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CONTRIBUTION TO THE SERBIAN COAL RANKING AND FLY ASH CHARACTERIZATION USING Pb ISOTOPIC RATIO

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Abstract

The Republic of Serbia generates the majority of its electricity at the thermal power plants (TE) Nikola Tesla, Kolubara, and Kostolac. Coal is extracted from the Kolubara basin, which produces approximately 70% of lignite (an average of 30 million tons per year), and the Kostolac basin, which produces 30% of lignite. Ash, fly ash, and slag are examples of coal combustion residues. Because of the high content of potentially hazardous elements such as As, Pb, Cd, and Cr, environmental pollution with ash and fly ash has been extensively researched. Stable isotopes of lead can be used to trace lead sources. It is possible to monitor the presence, transformation pathways, and environmental impact of Pb by determining its isotopic composition in coal and fly ash. For the first time, the isotopic composition of selected coal samples from the Kolubara and Kostolac mines, as well as fly ash from the Kolubara (A and B), Kostolac (A and B), and Nikola Tesla (TENT A3, A2, B2) thermal power plants, was investigated in this study. The obtained data for $^{206}Pb/^{207}Pb$ in coal serve as the foundation for ranking domestic coals, whereas the isotopic ratios $^{206}Pb/^{207}Pb$ and $^{208}Pb/^{207}Pb$ in fly ash can be used to monitor and control lead pollution from investigated sources.

Keywords: Pb isotopic fingerprint; coal combustion; emission; pollution.

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Introduction

Industrial growth has resulted in an increase in industrial waste, and its environmental impact necessitates a comprehensive approach aligned with sustainable development principles. Those aligned principles, which do not aim solely to preserve natural resources, will encourage future innovations in a sustainable direction. It is well known that the combustion of coal in thermal power plants results in the emission of pollutants, which can pollute the air, water, and land. Large amounts of waste, such as fly ash, bottom ash, and slag, are produced during combustion. It is also acknowledged that the primary causes of atmospheric Pb deposition are I coal combustion, (ii) vehicular exhausts, and (iii) industrial emissions [1].

Because the global industry is in need of raw materials, it is not surprising that the focus of research is on the potential of fly ash, a byproduct of thermal power plants that may contain valuable strategic elements and whose extraction results in financial and environmental benefits [2, 3]. The Science Fund of the Republic of Serbia identified the need for innovative waste management solutions for specific waste streams in Serbia, such as coal fly ash. One of the goals of the SIW4SE project is to develop a method for recovering rare earth elements/strategic elements from fly ash generated by Serbian thermoelectric power plants.

On the other hand, fly ash contributes significantly to air pollution and has a negative impact on human health. Lead, one of the components of fly ash, is well known for its negative environmental and human health effects. A significant number of studies are concerned with the monitoring of lead in soil, sediments, and plants; in addition to measuring concentrations, isotopic composition is also determined in order to determine the origin of lead and accompanying elements, as well as the source/sources of emission.

Tracing of pollution sources and atmospheric transport could be performed using lead isotope fingerprint. Lead emitted into the atmosphere through different anthropogenic processes including coal combustion can be deposited on soil and sediments. In the environment there are four stable isotopic forms of lead: ^{204}Pb (~1.4% of natural abundance), ^{206}Pb (~24.1%), ^{207}Pb (~22.1%) and ^{208}Pb (~52.4%). ^{208}Pb is formed from the radioactive decay of ^{232}Th, ^{207}Pb from ^{235}U, and ^{206}Pb from ^{238}U. ^{204}Pb has no radioactive parent, and it is referred to as common Pb. Due to different decay rates of the parents, uranium and thorium, predictable changes in Pb isotope ratios could be achieved [4].

Coal and fly ash, a coal-combustion product, were collected from selected coal-fired power plants in the Republic of Serbia for this study. The study's goal was to rank Serbian coal of various geological origins and examine the correlation with fly ash using measured Pb isotopic composition.

Materials and methods

The burning of lignite from surface mines in Kolubara and Kostolac provides 70% of electricity in the Republic of Serbia. The Kolubara basin has an area of 600 km^2, about 30 million tons of coal is mined annually and burning coal from this mine in the thermal power plants Nikola Tesla A and B, Kolubara A and Svilajnac provides 53% of electricity. About 9 million tons of lignite are mined annually from the Kostolac surface mine; coal from this mine is burned in the Kostolac Thermal Power Plant, which provides 17% of electricity.

Sample collection

The location of power plants and coal mines is presented in Figure 1. The Kolubara basin is located about 60 km SSW of Belgrade, and covers an area of almost 600 km^2, extending in the E–W direction up to 55 km, and in the S–N direction up to 15 km (Figure 1). The Kostolac basin is located at about 90 km east of Belgrade and covers an area of 145 km^2 [5]. Feed coal and fly ash at each plant were collected.

ICP-MS analysis

The samples were prepared for analysis by microwave digestion in a mixture of ultra-pure mineral acids, hydrochloric acid (30%, vv^{-1}) and nitric acid (65%, vv^{-1}), purchased from Sigma-Aldrich. The water was purified in a Milli-Q™ system (Millipore, Bedford, MA, USA) resulting in Ultra-pure water with >18 MΩ cm resistivity and was used for dilution of standards, for preparing samples and for final rinsing of the acid cleaned vessels. Approximately 0.4 g of each sample was digested in a microwave oven (Speedwave™ MWS-3+, Berghof) with 6 mL of HCl and 2 mL of HNO_3. Then the acid liquid phase was filtered using Whatman Nº 40 paper filter (Whatman International Ltd, Maidstone, UK). The solutions were made up to 25 mL volume with ultrapure water.

Pb concentration and isotopes were measured by inductively coupled plasma mass spectrometry (ICP-MS) using an Agilent 7500ce spectrometer, equipped with Octopole Reaction System (ORS), in FullQuant mode and in Isotope analysis mode. Calibration of ICP-MS was performed using lead standard solution (Agilent) prepared in 2% nitric acid, with six standard solutions in the range of 0.025–10 μg/L. The accuracy of Pb concentration determination was controlled by using the reference material NIST (National Institute of Standards and Technology) 1643e (trace elements in water). Pb isotopes were measured in Isotope analysis mode, and isotope ratios were calculated automatically by ICP-MS software based on each isotope's measured abundance. The precision of isotopic ratio measurements was assessed using the NIST SRM 981 certified isotopic standard (Common lead isotopic standard).

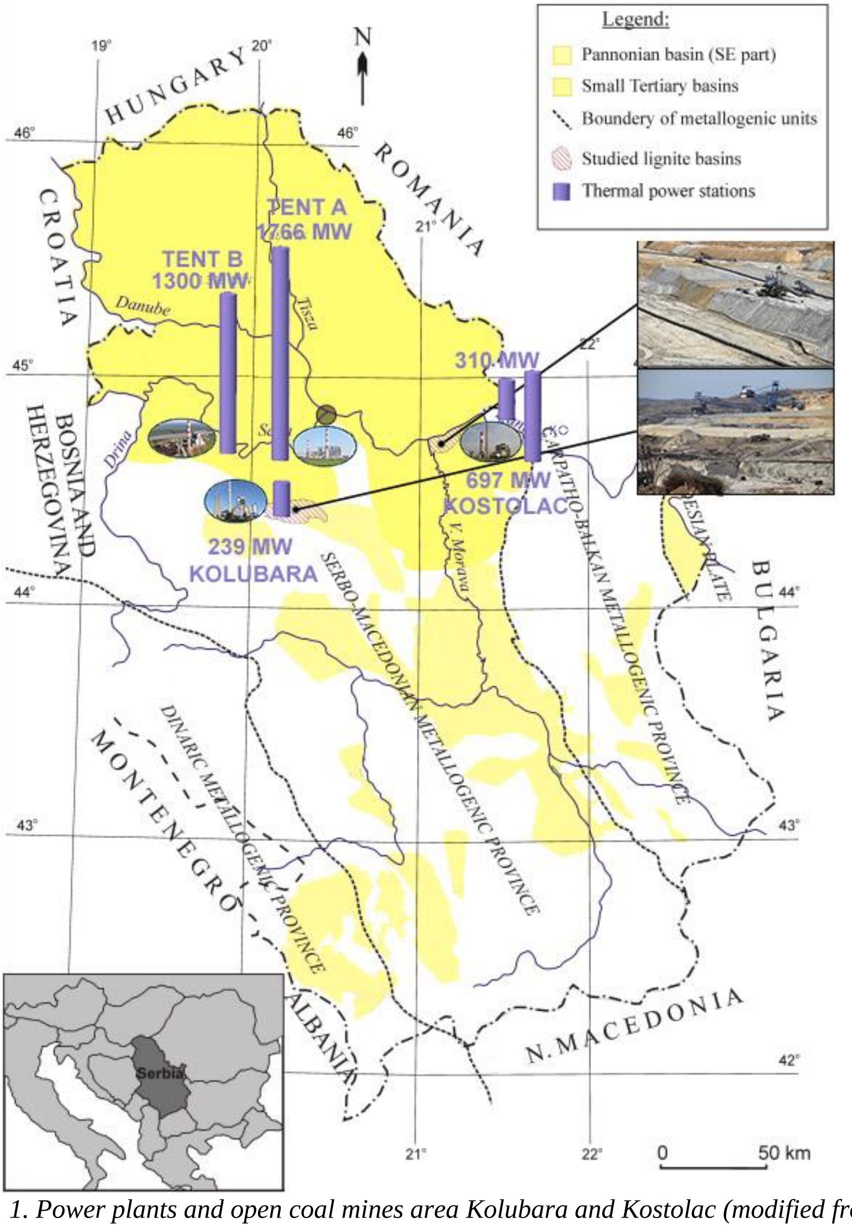

Fig. 1. Power plants and open coal mines area Kolubara and Kostolac (modified from [5]).

Results and disscusion

It is obvious that lignite is a vital resource for the production of electricity in the Republic of Serbia, as it accounts for up to 70% of total electricity generation. Industry and households are also considered lignite consumers in Serbia.

The Upper Miocene (Pontian-Messinian ICS) coal-bearing series from the Kolubara and Kostolac lignite basins are associated with sandy-clayey sediments that formed in the Pannonian basin System in shallow lacustrine, delta plain, and fluvial environments [5].

$^{206}Pb/^{207}Pb$ distribution in coal

In order to rank/compare Serbian lignite used in thermal power plants and coals with the data readily available for various parts of continental Europe, the isotopic ratio of lead isotopes ^{206}Pb and ^{207}Pb in coal within the geochronological context has been determined in this study. The samples of fly ash that were examined had a lead concentration of 20–30 mg/kg. This paper only discusses Pb concentrations in fly ash because Pb concentration in coal is common information that is presented in most studies.

Figure 2 summarizes the literature data, which were primarily gathered in a thorough study of the isotopic composition of 59 coal samples, which represented the world's major coal deposits [6]. Table 1 lists the type of coal and the time/period/epoch of formation.

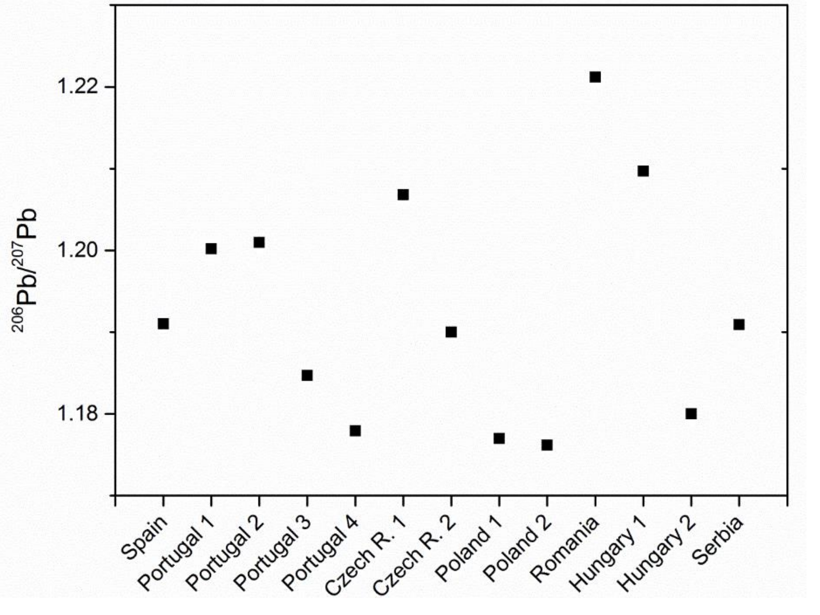

Fig. 2. $^{206}Pb/^{207}Pb$ variability in different European coal deposits.

Table 1. Properties of coal presented in Figure 2.

Country	Coal type	Period of formation	Reference
Spain	bituminous	Carboniferous	[6]
Portugal 1	lignite	Tertiary-Neogene	[6]
Portugal 2	lignite	Tertiary-Neogene	[6]
Portugal 3	lignite	Tertiary- Neogene	[6]
Portugal 4	lignite	Tertiary	[6]
Czech R. 1	bituminous	Carboniferous	[6]
Czech R. 2	no data	no data	[7]
Poland 1	bituminous	Tertiary	[8]
Poland 2	hard coal	No data	[9]
Romania	no data	no data	[6]
Hungary 1	lignite	Karpatian Stage of the Miocene	[6]
Hungary 2	hard coal	No data	[10]
Serbia	lignite	Upper Miocene/Neogene	This study

It can be seen that the $^{206}Pb/^{207}Pb$ ranges from 1.1762 (Poland 2) to 1.2212. (Romania). Except for two coals from Portugal (1 and 2) and Poland, the geographic distribution pattern of Pb isotopes cannot be identified. Observed Pb isotope patterns are influenced by a variety of complex processes that are difficult to connect and identify, such as heterogeneous Th/U-distributions, special geochronologies, coal formation conditions, the origin of incorporated lead, and so on.

$^{206}Pb/^{207}Pb$ and $^{208}Pb/^{206}Pb$ distribution in coal and fly ash

In Table 2. data from this study and similar studies performed in other coutries/regions worldwide are presented. $^{206}Pb/^{207}Pb$ is relatively important in studying the sources of lead in the environment, since it can be determined precisely. The ratio of $^{206}Pb/^{207}Pb$ in the coals was in the range of 1.14−1.26 and $^{208}Pb/^{206}Pb$ between 2.04 and 2.47. Moreover, the highest $^{206}Pb/^{207}Pb$ isotope ratio reported in these studies corresponds to China which makes wide use of coal.

Table 2. $^{206}Pb/^{207}Pb$ and $^{208}Pb/^{206}Pb$ in coal and fly ash from different locations.

Country origin	$^{206}Pb/^{207}Pb$		$^{208}Pb/^{206}Pb$		Source
	coal	fly ash	coal	fly ash	
India (Korba, Chhattisgarh, noncooking coal)	1.151-1.22	1.142	2.073-2.177	2.171	[11]
China Hebei power plant in north China	1.139-1.146	1.139-1.198	2.110-2.166	2.133-2.148	[11]
China Hubei power plant in central China	1.173-1.182	1.178-1.998	2.088-2.110	2.062-2.089	[12]
China Guizhou power plant in southwestern China	1.186-1.262	1.190-1.26	2.062-2.089	1.993-2.094	[12]
United States, Appalachian Basin, Illinois Basin, and Powder River Basin	-	1.2263-1.2284	-	2.0172-2.0253	[13]
United States,	1.19-1.24	1.16-1.20 (US-West) 1.18-1.25 (US-East)	-	-	[6]
Poland (Lower Silesia, SW Poland)	1.173-1.178	1.17-1.18	2.088		[9]
Hungary (lignite, Salgótarján)	1.18	1.18	2.47	2.46	[10]
Serbia (lignite Kolubara and Kostolac)	1.17-1.21	1.16-1.98	2.04-2.09	2.08-2.10	This study

In Figure 3, the isotopic ratio $^{206}Pb/^{207}Pb$ versus $^{208}Pb/^{206}Pb$ in coals from Europe and in fly ash from Serbia has been presented.

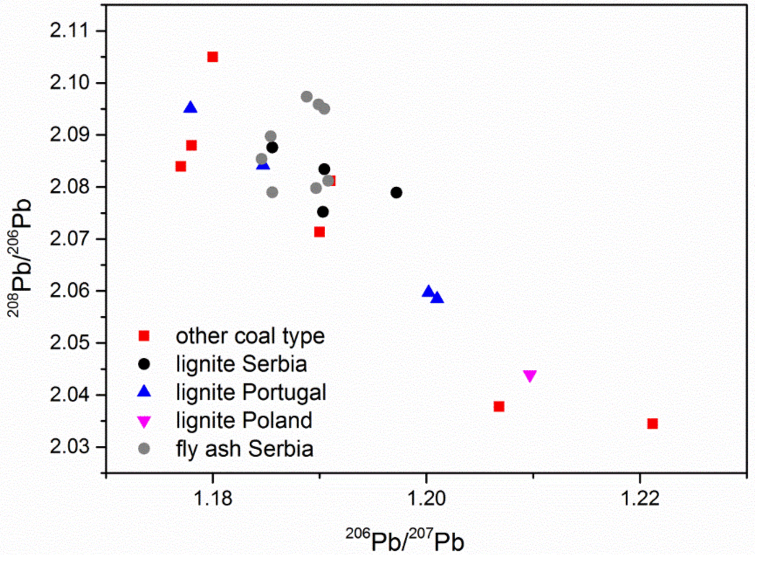

Fig. 3. The isotopic ratio $^{206}Pb/^{207}Pb$ versus $^{208}Pb/^{206}Pb$ in coals from Europe and in fly ash from Serbia.

The data for Serbian coals clearly fall within the range for lignites. The differences in isotope ratios may be due not only to the different origins of lead in different coals, but also to the presence of several lead species incorporated from various sources in a specific coal [14].

The variation in Pb isotopic ratios between Serbian coal and fly ash could be due to isotope fractination during coal combustion, as previously observed in similar research where it was shown that high-temperature coal combustion could lead to a very high degree of fractionation of some metal isotopes [15].

Identification of potential pb emission sources

Lead was once the most widely dispersed element on the planet, owing primarily to its use in gasoline additives. Given that traffic-related emissions are now much lower, one of the sources that can influence the increase in lead concentrations in the environment is fly ash. As a result, a few studies in Serbia have focused on the use of Pb isotope fingerprinting in lead source determination. Figure 4 depicts the $^{208}Pb/^{207}Pb$ versus $^{206}Pb/^{207}Pb$ ratio data for this study's fly ash samples and previous study's tree leaves as lead tracers in an urban environment [16].

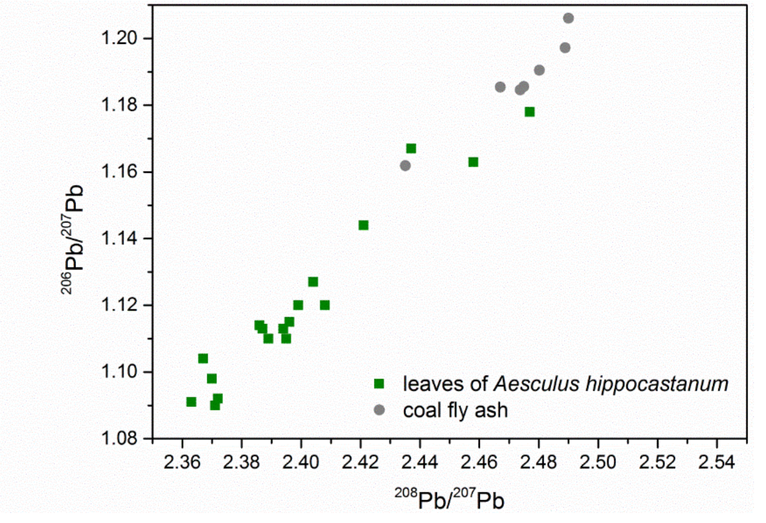

Fig. 4. The isotopic ratios of $^{208}Pb/^{207}Pb$ versus $^{206}Pb/^{207}Pb$ in Aesulus hippocastanum leaves sampled in Belgrade, Serbia and coal fly ash from selected thermal power plants.

Leaded gasoline was still widely used in Serbia in the year of the leaf collection (2009) despite the official ban beginning in 2011. According to Figure 4, the Pb isotopic ratios of fly ash can be distinguished from other anthropogenic sources of Pb, suggesting that coal combustion may be a significant source of lead pollution and that it may have an impact on the isotopic composition at a specific location. This isotopic signature can be used to track the environmental pollution caused by fly ash.

Conclusions

In this study the determination of lead isotopic composition in selected samples of Serbian coal and fly ash has been performed for the first time. The correlation between lead isotopic ratios in coal and fly ash could not be determined with precision because numerous complex processes have an impact on the observed Pb isotopic patterns. The results for $^{206}Pb/^{207}Pb$ in coal serve as the foundation for their ranking; the environment that coal formed in has a significant impact on the isotopic ratio. The fly ash isotopic ratios of $^{206}Pb/^{207}Pb$ and $^{208}Pb/^{207}Pb$ make a significant contribution to the lead isotopic database that is essential for interpreting various pollution sources. Additionally, coal combustion has a significant impact on the pollution of the atmosphere with Pb after the removal of leaded gasoline.

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