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Health risk assessment of potentially harmful substances from fly ashes generated by coal and coal waste combustion

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Abstract: Lignite and coal waste used as feed fuels in thermal power plants (TPPs) and semi-industrial fluidized bed boiler (FBB), as well as their representative fly ashes (FAs), were examined. Fly ashes were compared employing anions and cations content in correspondent water extracts, trace elements and polycyclic aromatic hydrocarbon concentrations, as well as health risk assessments of substances known to be of concern for public health. Fluoride and sulfate contents in water extracted FAs are far below the legislation limits for waste, classifying all investigated FAs as non-hazardous. Among investigated trace elements, Cd content is the lowest, while Mn content is the highest. The highest enrichment ratios are noticed for As, Pb, Hg, Cu, V and Cr. The results indicate that total PAHs content is elevated in FA from the combustion of coal waste (AFB), with fluoranthene prevailing. The cancer risk of As and the non-cancer risk of As and Ni in some FAs surpass their respective permissible limits. The incremental lifetime cancer risk of an adult population indicates a potential PAHs risk in AFB, whereas all other fly ashes are within safe limits.

Keywords: coal ashes; leaching; trace elements; PAHs; carcinogenic risk; total hazard impact.

INTRODUCTION

Despite limited coal supplies, its consumption in Europe is expected to rise due to the uncertainty of the energy sector, so therefore many EU countries extended the life of coal-fired power plants.[1,2] The choice of the appropriate coal as a feed fuel for particular combustion systems relies on coal characteristics, such as its moisture, ash content and gross calorific value.[3] Fluidized bed combustion is

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regarded as an environmentally friendly way of producing energy from low grade coals, due to continuous operation and low NOx and SO_2 emissions.[4,5]

Coal is the dominant energy source in Serbia, with over 7 billion tons of estimated lignite reserves. Annually, the Electric Power Industry (EPI) of Serbia produces around 560, 2010 and 7878 GWh in thermal power plants (TPPs) Kolubara A, Kostolac B and Nikola Tesla A, respectively, which brings to the generation of 246.60 kt, 610.82 kt and 2.08 Mt fly ash, accordingly.[6] Since lignite with particle sizes lower than 10 mm cannot be used further in thermal power plant boilers, it is considered waste. However, coal waste might have a significant energy perspective and can be used as a feed fuel in other combustion technologies, such as fluidized bed combustion.[4] In these circumstances, coal waste originating from the Kolubara basin, discarded as waste in TPP Kolubara A, was tested as a feed fuel in a semi-industrial FBB with a thermal power of up to 500 kW.

Most studies have shown that potentially harmful trace elements emitted during coal combustion are distributed in bottom ash, fly ash particles of different parameters and flue gases so that they can reach soil and water.[7] Content of heavy metals salts, such as chlorides or sulfates, affect leaching mechanisms of potentially harmful compounds in FAs.[8,9] Ca and Mg are the most dominant cations in fly ash water leachates, while anions primarily include sulfates, carbonates and fluorides.[10] Furthermore, anions and cations content were determined to complement the scarce literature data considering water extracted FAs.

In addition, persistent organic compounds, such as polycyclic aromatic hydrocarbons (PAHs), represent significant environmental pollutants generated during coal combustion.[11] The US Environmental Protection Agency (US EPA) regulated 16 priority PAHs due to their harmful effects on people and the environment.[12] Physicochemical properties of PAHs and, consequently, their environmental fate depends on their structure and number of fused aromatic rings.[13] PAHs are usually classified into low molecular weight (LMW), medium molecular weight (MMW) and high molecular weight (HMW). As the molecular weight of a particular PAH increases, its carcinogenicity rises, while its acute toxicity decreases.[14] The fate and partitioning of toxic elements and PAHs in coal combustion by-products depends on the used feed fuel, combustion temperature, burner type and structure.[10] Therefore, a thorough analysis of the used coals and produced FAs is necessary to optimize combustion processes in terms of environmental and health issues.[15] Intake of potentially toxic substances by humans can be through three pathways *i.e.* ingestion, inhalation and dermal contact. Model of human exposure (adults and children) to potentially harmful substances is developed by the US EPA guidelines.[16]

In this study, feed coals and FAs from TPPs Kolubara A (TPKb), Kostolac B (TPKs) and Nikola Tesla A (TPNT), as well as coal waste and FA from semi-

industrial FBB were investigated. This paper characterizes and compares different coals based on proximate and ultimate analysis, along with trace element concentrations, and analyzes corresponding fly ashes, determining their particle size diameters, trace elements and PAHs content, as well as anions and cations content in fly ash water leachates. The aim of this study was to perform a human health risk assessments of potentially harmful substances in fly ashes by estimating the carcinogenic and non-cancer risk for trace elements and the incremental life cancer risk of seven carcinogenic PAHs associated with different exposure routes.

EXPERIMENTAL

A sampling of coals and fly ashes

A sampling of coals from TPP Kolubara A (CKb), TPP Kostolac B (CKs), TPP Nikola Tesla A (CNT) and coal waste from a fluidized bed boiler (CFB) was done according to the standard method.[17] The same method was used for the collection of coal fly ashes from TPKb (AKb), TPKs (AKs), TPNT (ANT) and from the cyclone of FBB (AFB). The samples were prepared and stored in a glass container at a dark place under a temperature below 15 °C.[18,19]

Granulometric analysis of fly ashes

The granulometric analysis of investigated fly ashes was performed using a set of sieves with round hole diameters of 90 μm, 200 μm, 500 μm and 1000 μm.[20]

Proximate and ultimate analysis of coals

The proximate analysis of investigated coals was done by LECO TGA 701 according to a standard test method.[21] The ultimate analysis was performed by a LECO CHN 628 Series with a Sulfur add-on module.[22-24]

Determination of anions and cations by ion chromatography

5 g of each FA was mixed with 50 mL of deionized water in an IKA KS130 orbital shaker (800 rpm) for 180 min. Obtained extracts were filtered and further used to determine cations and anions by ion chromatograph Dionex. The details are given in the Supplementary material.

Determination of trace elements in coals and FAs

Extraction of 18 elements (As, Be, Cd, Co, Cr, Cs, Cu, Ga, Ge, Hg, Mn, Mo, Ni, Pb, Sb, Sr, U, V) was done by sequential extraction.[25] Trace elements concentrations were determined by the inductively coupled plasma mass spectrometry (ICP-MS) using an Agilent 7500ce instrument equipped with Octopole Reaction System in FullQuant mode. The details about ICP-MS measurements are described in the Supplementary material. Each element's total concentration is the sum of its six representative fractions.

PAHs analysis

The extraction of 16 priority PAHs (naphthalene, Nap; acenaphthylene, Acy; acenaphthene, Ace; fluorene, Flu; phenanthrene, Phe; anthracene, Ant; fluoranthene, Fla; pyrene, Pyr; benzo[a]anthracene, BaA; chrysene, Chry; benzo[b]fluoranthene, BbF; benzo[k]fluoranthene, BkF; benzo[a]pyrene, BaP; dibenzo[a,h]anthracene, DahA; benzo[g,h,i]perylene, BghiP and indeno[1,2,3-cd]pyrene, IP) from fly ashes was done according to literature.[26] The prepared extracts were analyzed by HPLC/DAD. The details are explained in the Supplementary material.

Enrichment ratios (ERs) of trace elements

The ER of a particular trace element was calculated as a quotient of its concentration in ash and correspondent coal. ER higher than 1 indicates trace elements enhancement in ash compared to the corresponding feed fuel.

Human health assessment for trace elements and PAHs from FAs

The human health assessment associated with trace elements and PAHs found in FAs was performed for adults and children.

Human health assessment comprises the calculation of total risk indexes (*R*) for carcinogenic substances (As^{cc}, Cd^{cc}, Cr^{cc}, Co^{cc}, Ni^{cc}), as well as total hazard indexes (*HI*) for non-carcinogenic substances (As^{ncc}, Pb, Hg, Cd^{ncc}, Cr^{ncc}, Co^{ncc}, Ni^{ncc} and Cu). Total *R* and *HI* were calculated for each element by the following equations:

$$R = D\mathrm{ig} \times SF\mathrm{ig} + D\mathrm{ih} \times SF\mathrm{ih} + D\mathrm{d} \times SF\mathrm{d} \quad (1)$$

$$HI = D\mathrm{ig} / RF\mathrm{ig} + D\mathrm{ih} / RF\mathrm{ih} + D\mathrm{d} / RF\mathrm{d} \quad (2)$$

D_i/ mg kg^{-1} day^{-1} is the daily intake dose, SF_i/ kg day mg^{-1} is the corresponding carcinogenicity slope factor and RF_i/ mg kg^{-1} day^{-1} is the reference dose for each exposure route i, where i stands for ingestion (ig), inhalation (ih) or dermal contact (d). Parameters used to calculate D_i are given in Supplementary material (Table S-I, a and S-II), and the toxicity values for RF_i and SF_i are in Table S-III.[27,28]

Generally, a risk less than 10^{-6} can be ignored; a carcinogenic risk in the range of 10^{-6} to 10^{-4} is acceptable or tolerable, while a risk exceeding 10^{-4} is considered unacceptable for any element. If *HI* is higher than 1, negative health effects are probable.

The incremental lifetime cancer risk (*ILCR*) was estimated as the sum of 7 carcinogenic PAHs (BaA, Chry, BbF, BkF, DahA, BghIP and IP) for three exposure routes. $ILCR \leq 10^{-6}$ generally denotes virtual safety, $10^{-4} < ILCR < 10^{-6}$ indicates potential risk, while $ILCR > 10^{-4}$ represents a high risk.

The health assessment calculations for PAHs and their parameter values are shown in Supplementary material (Table S-I, b and S-II).

RESULTS AND DISCUSSION

Proximate and ultimate analysis

The fuels used in four combustion facilities were examined by proximate and ultimate analysis and results on air dried basis are shown in Table I. Compared to coal waste, all feed fuels from TPPs have better properties as a combustion feedstock due to lower ash content, as well as higher volatile matter, carbon content and heating value.[29] Because high volatile matter can be associated with spontaneous combustion (particularly with low-rank coals such as lignite), knowing the volatile content of the coal simplifies transportation and handling. The total sulfur of CKs is fourfold higher than other coal samples. CKb, CNT and CFB originate from the same basin (Kolubara), while CKs derive from the Kostolac basin. The combustible sulfur proportion of CFB (36 %) is substantially lower than for other coals from the Kolubara basin (62 - 69 %).[30]

TABLE I. Proximate and ultimate analysis of lignite from TPPs Kolubara A (CKb), Kostolac B (CKs) and Nikola Tesla A (CNT) and coal waste from FBB (CFB)

	CKb	CKs	CNT	CFB
	Content, % (proximate analysis)			
Total moisture*	42.94	40.34	48.90	36.74
Inherent moisture**	6.04	8.18	7.14	7.04
Ash	37.21	36.29	36.86	61.85
Coke	61.55	60.56	57.31	77.43
Combustible	61.79	63.71	63.14	38.15
Volatile	38.45	39.44	42.69	22.57
C-fix	23.34	24.27	20.45	15.58
	Heating value, MJ kg^{-1}			
High	16.56	16.56	16.41	10.16
Low	15.75	15.62	15.60	9.75
	Content, % (ultimate analysis)			
Carbon	41.26	41.64	38.80	24.81
Hydrogen	3.74	3.78	3.74	1.96
Total sulfur	0.64	2.76	0.55	0.66
Combustible sulfur	0.43	1.91	0.34	0.26
Nitrogen	0.58	0.67	0.44	0.34
Oxygen	16.77	15.65	19.92	10.78

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

Granulometric analysis

Ash particle size is an important parameter since finer ashes provide a greater surface area for the sorption of harmful substances.[31] The granulometric analysis results are shown in Fig. 1. AKb mainly comprises finer particles with diameters less than 90 μm (64.61 %), while AFB has the highest yield in the F3 fraction (92.96 %). FAs from TPPs have mean particle diameters ranging from 126 μm to 131 μm, while for AFB, it is 341 μm. The variations of FAs particle size are affected by combustion system characteristics, burning temperatures, used feed fuels, as well as the system treatment of the gaseous effluents.[32]

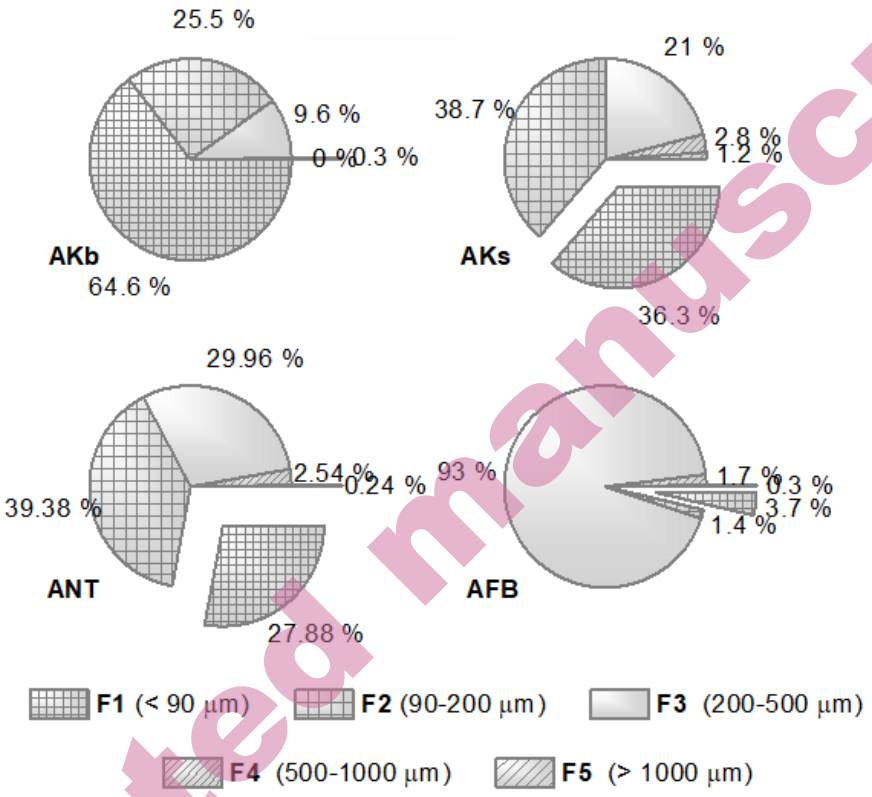

Fig. 1. Granulometric analysis of fly ashes from TPPs Kolubara A (AKb), Kostolac B (AKs), Nikola Tesla A (ANT) and from fluidized bed boiler (AFB)

Anions and cations content in water extracted fly ashes

Fig. 2 depicts the leaching of anions and cations in water extracted FAs. Among determined cations, calcium prevails with concentrations ranging from 2.06 mg/g (in ANT) to 5.32 mg/g (in AKs). It is in line with the literature since calcium salts easily dissolve.[33] Potassium is the most dominant in AKb with a concentration of 3.38 mg/g, which is more than tenfold higher than in other FAs. Sulfates are the most abundant among the other anions, ranging from 2.32 mg/g (in ANT) to 10.32 mg/g (in AKs), whereas chlorides, phosphates, and nitrates are undetected. Fluorides vary from 0.10 mg/g (in AKs) to 0.18 mg/g (in AKb). Most of the fluorides in FA are insoluble, while the water-soluble form of fluoride mainly originates from NaF and KF.[34]

All water extracted FAs can be regarded as non-hazardous waste since fluoride and sulfate contents are far below upper legislation limit values for waste classification given in Table S-IV.

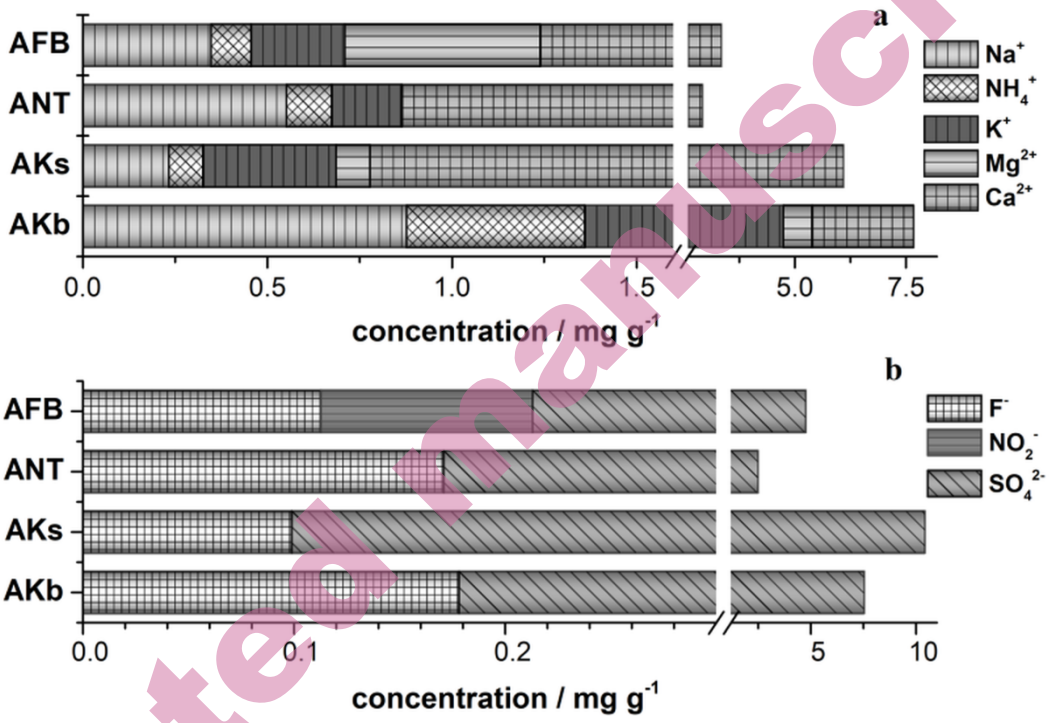

Fig. 2. Leaching of cations (a) and anions (b) in water extracted fly ashes from TPPs Kolubara A (AKb), Kostolac B (AKs), Nikola Tesla A (ANT) and from fluidized bed boiler (AFB)

The concentration of trace elements in coals and representative FAs; enrichment ratios (ERs)

Fig. S-1 and Table S-Ishow the overall trace elements concentrations in feed coals and their corresponding fly ashes. CFB has the lowest overall trace element content among all the investigated feed coals (256.72 mg/kg). Trace element concentrations in coals are the highest for Mn (up to 209.63 mg/kg), while decreased content for Hg and Ge is observed (Fig. S-1, a-b). Trace element contents in FAs vary from the lowest values for Cd (up to 0.76 mg/kg in AKs) to the highest content for Mn, ranging from 210.48 mg/kg in AFB to 607.29 mg/kg in AKb (Fig. S-1, c-d). Finer TPP ashes have elevated trace element concentrations than AFB due to higher concentrations in corresponding feed fuels and larger surface area of ash particles.[35] Furthermore, the reason for significantly lower concentrations of As, Co, Cs and Hg in AFB compared to other FAs from TPPs can be higher combustion temperatures in TPPs. It is known that higher combustion temperatures can imply enhanced trace element concentrations in flue gases which can further easily condensate on fly ash particles.[36] In contrast, Cu,

Ga, Ge and Sb contents in AFB are not the lowest of all FAs, which is consistent with the literature where these trace elements do not show a significant correlation with ash particle diameters.[31]

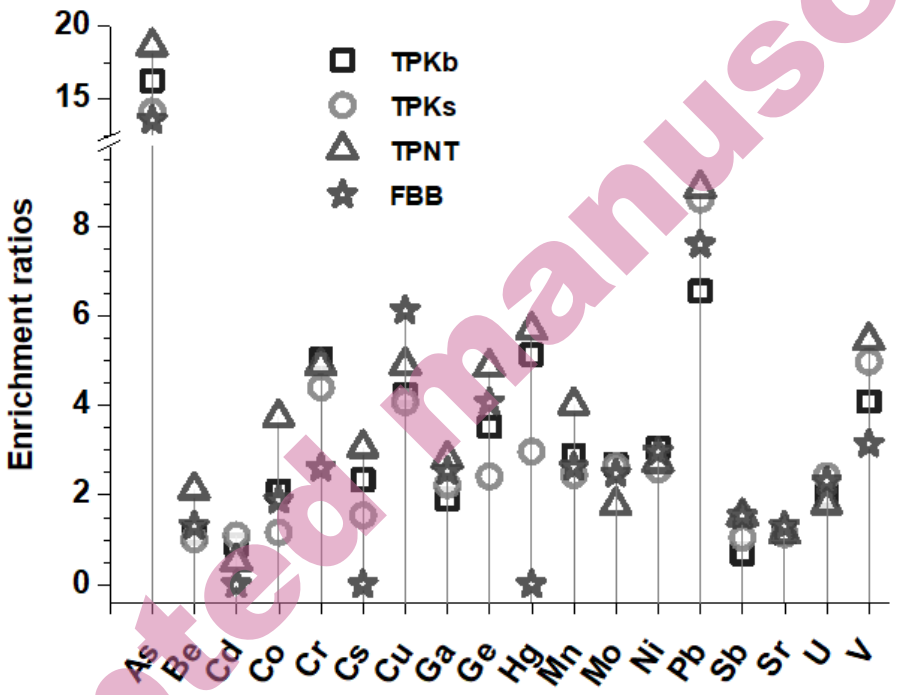

Fig. 3. Enrichment ratios for TPPs Kolubara A (TPKb), Kostolac B (TPKs), Nikola Tesla A (TPNT), and fluidized bed boiler (FBB)

The enrichment ratios (ERs) are presented in Fig. 3. As (from 13.58 to 18.60), Pb (from 6.55 to 8.85), Hg (from 2.97 to 5.68), Cu (from 4.08 to 6.13), V (from 3.14 to 5.45), and Cr (from 2.60 to 5.04) have the highest ER values. These elements are enhanced in FAs due to their vaporization during coal combustion and subsequent condensation on the fly ash particles.[37] At relatively low temperatures, arsenic easily forms volatile compounds.[38] In addition, Pb related to organic matters volatilizes at around 850 °C, while Hg may react with flue gas components and form oxidized mercury in a wide temperature range.[39] Other elements, such as Be, Co, Ni, U, Sb and Sr, have lower ERs because they are correlated with less volatile minerals.[5]

PAHs content in investigated FAs

Fig. 4a shows the distributions of LMW, MMW, and HMW PAHs. The total PAH content and the concentration of 10 PAHs defined in Serbian legislation for soil are presented in Fig. 4b. The total PAHs content varies from 278.95 ng/g

(ANT) to 32548.66 ng/g (AFB), which is consistent with PAHs ranges for FAs found in the literature.[40] The MMW PAHs are the most abundant in AKb (68.25 %) and AFB (70.03 %), while LMW PAHs prevail in AKs (75.23 %) and ANT (67.28 %). Among examined FAs, AFB and AKb contain the highest fluoranthene contents, while AKs and ANT have the highest fluorene concentrations (Table S-I,b). These findings are in accordance with literature revealing Fla and Flu as the most abundant PAHs due to incomplete combustion of fossil fuels.[26] The content of 10 PAHs is in the range from 124.13 ng/g (ANT) to 23075.48 ng/g (AFB), which is lower than permissible limits in Serbian soil guidance (Table S-IV).[41]

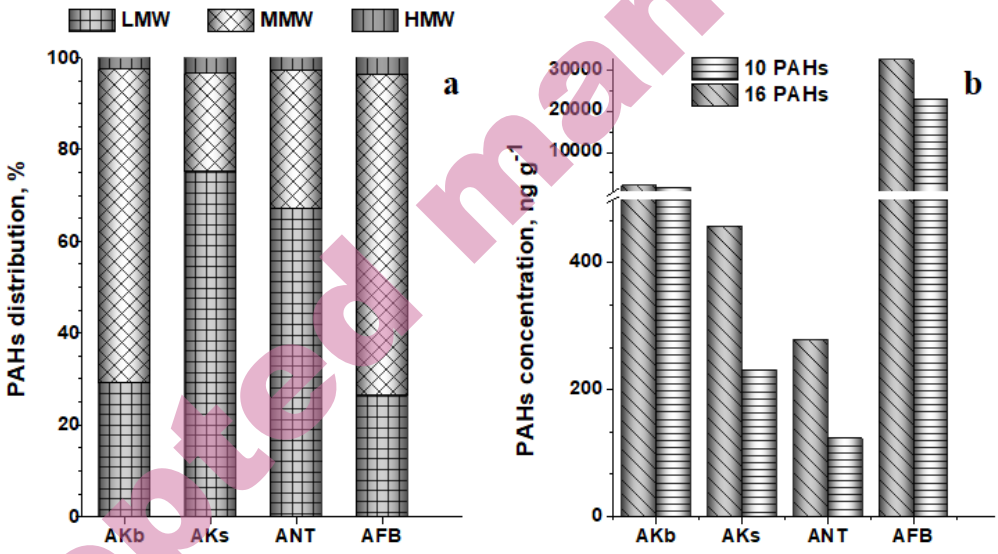

Fig. 4. Distribution of PAHs according to molecular weight (a); the overall and 10 PAHs content (b); fly ashes from TPPs Kolubara A (AKb), Kostolac B (AKs), Nikola Tesla A (ANT) and fluidized bed boiler (AFB)

Health impact for potentially toxic trace elements and PAHs from FAs

Risk indices, as well as total hazard indices for children and adults, are presented in Table II. The non-cancer risks for children demonstrate that Ni values in AKb, AKs and ANT, as well as As for all FAs, exceed the acceptable limit. Furthermore, *HI*s for adults are higher than safe values for As in AKb, AKs and ANT (Table II). Hazard indices for Cd^{ncc}, Co^{ncc}, Cu, Hg and Pb are about two orders lower than the regulatory level.[42] To acquire better insight into the health impact of each FAs, the overall *HIs*, as well as the overall *Rs,* are determined as the sum of *HI* or *R* for all investigated elements, respectively. The estimated overall *HI* is the highest for AKb (7.15 for children and 2.15 for adults). Trace elements hazard quotients (HQ_{ig}, HQ_{ih} and HQ_{d}) and risk indices (R_{ig}, R_{ih} and R_{d}) for three exposure routes are shown in Table S-V, a-b. The dominant exposure routes for

the non-cancer risk are dermal contact for As^{ncc}, Cd^{ncc}, Ni^{ncc} and Cu, and ingestion for Co^{ncc}, Cr^{ncc}, Hg and Pb.

TABLE II. Trace elements cancer risk (*R*) and total hazard impact (*HI*); PAHs total risk (*ILCR*) for fly ashes from TPPs Kolubara A (AKb), Kostolac B (AKs) and Nikola Tesla A (ANT) and from fluidized bed boiler (AFB)

Carcinogenic elements					
R/ unitless					
		AKb	AKs	ANT	AFB
Children	As	1.81×10^{-4}	1.51×10^{-4}	1.61×10^{-4}	4.82×10^{-5}
					4.82×10^{-5}
Adults	As	2.51×10^{-4}	2.09×10^{-4}	2.23×10^{-4}	6.69×10^{-5}
					6.69×10^{-5}
Non-carcinogenic elements					
HI/ unitless					
		AKb	AKs	ANT	AFB
Children	As	4.68	3.90	4.16	1.25
					2.95
Adults	As	1.30	1.08	1.16	3.47×10^{-1}
					9.40×10^{-1}
PAHs					
ILCR/ unitless					
		AKb	AKs	ANT	AFB
Children		1.32×10^{-7}	2.12×10^{-8}	1.65×10^{-7}	6.05×10^{-6}
Adults		4.29×10^{-7}	6.91×10^{-8}	5.40×10^{-7}	1.98×10^{-5}

AFB displays the lowest total risk index (4.82×10^{-5} for children and 6.69×10^{-5} for adults). The calculated total risk indices decrease in the following order: $As^{cc}>Co^{cc}>Ni^{cc}>Cr^{cc}>Cd^{cc}$ (Table II). Total cancer risk of As (up to 2.51×10^{-4} in AKb) exceed the safe limits, while Co^{cc}, Ni^{cc}, Cr^{cc} and Cd^{cc} risk values are far below permissible limit values. The arsenic content should be thoroughly monitored and controlled. The most dominant exposure route among carcinogenic substances is the inhalation for Co^{cc}, Ni^{cc}, Cr^{cc} and Cd^{cc}, while for As^{cc} it is dermal contact (Table S-V, a-b).

Three exposure routes were used, both for children and adults, to determine human health issues caused by PAHs. Table II demonstrates that only AFB for adults indicates a potential risk for PAHs, while all other FAs are within safe limits. The literature provides health assessments of PAHs for various soil types, while there is a lack of information regarding health assessments of PAHs from FAs generated during coal combustion.[43]

CONCLUSIONS

Potassium is the most dominant among cations (AKb), while sulfates have the highest content in all FAs among anions. Investigated FAs can be considered non-hazardous since fluorides and sulfates content are far below legislation limits for waste classification. The ERs are the highest for As, Pb, Cu, V, Hg and Cr. Among all investigated FAs, the highest concentration of Fla was noticed in AKb and AFB, while Flu concentrations are maximal in AKs and ANT. Health calculations associated with trace elements and PAHs in FAs lead to some general conclusions:

- The obtained results for non-cancer risk show that Ni in AKb and AKs and ANT, as well as As for all FAs, exceed the permissible limit for children, while HIs for adults are higher than safe values for As in AKb, AKs and ANT.
- As exceeds the safe limit for cancer risk in all FAs, apart for AFB.
- PAHs potential risks for adults (except for AFB) are within safe values.

Due to a lack of information on anions and cations analysis in water extracted FAs, as well as health risks related with exposure to PAHs and trace elements, this research could contribute to the current state of knowledge for health issues associated with fly ash disposal.

SUPPLEMENTARY MATERIAL

Supplementary Materials are available electronically from https://www.shd-pub.org.rs/index.php/JSCS/article/view/12208, or from the corresponding authors on request.

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И З В О Д

ПРОЦЕНА РИЗИКА ЗА ПОТЕНЦИЈАЛНО ОПАСНЕ СУПСТАНЦЕ ИЗ ЛЕТЕЋИХ ПЕПЕЛА ДОБИЈЕНИХ САГОРЕВАЊЕМ УГЉА И ОТПАДНОГ УГЉА

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У овом раду, испитивана су горива (лигнит и отпадни угаљ) која се користе у термоелектранама (ТЕ) и полуиндустријском постројењу са флуидизованим слојем (ФББ), као и летећи пепели добијени њиховим сагоревањем. Летећи пепели су упоређени на основу: садржаја анјона и катјона у њиховим воденим екстрактима, концентрације елемената у траговима и полицикличних ароматичних угљоводоника (ПАХ-ова), као и процене здравственог ризика који потиче од претходно поменутих потенцијално опасних супстанци. Садржај флуорида и сулфата у воденим екстрактима летећих пепела далеко је испод законски дозвољених граница за отпад, на основу чега се могу сврстати у безопасне. Од испитиваних елемената у траговима, садржај Cd је најнижи, док је концентрација Mn највиша. Највеће обогаћење пепела у односу на одговарајући угаљ, примећено је за As, Pb, Hg, Cu, V и Cr. На основу добијених резултата показано је да је укупни садржај ПАХ-ова највећи за летећи пепео добијен сагоревањем отпадног угља. Међу испитиваним ПАХ-овима, највишу концентрацију има флуорантен. Ризици који потичу од арсена (међу канцерогеним елементима), као и арсена и никла (међу неканцерогеним елементима), премашују дозвољене граничне вредности. Вредност процењеног ризика од рака код одрасле популације у случају ПАХ-ова, показује да за летећи пепео добијен сагоревањем отпадног угља постоји потенцијални ризик, док су вредности за остале пепеле унутар дозвољених граница.

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