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Lignite combustion in Thermal power plant Kolubara A as a source of mercury pollution

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Abstract: Coal combustion is a major contributor to environmental pollution, releasing various harmful pollutants, including mercury, which poses significant risks to soil and water quality through atmospheric deposition. For this reason, some countries have established regulatory limits on mercury emissions from coal combustion, requiring the use of advanced pollution control technologies to capture and effectively reduce mercury emission. In this study, the mercury content in coal, coal ash samples and flue gas from the Kolubara A thermal power plant is determined. The results show that the mercury concentration in coal was 0.73 mg/kg, whereas the concentrations in fly ash and bottom ash were 0.02 mg/kg and 0.03 mg/kg, respectively. The mercury concentrations in coal and coal byproducts were in accordance with existing literature. In addition, the overall mercury content in flue gas was 38.73 µg/Nm³, falling within the permissible emission limit for thermal waste treatment in Serbia. The calculated mercury emission factor was below the lower limit specified in the Air Pollutant Emission Inventory Guideline of the European Monitoring and Evaluation of Air Pollutants (EMEP/EEA). These findings provide useful data for long-term environmental monitoring and regulation of mercury emission from coal combustion in Serbia.

Keywords: coal, coal ash, mercury, emission, direct mercury analyzerIntroduction

In many countries coal is considered as the primary source of energy, but also one of the major anthropogenic sources of environmental pollution [1]. The rise of renewable energy and international climate agreements are pushing many countries to reduce coal dependency, leading to economic shifts in coal-producing regions. Lignite is one of Serbia's most abundant energy resources. With significant reserves concentrated in the Kolubara and Kostolac basins, lignite plays a crucial role in the country's energy sector, primarily as a fuel for electricity generation in thermal power plants (TPPs) where these plants provide around 60% of Serbia's electricity [2].

Coal combustion generates wastes such as fly ash, bottom ash and flue gas [3]. The pollution of water, air, and soil by some trace elements contained in the ashes and/or flue gases produced during coal combustion drew attention since most of them are extremely dangerous and carcinogenic [4]. Trace elements (TEs) found in coal, such as mercury, arsenic, selenium, lead, cadmium and chromium are recognized to pose serious environmental and public health risks [5]. These element concentrations in combustion byproducts are dependent on operating conditions, coal and combustor type [6]. Among mentioned trace elements, mercury is one of the most significant environmental pollutants and one of the top 10 chemicals of major public health concern designed by the World Health Organization (WHO) [7], causing concern due to its severe toxicity to human health, long-range transport, persistence, and bioaccumulation in the environment [8]. Mercury transformation during coal combustion can be divided into homogeneous (without fly ash) and heterogeneous (with fly ash) reaction, which are influenced by the coal types, flue gas components, flue gas temperature, combustion atmosphere, coal ash properties, etc [9]. Mercury emitted from coal combustion can be present in various forms, such as elemental mercury (Hg^0), gaseous oxidized mercury (Hg^{2+}), and particulate mercury

(Hg^p) [9]. Then, Hg^{2+} and Hg^p can combine with organic molecules to form methyl mercury (MeHg), which is the most toxic form of mercury. The results indicated that Hg was the predominant in flue gas with more than 90% [10].

Today's coal-fired power plants use selective catalytic reduction (SCR), electrostatic precipitators (ESPs), and flue gas desulfurization (FGD) to manage NOx, particulates, and SOx[11]. Dust removal equipment, such as the ESP which is used in TPP Kolubara A, can efficiently reduce the concentration of Hg^P from flue gas.

Coal combustion emits around 475 tons of mercury into the atmosphere globally each year, according to the most recent air emissions inventory. In comparison, other fossil fuels contribute with 10 tons. Figure 1 shows mercury emissions from coal combustion in some countries [12].

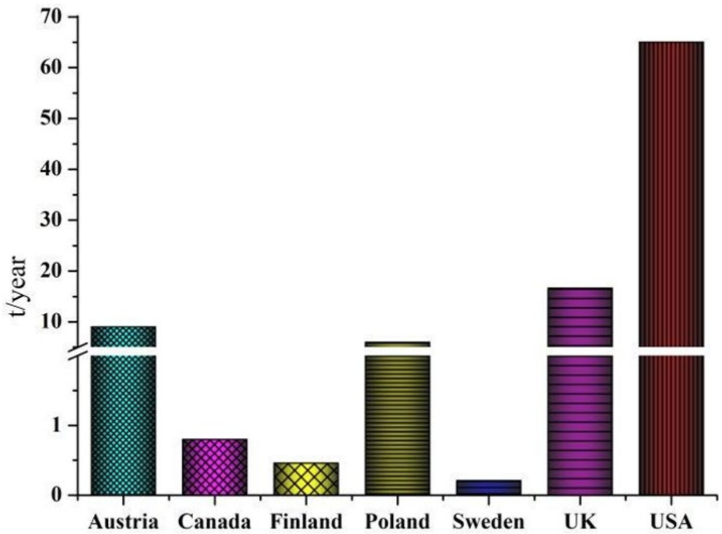

Figure 1. Mercury emissions from coal combustion in the UK, Austria, Canada, Finland, Sweden, Poland and the USA.

Furthermore, the large increase in worldwide anthropogenic mercury emissions demonstrates the critical need for effective solutions to reduce coal use and regulate mercury emissions. This understanding is essential for accurate mercury emission estimations and the development of effective mercury removal technologies, particularly during coal combustion for power generation. Addressing these challenges is important for protecting human health and the environment in the face of the ongoing utilization of coal. Given the public health and ecological risks associated with mercury in coal, the aim of this work is to determine mercury content and its distribution in coal, as well as in flue gas and coal byproducts.

1. Materials and Methods

1.1. Collection and storage of coal, fly and bottom ash

Lignite originated from the Kolubara basin and fly ash from the electrostatic precipitator, as well as bottom ash were sampled in TPP Kolubara A (44° 28' 49" N, 20° 17' 37" E). The total installed capacity of the TPP Kolubara A block is 245 MW [13], with rates of lignite consumption of 350 t/h and ash production of 64 t/h. Three lignite from three regimes samples were collected and mixed. Sampling and sample preparation was done according to standard methods . Fly ash was sampled from an electrostatic precipitator, and its temperature was around 160°C. The sampling of fly and bottom ashes was carried out in each of the three operational regimes (different air and fuel flow, and maximal boiler power) separately. The ashes from each of the regimes were combined according to the standard method [14]. Before analysis, ash samples were homogenized [14] and stored in a glass container [15] at a dark place under the temperature below 15°C.

1.2. Sampling of flue gas from TPP Kolubara A

Flue gas was extracted representatively from a chimney over a certain period of time with a controlled flow and a known volume according to the standard method [16]. Flue gas flows and parameters are shown in Table 1. Sampling was performed by the isokinetic sampling system. Dust in the sampled gas stream is collected on a quartz filter Munktell with an efficiency of more than 99,9%, whereafter the gas passed through a series of absorbers, which contains absorbed solution (2%w/w $KMnO_4$/10

%w/w H_2SO_4). At the end of the sampling period the filter, the absorption solution and the rinsing solution are collected in the glass container and stored at room temperature.

Table 1. Flue gas parameters and flows for TPPs under working conditions (f_W), under standard conditions and dry flue gas (f_{st}), and under standard conditions for dried flue gas and oxygen content of 6% (f_R)

TPP Kolubara A	
Temperature of flue gas (°C)	197.9
Oxygen content in flue gas (%)	10.70
Volume ratio of moisture in flue gas (%)	16.73
Mean velocity of flue gas (m/s)	10.19
f_W (m^3/h)	524003
f_{st} (Nm^3/h)	250614
f_R (Nm^3/h)	172099

1.3. Proximate and ultimate analysis of lignite and coal ash samples

The proximate and ultimate analyses of lignite from TPP Kolubara, fly and bottom ash samples were done. The proximate analysis was done by LECO TGA 701 using the standard test method [17]. The high heating value of coal was determined by an IKA C200 calorimeter while low heating values was calculated according to standard method [18]. The ultimate analysis was done by a LECO CHN 628 Series with a Sulfur add-on module using the standard test methods [19,20]. The calculation for oxygen content was outlined in [21].

1.4. Mercury analysis of flue gas and coal, fly ash and bottom ash on Direct Mercury Analyzer- DMA1 evo

Samples of coal, fly and bottom ash were analysed on DMA1 evo directly.

After sampling flue gas, two bottles of absorption solution, were prepared for analysis. A previously prepared 10% solution of hydroxyammonium chloride is slowly added to the bottles containing the absorption solution until the solutions turn discolored. Then, aliquots of these absorption solutions, aliquots of rinsing solution and filters were directly analysed on Direct Mercury Analyzer- DMA1 evo.

1.5. Mercury emission factor (MEF)

Mercury emission factor (mg/GJ) represents mercury emission from flue gas per unit of low heating value of coal. It is calculated using the following equations:

$$MEF= m/GQ \quad (1)$$

$$m=VC \quad (2)$$

where, m (mg/h) is the emission of mercury from flue gas; G (ton/h) is coal consumption; Q (kJ/kg) is the low heating value (LHV) of feed coal; V (Nm^3 /h) is the flow rate of flue gas; C (μg/Nm^3) is mercury content in flue gas.

2. Results and Discussion

Coal can be characterized by its physical and chemical properties, and the quality of coal is evaluated by proximate, ultimate analysis and upper heating value. A complete proximate analysis of coal determines: total (analytical moisture and total moisture), ash content, combustible substances, volatile substances, fixed carbon content (Cfix), upper and lower heating values. The ultimate analysis includes determining the total carbon, hydrogen, nitrogen, and oxygen content, as well as the total, bound, and combustible sulfur content. Foreign authors first classified domestic coals based on volatile substances (V), carbon (C), hydrogen (H) and oxygen (O). Furthermore, it can be seen that lignites have lower carbon values but higher volatile values [22]. Lignite used as a feed fuel in TPP Kolubara A was examined and the results of its proximate and ultimate analysis are presented in Table 2A. When these results are compared to literature data [23,24] lignite from TPP Kolubara A is regarded as low grade coal due to its high ash content and low Cfix value. Furthermore, examined lignite can be categorized as medium-sulfur coal since its sulfur level ranges between 1% and 3% [25].

Table 2A. Proximate analysis and ultimate analysis of coal from TPP Kolubara

			Coal
Proximate analysis	Total moisture*		47.43
	Inherent moisture**		3.39
	Ash	%	33.73
	Total sulfur		1.52
	Cfix		25.97
	Volatile		40.31
Heating value	Upper	MJ/kg	17.8
	Lower		16.9
Ultimate analysis	Total carbon		44.33
	Hydrogen		3.90
	Comb. sulfur	%	0.80
	Nitrogen		0.75
	Oxygen		16.50

*as-received; **as determined; all other data are given on a dry basis

The proximate analysis results for fly ash indicate a low combustible content (Table 2B), suggesting almost complete coal combustion in TPP Kolubara A. As indicated in Table 2B, bottom ash has substantially lower ash content than fly ash, which is expected given its high proportion of unburned carbon [26].

Table 2B. Proximate analysis of bottom and fly ash from TPP Kolubara

	Bottom ash	Fly ash
Inherent moisture**	2.39	0.04
Ash	65.80	99.70
Combustible	34.20	0.30
Total sulfur	0.94	0.73
Comb. sulfur	0.35	0.02

**as determined; all other data are given on a dry basis

The measured mercury concentration in lignite is 0.73 mg/kg, while literature data for mercury content found in different types of coals goes to 10.5 mg/kg (Figure 2). There is limited data on mercury concentrations in Serbian coals and their corresponding fly and bottom ashes. However, as illustrated in Figure 2, the findings from this study align closely with mercury concentrations found in Indian, Polish, and Russian coals utilized in different power plants, whereas the levels are significantly lower than those reported for certain Chinese coals.

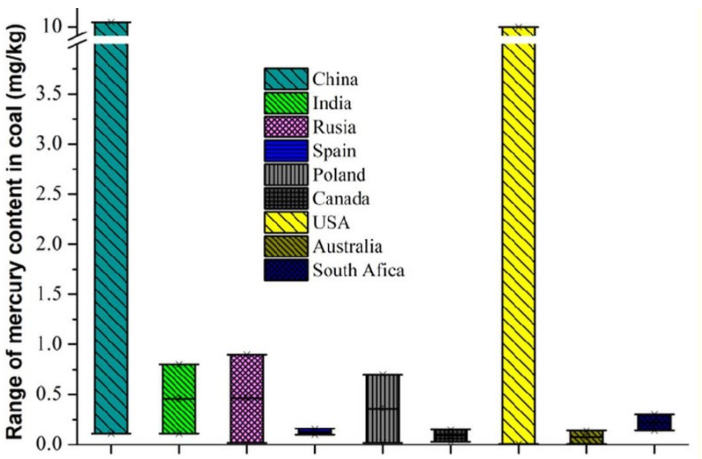

Figure 2.Range of mercury content in coals from different countries [9,10,27-29]

The mercury content in bottom ash is 0.03 mg/kg, whereas fly ash has 0.02 mg/kg. Mercury content in fly and bottom ashes can vary significantly depending on the type of coal and combustion conditions. Understanding these dynamics is crucial for assessing the environmental impact of coal combustion and developing effective remediation strategies. Figure 3 shows that the mercury contents in the fly ash and bottom ash studied in this study are similar to the literature.

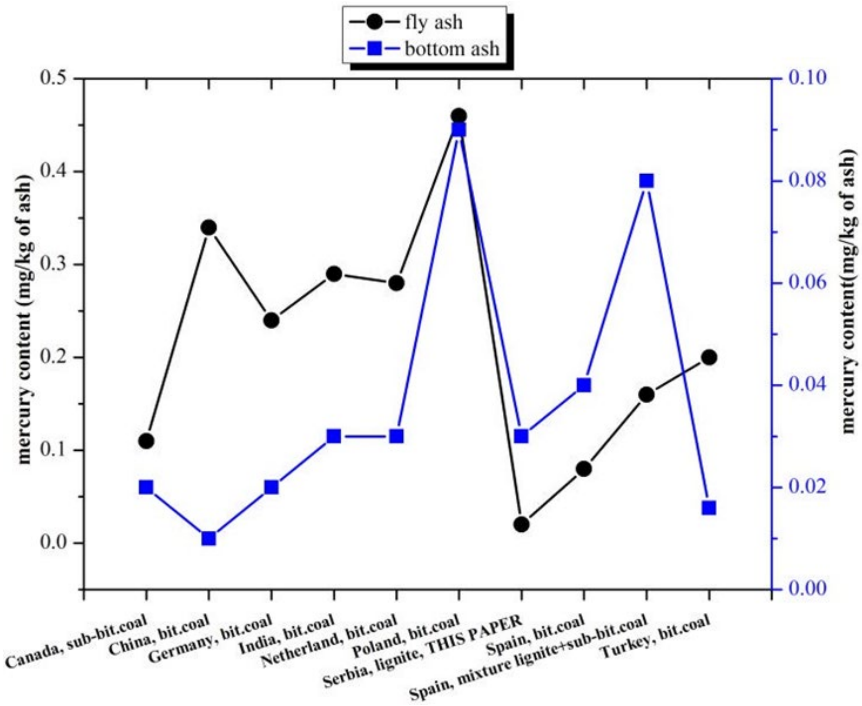

Figure 3.Mercury content in fly and bottom ashes from different countries [9,10,27-31] and determined in this paper

Mercury in coal is highly related to sulfur content in most coals, with pyritic mercury being the most common form, although organic- and sulfide-bound mercury (mainly pyritic mercury) are the predominant species in low-sulfur coals. Although higher mercury concentration is expected for fly ashes than bottom ashes [32], in our instance, the higher mercury concentration in bottom ash is most likely related to its higher sulfur content (Table 2B).

Total mercury emission in flue gas from TPP Kolubara A was 12.72 µg/m3 (Table 2) , or 38.73 µg/Nm3 under standard conditions for dried flue gas and oxygen content of 6%. Mercury emissions in this paper are significantly higher than those in Poland but substantially lower than those in India (Table 3).

Table 3. Literature data for the distribution of mercury in flue gas and particulate phase assocciated with flue gas

Coal Type, thermal power plant capacity	Literature	Flue gas with particulate associated with flue gas (µg/m3)
Bituminous coal, India, TPP 220MW	[29]	22.72
Mixture of lignite and sub-bituminous coal, Spain, TPP 350MW	[10]	20.5
Bituminous coal, Poland, TPP 113MW	[28]	2.49
Bituminous coal, Poland, TPP 160MW	[28]	1.88
Bituminous coal, Poland, TPP 560MW	[28]	1.51
Total mercury content in flue gas	THIS PAPER	12.72

Legislation regarding mercury emission is established in some countries, but mercury maximum limit values are applicable to different industries or processes. In Serbia, the limit value for Hg emission is 0.05 mg/Nm^{3,} but that limit value is applicable to the thermal treatment of waste, while Austria has a value for mercury emission that is applicable exclusively to coal-fired power stations. The measured mercury concentration in flue gas from TPP Kolubara A is below all limit values for mercury emission given in Table 4.

Table 4. National guidelines and legislation regarding mercury emission

Country	Limit value for Hg* (mg/Nm^3)	Applicable to
Australia	3	Any industry or process
Austria	0.05	Coal-fired power stations
Canada	1	New or recently modified utility boilers
Netherland	0.20	Any industry or process
Serbia	0.05	Thermal treatment of waste

*mercury limit value is given under standard conditions for dried flue gas and oxygen content of 6%

The calculated Mercury Emission Factor value is 1.12 mg/GJ, which is significantly lower than the lower limit value given in the EMEP guidebook [33], for medium size non-residental sources, coal fuels and capacity from 1MW to 50 MW.

3. Conclusion

This study provides a comprehensive analysis of mercury content in coal and coal byproducts in TPP Kolubara A, which is crucial given its major influence on environmental contamination. The mercury content found in the lignite aligns closely with contents reported in coals from India, Poland, and Russia, while being significantly lower than those found in certain Chinese coals. The investigation into the mercury concentrations in fly and bottom ash indicates that the observed values are consistent with existing literature, emphasizing the influence of coal type and combustion conditions on mercury distribution in ash byproducts. These findings underscore the importance of understanding the dynamics of mercury emissions in relation to combustion technologies, which is essential for evaluating the environmental impacts of coal-fired power generation.Total mercury emissions from TPP Kolubara A were measured at 38.73 µg/Nm^3, adhering to the existing legislative limits for mercury emissions in Serbia. The calculated Mercury Emission Factor of 1.12 mg/GJ is below the lower limit set in the EMEP guidebook for medium-sized non-residential sources. This indicates that the facility is operating within acceptable limits and suggests the potential for effective mercury management strategies in coal combustion processes. Overall, this research contributes valuable data to the limited knowledge surrounding mercury content in Serbian coals and their byproducts, highlighting the need for continued monitoring and the development of stringent regulatory frameworks to mitigate the environmental impacts of coal combustion.

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