentration from plants/ metal concentration in soil adjacent to of the plant. According to the literature [5] a coefficient of transfer from soil to plants around 0.1 indicates no metal bioaccumulation in tissues, while values around 0.5 indicates a build that should be considered food safety for change in the human body through food. Lift coefficients worthy of consideration in terms phytotoxic (fig. 4) indicates the following trend: cadmium in *Hypericum perforatum* (0.47), *Artemisia absinthium* (0.43), *Chelidonium majus* (0.18), *Crataegus monogyna* (0.15), mercury and cadmium in *Crataegus monogyna* (0.15).

Lead (Pb) is the most frequently occurring and stable heavy metal in nature, a serious cumulative body poison. Levels of lead beyond the permissible limits, use of these contaminated plants could lead to toxicity characterized by colic, anemia, chronic nephritis, headache convulsions, brain damage and central nervous system [32]. In the present study, lead was detected in all medicinal herbs, average values from 2.37- 7.21 mg.Kg^{-1} (table 3). The values found for lead, exceeding Maximum Permissible Limit (MPL) specified by Ph.Eur.(2008) [15]: *Artemisia absinthium L* (5.37mg.Kg^{-1}), *Hypericum perforatum* (7.21mg.Kg^{-1}).

Cadmium (Cd) is a non-essential trace element causes hypertension, liver and kidney damage. Cadmium

Table 2
HEAVY METAL CONCENTRATIONS IN ASH, SLAG, SOIL AND COAL (TOTAL FORMS)

Sample	Pb(mg. Kg^{-1})		Hg(mg. Kg^{-1})		Cd(mg. Kg^{-1})	
	c	sd	c	sd	c	sd
Filter ash (n=3)	47.63	1.23	0.037	0.01	1.024	0.042
Ash dump (n=4	31.80	0.75	0.020	0.01	0.139	0.054
Coal (n=4)	31.40	0.87	0.019	0.01	0.331	0.13
Soil area (n=16)	55.10	3.69	0.082	0.02	0.27	0.03
NL (soil)	20		0.1		1	
MPL (soil)[a]	100		1		3	

[a] Sensitive soils, Source: Romanian Ordinance Ministry No. 756/1997, NL: Normal Levels, MPL: Maximum Permissible Limit, c: concentration, sd: standard deviation

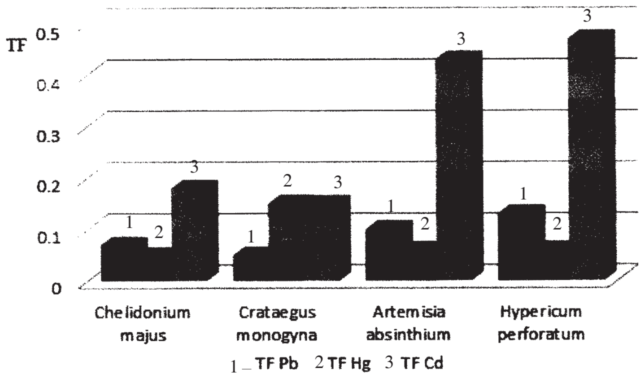

Fig. 4. Transfer factor in medicinal plants

Table 3
HEAVY METALS IN MEDICINAL PLANTS (AVERAGE CONCENTRATION, TOTAL FORMS, n = 4/PLANT)

Plants	Pb(mg. Kg^{-1})		Hg(mg. Kg^{-1})		Cd(mg. Kg^{-1})	
	c	sd	c	sd	c	sd
Chelidonium majus L	3.64	0.17	0.004	0.001	0.053	0.01
Crataegus monogyna	2.37	0.12	0.002	0.002	0.042	0.01
Artemisia absinthium L.	5.37	0.28	0.005	0.001	0.118	0.03
Hypericum perforatum	7.21	0.34	0.005	0.002	0.128	0.04
MPL[a]	5		0.1		0.2	

[a] MPL: Maximum Permissible Limit, Sources: (Ph.Eur.2008), c: concentration, sd: standard deviation.

poisoning causes a disease: Itai-itai, characterized by softening of bones, anemia, renal failure and ultimately death [33]. The maximum allowable limit of Cd in raw herbs (0.2 mg.Kg^{-1}) stated in the Ph Eur (2008) [15] do not exceed the average concentrations detected in the present analysis (0.042-0.168 mg.Kg^{-1}). *Hypericum perforatum* plants are known for their ability to store [34], is traditionally used for the treatment of several diseases such as skin wounds, eczema, burns, inflammatory and psychological disorders. The average value of Cd in *Hypericum perforatum* (0.128 mg.Kg^{-1}), as compared to other plants, confirming the literature data on hyper accumulation capacity of this plant: 0.731 mg.Kg^{-1} [35,] and 0.95 mg.Kg^{-1} [17].

Exposures to high concentrations of metallic mercury, inorganic or organic compounds permanently can damage the brain, kidneys, and developing fetus [36]. Reporting mercury concentrations obtained with the permissible limit FAO / WHO, 0.02 ppm in edible plants and 0.1 ppm medicinal herbs, it is found that all four selected herbs have the concentration below the limit set by FAO / WHO (2007) [14] and Ph Eur (2008) [15].

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Conclusions

Due to increased interest in the use of natural plant products and foodstuffs sanogenic meanings, it is necessary to carefully assess their quality, especially in areas where major pollution sources and manifestations of toxicity of pollutants on vegetation are evident. Coal power plant area presents the anthropogenic loading of potentially toxic heavy metals, plants selected have a moderate coefficients transfer level. Transfer factor (TF) calculated for selected medicinal plants shows moderate values, the highest value was recorded in *Hypericum perforatum* (0.47), which confirms the ownership of the plant to hyper accumulate cadmium. Knowing the level of potentially toxic metal contamination of medicinal plants from the spontaneous flora, provides an indication of the impact of emissions on the area around thermal coal power plants about risk to human and animal health fact which imposes the need for a systematic control. Atomic absorption spectrometry is the analytic technique most employed for traces of heavy metals analysis due to low interference level and reasonable parameters including: linearity, sensitivity, precision and accuracy.

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