

# Monitoring of Mercury Content in the Main Environmental Components Caused by Lignite Combustion in Large Thermal Power Plants

DELIA NICA BADEA<sup>1\*</sup>, MIHAELA GABRIELA DUMTRU<sup>2</sup>, IGOR CRETESCU<sup>3</sup>

<sup>1</sup>Constantin Brancusi University of Targu Jiu, Faculty of Technical, Medical and Behavioral Sciences, 30 Calea Eroilor, 210135, Targu Jiu, Romania

<sup>2</sup>University of Craiova, Faculty of Sciences, Department of Chemistry, 1071 Calea Bucuresti, 200585, Craiova, Romania

<sup>3</sup>Gheorghe Asachi Technical University of Iasi, Faculty of Chemical Engineering and Environmental Protection, 73 D. Mangeron Blvd., 700050, Iasi, Romania

*The aim of experiment was to evaluate the local impact of mercury accumulations, discharge from coal power plants, by examining samples of ash, slag, soil, spontaneous vegetation and crop plants, using as analytical techniques the cold vapor atomic absorption spectroscopy. Mercury determined in samples of lignite (0.020 mg.Kg<sup>-1</sup>), is found in fly ash samples retained by filters (0.037 mg.Kg<sup>-1</sup>), bottom ash transported hydraulic in deposit (0.022 mg.Kg<sup>-1</sup>), adjacent soils landfill and the power plant (0.12 mg.Kg<sup>-1</sup> or 0.049 mg.Kg<sup>-1</sup>). The mercury content in vegetation presents differentiated values depending on the bioavailability of plant, area and the positioning of the emission source, reaching values between 0.014 at 0.005 mg.Kg<sup>-1</sup> in the wild flora and 0.022 mg.Kg<sup>-1</sup> to 0.004 mg.Kg<sup>-1</sup> for plants crop. Data obtained for plants, confirmed that most families tend to accumulate mercury plant in larger quantities in the roots (0.022 ± 0.0016 mg.Kg<sup>-1</sup>) and moderate quantities in the foliar level by translocation or by direct vapor absorption.*

*Keyword: coal combustion, mercury concentration, soil plant accessibility, CVAAS*

Mercury is one of heavy metal that is widespread in the environment in many physical and chemical forms: elemental Hg (Hg<sup>0</sup>), inorganic Hg (Hg<sup>2+</sup>), associated with ions (HgS, HgCl<sub>2</sub>), mercurous chloride or calomel (Hg<sub>2</sub>Cl<sub>2</sub>) and organic Hg (e.g., CH<sub>3</sub>-Hg). There are two main types of reactions which convert the mercury in the mercury cycle through its various forms: oxidation-reduction, and methylation-demethylation. Mercury abundance in the Earth's crust is very low being in the range 0.02 to 0.06 mg.Kg<sup>-1</sup>, although it is likely to be more concentrated in argillaceous sediments and in coal [1]. Concentrations of mercury in soils in the world [2] have the values: UK rural soils (0.07 to 1.22 mg.Kg<sup>-1</sup>, mean 0.13 mg.Kg<sup>-1</sup>); Greek soils (0.033–0.101 mg.Kg<sup>-1</sup>); Peats in Poland (0.05–1.4 mg.Kg<sup>-1</sup>, mean 0.09 mg.Kg<sup>-1</sup>); Russian soils – Asia (0.01–0.29 mg.Kg<sup>-1</sup>, mean 0.08 mg.Kg<sup>-1</sup>).

Burning coal is the main source of mercury emitted into the environment, burning fossil fuels produces 45% of the total mercury emitted from human activity worldwide [3, 4]. The spatial dispersion and deposition level of mercury around coal power plants is non uniform [5] and depends on many factors: the level of emissions, chemical form of mercury emitted, exhaust chimney height, exhaust temperature and weather conditions [6]. The analysis of the products and by-products involved in the processes of energy production from coal is an indispensable tool for controlling and preventing environmental problems caused by mercury emissions. Hg in soils is related mainly with atmospheric deposition [7].

A number of studies have reported that presence and accumulation of Hg in soils and vegetation around power plants. The soil around power plant has been shown to be rich in Hg: Albufera Mallorca of Spanish (100-150 µg.Kg<sup>-1</sup>), [5]; Baoji Power plant of China (1.000µg.Kg<sup>-1</sup>), [6] and 2.100 µg.Kg<sup>-1</sup> in the Serbian Nikola Tesla power plant [7]. The extant computer modeling for this study suggests that increased local deposition will occur on a local (2 to10

km) to regional scale (20 to 50 km) with local increases a small percentage of background deposition on the regional scale.

Mercury is one of the most hazardous contaminants emitted to the atmosphere due to its toxic effects on the environment and human health. Excessive exposure to mercury is associated with a wide range of adverse health effects, including damage to the central nervous system (neurotoxicity), kidney, developing fetus (organic mercury, methylmercury), can cause birth defects and attention deficit hyperactivity disorder [8]. Lethal dose by ingestion (LD50) it is 0.02. Kg<sup>-3</sup>. Due to these considerations limits have been established for food and medicines by health authorities. Maximum levels (MLs) for mercury, lead, cadmium and tin in foodstuffs (milk, meat, fish, cereals, vegetables, fruit and fruit juices, fish and fish products) have been set by European Commission, [9]. Starting from literature data to estimate the local impact of mercury accumulations was studied local transport of mercury released from coal power stations, by examining samples of ash, slag, soil, vegetation and plants crop, by applying analytical techniques: cold vapor atomic absorption spectroscopy (CVAAS).

## Experimental part

### Maerial and methods

The area of Power Plant Turceni, Gorj-Romania is characterized by emphasizing the drainage favored marmo-loose rocks and clay, clays, sands, gravels. The hydrographic network is continuously deepened and widened under the action of tectonic factors, climatic and works. From a climate perspective is influenced mainly Mediterranean climate, with movement of southern and western part, interfering with air circulation in the passageway Jiu, NW-SE direction. Forests and natural vegetation represented by its narrow gradually, giving way to grasslands and crops.

\* email: nicabadeadelia@yahoo.com

Monitoring of environmental pollutants include compounds for investigating multiple areas - air, water, soil, vegetation in urban and in rural areas. Soil and plant sampling was conducted on the Jiu river corridor, between the localities, Brăne'ti - Ceplea and Ilie'ti Jilu, in the NW-SE direction, considering the relief of the area and the predominant directions of the atmospheric circulation adjacent to the pollution sources (power plant and cinder deposit). The type, number and positioning of the collected samples are shown in figure 1.

The solid samples lignite, bottom ashes, filter ashes, slag and ash deposits, soil were prepared in laboratory for the determination of total mercury content. The samples were crushed and dried at room temperature for 48 h and passed through a 2 mm sieve. A portion of 2.5 g was taken and subjected to mineralization with aqua regia and hydrogen peroxide according to ISO 11466:1999. The sample preparation for the determination of mercury solid samples was done according to MA079 Re.0/2006 Microwave Operating Manual, wet mineralization HNO<sub>3</sub>, HCl and H<sub>2</sub>O<sub>2</sub> 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 CVAAS.

About 500 g of each plant species in each sampling locations was collected, put in clean plastic bags and transported to the laboratory. The plant samples were thoroughly segregated, purified and washed with tap water and then with distilled water placed in a ventilated room and were oven dried at 80° C to constant weight. The dried samples were ground and a portion of 1.0 g was subjected to extraction with aqua regia and hydrogen peroxide

following the method from ISO 11466:1999. 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 mercury total forms in coal, ash, slag, soil and plants.

The determination of mercury concentration, total forms in lignite used as fuel, solid combustion by product, soil and plant was carried out by Cold Vapor Atomic Absorption Spectroscopy [10] according to standards international with a spectrometer Thermo Electron Model S Series AA SOLAAR, software platform. 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.

## Results and discussions

Numerous standard procedures for determining traces of mercury in environmental samples using cold vapor atomic absorption spectroscopy method were reviewed and discussed, the differences consist in the method of oxidation and dissolution of mercury [11, 10]. The basic physicochemical parameters, technical characteristics of the Solaar Cookbook: spectrometer and vapour method, are shown in table 1.

Specific data calibration and plotting calibration curves using software connected to high standards spectrometer for analysis of mercury, total forms in samples collected are presented in figure 2. Mercury, total forms, was quantified by CVAAS, the method recommended for the determination of elements in low concentrations (of 0.01

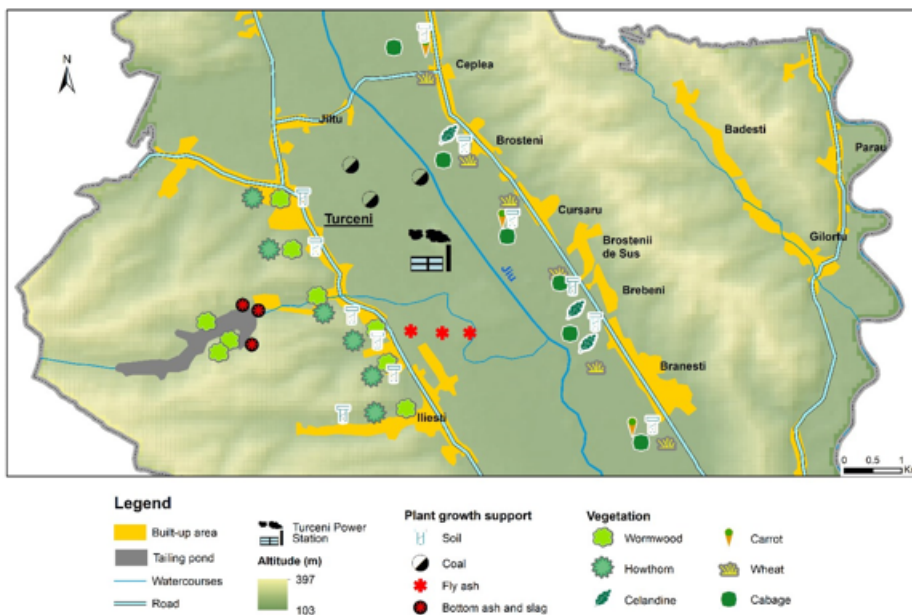


Fig. 2. 1. Map of sampling areas

Solaar Cookbook, Spectrometer		Solaar Cookbook, Vapour method	
Characteristics	Database	Characteristics	Database
Primary wavelength	253.7nm	Measurement delay	40-70 seconds
Bandpass	0.5 nm	Carrier gas flow	50 – 150 mL/min
Secondary wavelength	253.7nm	Pump speed	30 -40 RPM
Flame characteristic concentration	2.7mg/L: lamp current 75%, normal use	Reductant	0.5% m/V sodium hydroxide, 0.5 – 5% m/V Sn Cl <sub>2</sub> solution
Furnace characteristic mass	58pg: lamp current 75%, best sensitivity	Acid reagent	5% V/V, 0.5M hydrochloric acid
Vapour characteristic concentration	0.2ug/L: lamp current 75%; best precision	Sginal	6ug/L gives about 0.1A

**Table 1**  
TECHNICAL CHARACTERISTICS OF THE SOLAR COOKBOOK

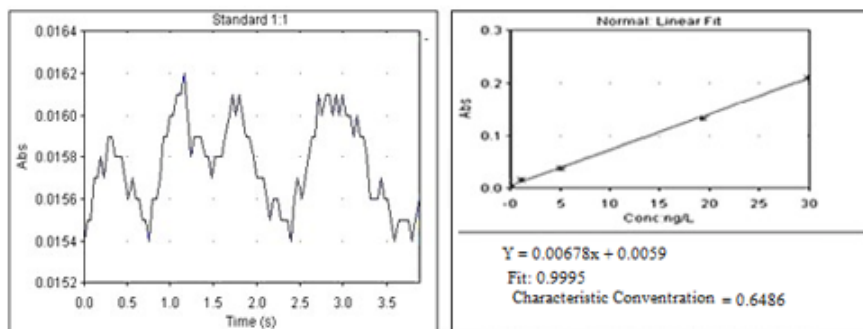


Fig. 2. Mercury calibration signal and calibration graph

No.	Samples	Area sampling	Hg (mg·Kg <sup>-1</sup> ) average± sd	Reporting basis mg·Kg <sup>-1</sup>
1	Coal (n=3)	Coal deposit	0.020±0.012	0.01 to 1.0 [12]
2	Fly ash (n=3)	Dedusting filters	0.037±0.012	0.02 to 2.00 [14]
3	Ash and slag (n=3) h = 020cm	Ash deposit Ceplea	0.022±0.011	NV: 0.1 [13, 1] 0.06 [15] 0.07 to 1.22 [2]
4	Soil (n=6) h = 0-20cm	Border zone ash deposit Turceni-Iliești	0.102±0.054	NV:0.1 [13, 1] 0.06 [15] 0.07 to 1.22 [2]
5	Soil (n=6) h = 0-20cm	Neighboring power plant: Brănești-Ceplea	0.049±0.013	NV: 0.1 [13, 1] 0.06 [15] 0.07 to 1.22 [2]
6	Wormwood leaves- flowers (n=3)	Ash deposit Ceplea	0.014±0.010	0.10 [17, 18] 0.020 [19] 0.5 [20]
7	Wormwood leaves- flowers (n=6)	Border ash deposit Ceplea, Turceni-Iliești	0.005±0.001	0.10 [19,17, 18] 0.020 [19] 0.5 [20]
8	Hawthorn fruit (n=6)	Border ash deposit Turceni-Iliești	0.012±0.0018	0.10 [19,17, 18] 0.020 [19] 0.5 [20]
10	Celandine (n=3)	Brănești – Ceplea	0.004±0.0012	0.10 [19, 17, 18] 0.020 [19] 0.5 [20]
11	Carrot (n=3)	Brănești – Ceplea	0.022±0.0016	0.003-0.01 [21] 0.009-0.048 [22] 0.020 [20]
	Cabbage (n=4)	Brănești – Ceplea	0.006±0.0011	0.003-0.01 [21] 0.009-0.048 [22] 0.020 [19]
13	Wheat (n=4)	Brănești – Ceplea	0.005±0.0011	0.003-0.01 [21] 0.009-0.048 [22] 0.020 [19]

**Table 2**  
CONCENTRATION LEVELS  
OF MERCURY IN SAMPLES  
(TOTAL FORMS)

\*sd: Standard deviation; n: number of samples; k: height; NV: Normal value

to 0.2 ng.mL<sup>-1</sup>), calibration curve was linear in the concentration range 0 at 30 ng. L<sup>-1</sup>, regression coefficient is 0.9995, covering the range of 0.9 at 1.0% RSD, standard deviation value varied from 0.0001 to 0.00022.

Analyzing the mercury content, total forms of samples (table 2), it is noted that mercury and its compounds it is found in varying concentrations in the chain of accumulation: lignite, ash and slag, soil and vegetation spontaneous or cultivated, in areas adjacent to the power plant: the localities Brănești – Ceplea and Iliești – Jilu, in the NW-SE direction. The average concentration determined in lignite used as fuel mean value of 0.020 mg. Kg<sup>-1</sup>, is at a low level, relative to the concentrations worldwide reported, ranging from 0.01 to 1.00 mg.Kg<sup>-1</sup> [12]. Fly ash, average concentration, collected by dust extraction filters is estimated at 0.037 mg.Kg<sup>-1</sup>. The ash and slag deposit, has an average mercury concentration of 0.020 mg.Kg<sup>-1</sup>, being shipped in a mixture with water from Jiu River, which

crosses many zones of mining and processing of the coal. Analyzing the data listed, is noted that, the mercury content in bottom ash, filters ash, ash and slag deposit, do not exceed the normal soils content (0.1 mg.Kg<sup>-1</sup>), or alert values from sensitive soils (1.00 mg.Kg<sup>-1</sup>), provided by national standards [13]. The determined values for mercury in fly ash (0.037 mg.Kg<sup>-1</sup>) is at minimum emission values relative to emissions by combustion in a Spanish fluidized bed combustion plant (0.02 to 2.00 mg.Kg<sup>-1</sup>) [14].

The dynamics between the amount of mercury, which exist in soil, and its adoption by the plant is non-linear and depends on several variables: cation exchange capacity, soil pH, soil ventilation, as well as plant species. Soil samples taken at the base southeast of the deposit of ash and slag (Locality: Turceni – Iliești), have recorded values of 0.102 ± 0.054 mg. Kg<sup>-1</sup>, concentrations above the normal levels of mercury [13]. But these concentrations are situated in the range 0.07 to 1.22 mg.Kg<sup>-1</sup> for soils in rural



areas reported by the UK Environment Agency [2] and exceeding the limit of  $0.06 \text{ mg.Kg}^{-1}$ , reported by Lee Susan (1990) [15]. Concentrations of mercury in soil samples, collected in the direction of propagation of atmospheric emissions (Locality: Branesti - Ceplea), with values of  $0.049 \pm 0.013 \text{ mg.Kg}^{-1}$ , are located well below the normal value of national rules but very near the limit of  $0.06 \text{ mg.Kg}^{-1}$ , reported in the literature for dry and uncontaminated soils [15] or mercury abundance in the Earth's crust [1].

The mercury may enter into the structure of the plant by two main ways: 1) the absorption of the oxidized form of Hg (II) or methyl-mercury adsorbed on soil particles and / or dissolved in ground water by roots; 2) absorption of Hg<sup>0</sup> vapor in the atmosphere through stomata, or derived from volatilization of mercury from the mercury-rich soil surface. Route 1 is specific to plant roots, lane 2 is a characteristic of foliage segment of the plants [16]. Therefore, spontaneous flora, plants grown inside deposit of ash and slag accumulated mercury at a concentration of  $0.014 \text{ mg.Kg}^{-1}$  for wormwood. Spontaneous vegetation around the deposit (Locality: Ilie'ti - Jilu) accumulated mercury in concentrations of  $0.012 \text{ mg.Kg}^{-1}$  for hawthorn fruit and  $0.005 \text{ mg.Kg}^{-1}$  for wormwood, while on the east side of the power plant (Branesti-Ceplea) samples celandine values are  $0.004 \text{ mg.Kg}^{-1}$ . These plants from spontaneous flora are classified as medicinal herbs whose permissible concentration limits are set to  $0.1 \text{ mg.Kg}^{-1}$  [17, 18],  $0.020 \text{ mg.Kg}^{-1}$  EC 396/ 2005 [19] and the value of  $0.5 \text{ mg.Kg}^{-1}$  in Brazil medicinal herbs [20]. Samples of plants grown from the area of influence of the thermal power plant emissions (Locality: Branesti- Ceplea), highlights mercury values of  $0.022 \text{ mg.Kg}^{-1}$  for carrot – root,  $0.006 \text{ mg.Kg}^{-1}$  for cabbage and  $0.005 \text{ mg.Kg}^{-1}$  for wheat. The samples concentration of carrot root ( $0.022 \pm 0.0016 \text{ mg.Kg}^{-1}$ ) exceeding the concentration of mercury in plants reported by European Commission ( $0.02 \text{ mg.Kg}^{-1}$ ), [19]. The obtained data ranged between  $0.022$  and  $0.006 \text{ mg.Kg}^{-1}$ , detected in crop plants (carrot root, cabbage and wheat), can be found in concentration ranges determined by a number of agro food products research: ranged between  $0.003$  and  $0.01 \text{ mg.Kg}^{-1}$  [21]; between  $0.009$  and  $0.048 \text{ mg.Kg}^{-1}$  [22].

Data obtained in this study, on the concentrations of total mercury accumulated in the plants of spontaneous or locally grown under the influence of the coal power plant emissions, confirmed the data reported in the literature, that most plant families tend to accumulate mercury in larger quantities in the roots [1, 2] and moderate quantities in the foliar segment by translocation or by direct vapor absorption.

## Conclusions

Burning coal in power plants is the main source of anthropogenic mercury emitted

environment. Mercury is recognized as a global contaminant, because it can be transported at local level (2-10 Km), regional (20-50 Km) and at long distances in the atmosphere, is persistent in the environment, accumulate in the food chain soil-plant-animal-food. Cold vapor techniques atomic absorption spectrometry is much more sensitive, reaching mercury detection limits as low  $0.01$  to  $0.2 \text{ ng.mL}^{-1}$ .

The performance of analytical method (CVAAS) applied in this study, permit the mercury detection in all the analyzed samples from local environment with values between  $0.004$  to  $0.12 \text{ mg.Kg}^{-1}$ . Analyzing mercury content as total forms, confirm the presence of both mercury and its compounds in the distribution chain and accumulation: lignite, ash and slag, soil and spontaneous or cultivated vegetation in the power plant area of influence, slag and

ash deposit on the flanks of Jiu river corridor, between Branesti-Ceplea and Turceni- Ilie'ti localities situated in NW-SE direction.

The xenobiotic heavy metals such as: mercury, cadmium, lead, released from the matrix of coal distributed in space, are considered persistent pollutants, being characterised by high residence times (thousands of years), having the tendency for hyper-accumulation and concentration in soil, plants and animals, leading to harmful effects toward the human organism, considered the final consumer of the food chain soil-plant-animal-food.

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