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Supplementary material

SUPPLEMENTARY MATERIAL TO

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

JOVANA Z. BUHA MARKOVIĆ[1]*, ANA D. MARINKOVIĆ[1], JASMINA Z. SAVIĆ[1], ALEKSANDAR D. KRSTIĆ[1], ANDRIJA B. SAVIĆ[1] and MIRJANA Đ. RISTIĆ[2]

[1]*University of Belgrade, Vinča Institute of Nuclear Sciences - National Institute of the Republic of Serbia, Belgrade, Serbia and* [2]*University of Belgrade, Faculty of Technology and Metallurgy, Karnegijeva 4, Belgrade, Serbia*

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DETERMINATIONS OF ANIONS AND CATIONS BY ION CHROMATOGRAPHY

Cations (sodium, potassium, magnesium, calcium, and ammonium ions) in aqueous extracts of ash samples were determined by ion chromatograph Dionex with a conductivity detector and Dionex IonPack CS12 (4×250 mm) column with pre-column CG12 (10-32) (4×50 mm). The mobile phase contained 0.02 M methane sulfonic acid (flow rate of 0.7 mL min^{-1}).

Anions (sulphates, Su; nitrates, NA; nitrites, NI; phosphates, Ph; chlorides, Ch and fluorides, Fl) were determined by ion chromatograph Dionex with a conductivity detector and Dionex IonPack AS14 (4×250 mm) column with pre-column AG14 (4×50 mm). The mobile phase contained 0.5 mM $NaHCO_3$ and 2 mM Na_2CO_3 (flow rate of 0.9 mL min^{-1}). The injection volume for cations and anions determination was 20 μL.

ICP-MS ANALYSIS

The measurements of every subsample were done in 3 replicates. ICP-MS was calibrated using Agilent Multi-Element Calibration Standards (standards 2, 3 and 4) with six standard solutions. Standard solutions and blanks were prepared in 2 % HNO_3. A tuning solution containing 1 μg/L Li, Mg, Co, Y, Ce and Tl (Agilent) was used for the instrument optimization. The limits of detection of measured elements were: As 0.015, Be 0.046, Cd 0.002, Co 0.001, Cr 0.015, Cs 0.01, Cu 0.005, Ga 0.007, Ge 0.006, Hg 0.01, Mn 0.098, Mo 0.07, Ni 0.022, Pb 0.005, Sb 0.01, Sr 0.163, U 0.005, V 0.001(all in μg/L). Quality control was performed using the certified reference material SLRS-5 (River water reference

* Corresponding author. E-mail: jbuha@vin.bg.ac.rs

material for trace metals, National Research Council of Canada). Accuracy was in the range of 88 – 112 %.

HPLC ANALYSIS

A Thermo Fisher Scientific Dionex UltiMate 3000 HPLC system with a diode array detector (DAD) and Envirosep-PP 125×2 mm column, with particle size 5 μm (Phenomenex) was used. A portion of 5 g of coal, coal waste, or ash was mixed with 50 mL of hexane:acetone mixture (1:1, v/v). PAHs extraction lasted 70 min, and was carried out by Grant XUB ultrasonic bath, Grant Instruments (Cambridge) Ltd, UK. After that, the mixture of ash samples with solvents was filtered through Whatman No. 44 filter paper, and ash was washed out several times with a total of 20 mL of acetone: hexane mixture (1:1). Then, the extract was transferred quantitatively into separating funnel; deionized water was added, and after shaking extract was divided into two layers: the upper hexane layer and downer polar layer (acetone-water). The downer layer was removed from the separating funnel. The hexane layer was dried with anhydrous Na_2SO_4 and concentrated up to 1 mL by a vacuum rotary evaporator (Heidolph Instruments GmbH, Germany). After that, the concentrated extract was evaporated to dryness in a nitrogen stream; 0.5 mL of acetonitrile was added and filtered by 0.22 μm nylon syringe filter ESF-NY-13-022 of 13 mm (Kinesis) before further PAHs analysis. The procedure was done in triplicate to check the reproducibility of extraction.

HUMAN HEALTH ASSESSMENT

The dose received through each of the three pathways was calculated by the following equations:

$$Dig = C \times \frac{IRig \times EF \times ED \times CF_1}{BW \times AT} \tag{1}$$

$$Dih = C \times \frac{IRih \times EF \times ED}{PEF \times BW \times AT} \tag{2}$$

$$Dd = C \times \frac{SA \times SL \times ABS \times EF \times ED \times CF_1}{BW \times AT} \tag{3}$$

C/ mg kg^{-1} - concentration of each representative metal in fly ash samples (given in Table S-I, a). Values for all other parameters used in health assessment calculations are presented in Table S-II.

TABLE S-I, a. Concentration of elements in fly ash samples (C/ mg kg^{-1})

Elements content- C/ mg kg^{-1}				
Element	AKb	AKs	ANT	AFB
As	63.26	52.78	56.26	16.87
Pb	23.17	24.95	29.44	16.47
Hg	1.65	1.075	1.99	0.46
Cd	0.44	0.76	0.26	/
Cr	158.02	120.58	183.09	107.98
Co	13.96	10.04	19.24	6.12
Ni	107.19	98.89	90.79	70.02
Cu	59.32	121.45	68.75	97.50

TABLE S-I, b. Individual PAHs concentration in fly ash samples (C/ ng kg^{-1})

PAHs content - C/ ng kg^{-1}					
PAHs	Abbreviation	AKb	AKs	ANT	AFB
Naphthalene	Nap	23.54	10.88	7.33	21.80
Acenaphthylene	Acy	2.77	49.36	38.05	745.23
Acenaphthene	Ace	6.56	8.29	3.25	104.70
Fluorene	Flu	150.06	144.76	92.01	1576.70
Phenanthrene	Phe	385.87	129.26	44.90	4993.90
Anthracene	Ant	17.20	1.87	2.14	1159.98
Fluoranthene	Fla	795.89	55.31	50.24	9509.68
Pyrene	Pyr	410.35	13.01	14.17	6999.46
Benzo[a]anthracene	BaA	84.37	20.39	15.32	3838.38
Chrysene	Chry	77.25	8.89	4.09	2445.81
Benzo[b]fluoranthene	BbF	25.05	0.00	1.39	491.95
Benzo[k]fluoranthene	BkF	4.32	7.61	1.33	53.56
Benzo[a]pyrene	BaP	5.59	0.00	21.06	338.25
Dibenzo[a,h]anthracene	DahA	0.04	0.00	0.00	25.29
Benzo[g,h,i]perylene	BghIP	10.66	3.54	1.49	115.92
Indeno[1,2,3-cd]pyrene	IP	4.51	0.46	0.17	128.05

TABLE S-II. Parameters used for risk assessment of trace elements and PAHs

Parameter, unit	**Abbr.**[ref]	**Children**	**Adults**
Body weight, kg	BW[2,3]	18.6	80
Exposure frequency, day year^{-1}	*EF*	350	350
Exposure duration, year	*ED*	6	30
Dust ingestion rate, mg day^{-1}	*IR*ig[2,3,5]	200	50
Inhalation rate, m^3 day^{-1}	*IR*ih[2,3]	41.76	56.16
Dermal exposure area, cm^2	*SA*[2]	2625	6475
Dermal adsorption factor (for elements)	*ABS*[6,9]	As (0.03), Pb (0.006), Hg (0.05), Cd (0.14), Cr and Co (0.001), Cu (0.1), Ni (0.35)	
Skin-soil adherence factor	*SL*[2]	1.2	0.98
Dermal adherence factor, mg cm^{-2}	*AF*[4]	0.2	0.07
Dermal adsorption factor (for PAHs), unitless	*ABS*[4,8]	0.13	0.13
Averaging time (for elements), year	*AT*[4,5]	6* 70**	30* 70*
Averaging lifespan (for PAHs), day	*AT*[9]	25550	25550
Particle emission factor, m^3 kg^{-1}	*PEF*[6]	6.8×10^8	6.8×10^8
Unit conversation factor, unitless	CF_1	10^{-6}	10^{-6}
Carcinogenic slope factor ih, kg day mg^{-1}	*CSF*ih[7]	3.85	3.85
Carcinogenic slope factor ig, kg day mg^{-1}	*CSF*ig[7]	7.30	7.30
Carcinogenic slope factor d, kg day mg^{-1}	*CSF*d[7]	25.00	25.00

*for non-carcinogenic, AT=ED, 6×365=2190 days for children and 30×365=10950 days for adults, ** for carcinogenic effect, 70×365=25550 days

TABLE S-III. Cancer slope factors (SF_i/ kg day mg^{-1}) for carcinogenic elements and Reference dose factors (RF_i/ mg kg^{-1} day^{-1}) for non-carcinogenic elements, for three exposure routes

Element	SF_{ig}	SF_{ih}	SF_d
Cancer Slope factor - SF_i/ kg day mg^{-1}			
As	1.5	3.66	15
Cd	/	/	6.3
Cr	/	/	42
Co	/	/	9.8
Ni	/	/	0.84
Reference dose - RF_i/ mg kg^{-1} day^{-1}			
As	3×10^{-4}	1.23×10^{-4}	3×10^{-4}
Pb	3.5×10^{-3}	5.25×10^{-3}	3.5×10^{-3}
Hg	3×10^{-4}	3×10^{-4}	8.6×10^{-5}
Cd	2×10^{-2}	1.6×10^{-2}	5.71×10^{-6}
Cr	3×10^{-4}	6×10^{-5}	3×10^{-5}
Co	2×10^{-2}	1.6×10^{-2}	5.71×10^{-6}
Ni	2×10^{-2}	5.4×10^{-3}	2×10^{-2}
Cu	4×10^{-2}	1.2×10^{-2}	4×10^{-2}

The *ILCR* were calculated for ingestion, inhalation and dermal route using the following equations:[1]

$$ILCRig = \frac{C_s \times \left(CSFig \times \sqrt{\left(\frac{BW}{70} \right)} \right) \times IRig \times EF \times ED}{BW \times AT \times 10^6} \quad (4)$$

$$ILCRih = \frac{C_s \times \left(CSFih \times \sqrt{\left(\frac{BW}{70} \right)} \right) \times IRih \times EF \times ED}{BW \times AT \times PEF} \quad (5)$$

$$ILCRd = \frac{Cs \times \left(CSFd \times \sqrt{\left(\frac{BW}{70} \right)} \right) \times SA \times AF \times ABS \times EF \times ED}{BW \times AT \times 10^6} \quad (6)$$

Health assessment calculations, according to literature data, are given in Table S-II.[2-9]

Concentrations of all 16 PAHs are shown in Table S-I, b, while Cs represent sum of converted PAHs concentrations for 7 CarPAHs based on toxic equivalents of BaP using the toxic equivalency factor in ng g^{-1}.[7]

TABLE S-IV. Literature data and permissible limits for anions and cations, trace elements and PAHs leaching

Analytes	C/ mg kg^{-1}	Data description,[reference]
		Anions and cations
F^-	10 - 500	Limit values for waste classification,[11]
SO_4^{2-}	1000-50000	
Na^+	189.92	Leaching from class F FA,[12]
NH_4^+	9.0-12.20	Leaching from Australian FAs,[13]
K^+	181.7	Leaching from class F FA,[12]
Ca^{2+}	42.32-52.42	Leaching from class F FA and Serbian FA,[12,14]
Mg^{2+}	2042.3	Leaching from class F FA,[12]
		Trace elements
As	29-55	Legislation limits for metals in soil,[15,16]
Be	1.1-30	
Cd	0.8-2	
Co	9-240	
Cr	100-380	
Cu	36-190	
Hg	0.3-10	
Ni	35-210	
Pb	85-530	
Mo	3-200	
U	42-250	
		PAHs
10 PAHs	1-40	Legislation limits for PAHs in soil,[15]

TABLE S-V. a. Risk indices (R_{ig}, R_{ih} and R_d) and hazard quotients (HQ_{ig}, HQ_{ih} and HQ_d) for three exposure routes for fly ashes from TPPs Kolubara (AKb) and Kostolac (AKs)

AKb						
	Children			Adults		
Element	R_{ig}*	R_d	R_{ih}	R_{ig}	R_d	R_{ih}
As^{cc}	8.39×10^{-5}	9.67×10^{-5}	1.07×10^{-8}	2.44×10^{-5}	2.26×10^{-4}	1.68×10^{-8}
Cd^{cc}	0.00	0.00	2.87×10^{-17}	0.00	0.00	4.49×10^{-17}
Cr^{cc}	0.00	0.00	4.25×10^{-11}	0.00	0.00	6.65×10^{-11}
Co^{cc}	0.00	0.00	1.55×10^{-9}	0.00	0.00	2.42×10^{-9}
Ni^{cc}	0.00	0.00	1.24×10^{-10}	0.00	0.00	2.26×10^{-9}
Element	HQ_{ig}*	HQ_d	HQ_{ih}	HQ_{ig}	HQ_d	HQ_{ih}
As^{ncc}	2.17	2.51	2.78×10^{-5}	1.26×10^{-1}	1.17	8.70×10^{-6}
Pb	6.83×10^{-2}	4.30×10^{-2}	8.73×10^{-7}	3.97×10^{-3}	2.01×10^{-2}	2.73×10^{-7}
Hg	5.68×10^{-2}	4.47×10^{-2}	2.54×10^{-6}	3.30×10^{-3}	2.10×10^{-2}	7.93×10^{-7}
Cd^{ncc}	2.29×10^{-4}	6.31×10^{-4}	1.03×10^{-5}	1.33×10^{-5}	2.96×10^{-4}	3.21×10^{-6}
Cr^{ncc}	5.43×10^{-1}	4.28×10^{-1}	6.95×10^{-4}	3.16×10^{-2}	2.00×10^{-1}	2.17×10^{-4}
Co^{ncc}	7.20×10^{-3}	1.42×10^{-4}	3.23×10^{-4}	4.18×10^{-4}	6.64×10^{-5}	1.01×10^{-4}
Ni^{ncc}	5.53×10^{-2}	1.13	7.07×10^{-7}	3.21×10^{-3}	5.28×10^{-1}	2.21×10^{-7}
Cu	1.53×10^{-2}	8.03×10^{-2}	1.96×10^{-7}	8.89×10^{-4}	3.76×10^{-2}	6.12×10^{-8}
AKs						
	Children			Adults		
Element	R_{ig}	R_d	R_{ih}	R_{ig}	R_d	R_{ih}
As^{cc}	7.00×10^{-5}	8.07×10^{-5}	8.95×10^{-9}	2.03×10^{-5}	1.89×10^{-4}	1.40×10^{-8}
Cd^{cc}	0.00	0.00	4.92×10^{-17}	0.00	0.00	7.69×10^{-17}
Cr^{cc}	0.00	0.00	3.25×10^{-11}	0.00	0.00	5.08×10^{-11}
Co^{cc}	0.00	0.00	1.11×10^{-9}	0.00	0.00	1.74×10^{-9}
Ni^{cc}	0.00	0.00	1.14×10^{-10}	0.00	0.00	2.08×10^{-9}
Element	HQ_{ig}	HQ_d	HQ_{ih}	HQ_{ig}	HQ_d	HQ_{ih}
As^{ncc}	1.81	2.09	2.32×10^{-5}	1.05×10^{-1}	9.79×10^{-1}	7.26×10^{-6}
Pb	7.35×10^{-2}	4.63×10^{-2}	9.40×10^{-7}	4.27×10^{-3}	2.17×10^{-2}	2.94×10^{-7}
Hg	3.70×10^{-2}	2.91×10^{-2}	1.65×10^{-6}	2.15×10^{-3}	1.36×10^{-2}	5.16×10^{-7}
Cd^{ncc}	3.93×10^{-4}	1.08×10^{-3}	1.76×10^{-5}	2.28×10^{-5}	5.07×10^{-4}	5.50×10^{-6}
Cr^{ncc}	4.14×10^{-1}	3.26×10^{-1}	5.30×10^{-4}	2.41×10^{-2}	1.53×10^{-1}	1.66×10^{-4}
Co^{ncc}	5.18×10^{-3}	1.02×10^{-4}	2.32×10^{-4}	3.01×10^{-4}	4.77×10^{-5}	7.25×10^{-5}
Ni^{ncc}	5.10×10^{-2}	1.04×10	6.52×10^{-7}	2.96×10^{-3}	4.88×10^{-1}	2.04×10^{-7}
Cu	3.13×10^{-2}	1.64×10^{-1}	4.01×10^{-7}	1.82×10^{-3}	7.70×10^{-2}	1.25×10^{-7}

* Cancer risk (*R*) and hazard quotient (*HQ*) are unitless parameters

TABLE S-V. b. Risk indices (R_{ig}, R_{ih} and R_d) and hazard quotients (HQ_{ig}, HQ_{ih} and HQ_d) for three exposure routes for fly ashes from TPP Nikola Tesla (ANT) and fluidized bed boiler (AFB)

ANT						
	Children			Adults		
Element	R_{ig}*	R_d	R_{ih}	R_{ig}	R_d	R_{ih}
As^{cc}	7.46×10^{-5}	8.60×10^{-5}	9.54×10^{-9}	2.17×10^{-5}	2.01×10-04	1.49×10-08
Cd^{cc}	0.00	0.00	1.70×10^{-17}	0.00	0.00	2.66×10-17
Cr^{cc}	0.00	0.00	4.93×10^{-11}	0.00	0.00	7.71×10-11
Co^{cc}	0.00	0.00	2.13×10^{-9}	0.00	0.00	3.33×10-09
Ni^{cc}	0.00	0.00	1.05×10^{-10}	0.00	0.00	1.91×10-09
Element	HQ_{ig}*	HQ_d	HQ_{ih}	HQ_{ig}	HQ_d	HQ_{ih}
As^{ncc}	1.93	2.23	2.47×10^{-5}	1.12×10^{-1}	1.04	7.74×10^{-6}
Pb	8.67×10^{-2}	5.46×10^{-2}	1.11×10^{-6}	5.04×10^{-3}	2.56×10^{-2}	3.47×10^{-7}
Hg	6.86×10^{-2}	5.40×10^{-2}	3.06×10^{-6}	3.99×10^{-3}	2.53×10^{-2}	9.57×10^{-7}
Cd^{ncc}	1.36×10^{-4}	3.74×10^{-4}	6.09×10^{-6}	7.89×10^{-6}	1.75×10^{-4}	1.90×10^{-6}
Cr^{ncc}	6.29×10^{-1}	4.96×10^{-1}	8.05×10^{-4}	3.66×10^{-2}	2.32×10^{-1}	2.52×10^{-4}
Co^{ncc}	9.92×10^{-3}	1.95×10^{-4}	4.45×10^{-4}	5.77×10^{-4}	9.15×10^{-5}	1.39×10^{-4}
Ni^{ncc}	4.68×10^{-2}	9.56×10^{-1}	5.99×10^{-7}	2.72×10^{-3}	4.48×10^{-1}	1.87×10^{-7}
Cu	1.77×10^{-2}	9.30×10^{-2}	2.27×10^{-7}	1.03×10^{-3}	4.36×10^{-2}	7.09×10-8
AFB						
	Children			Adults		
Element	R_{ig}	R_d	R_{ih}	R_{ig}	R_d	R_{ih}
As^{cc}	2.24×10^{-5}	2.58×10^{-5}	2.86×10^{-9}	6.50×10^{-6}	6.04×10^{-5}	4.47×10^{-9}
Cd^{cc}	0.00	0.00	0.00	0.00	0.00	0.00
Cr^{cc}	0.00	0.00	2.91×10^{-11}	0.00	0.00	4.54×10^{-11}
Co^{cc}	0.00	0.00	6.79×10^{-10}	0.00	0.00	1.06×10^{-9}
Ni^{cc}	0.00	0.00	8.08×10^{-11}	0.00	0.00	1.47×10^{-9}
Element	HQ_{ig}	HQ_d	HQ_{ih}	HQ_{ig}	HQ_d	HQ_{ih}
As^{ncc}	5.80×10^{-1}	6.68×10^{-1}	7.42×10^{-6}	3.37×10^{-2}	3.13×10^{-1}	2.32×10^{-6}
Pb	4.85×10^{-2}	3.06×10^{-2}	6.21×10^{-7}	2.82×10^{-3}	1.43×10^{-2}	1.94×10^{-7}
Hg	1.57×10^{-2}	1.23×10^{-2}	7.00×10^{-7}	9.11×10^{-4}	5.78×10^{-3}	2.19×10^{-7}
Cd^{ncc}	/	/	/	/	/	/
Cr^{ncc}	3.71×10^{-1}	2.92×10^{-1}	4.75×10^{-4}	2.16×10^{-2}	1.37×10^{-1}	1.48×10^{-4}
Co^{ncc}	3.16×10^{-3}	6.21×10^{-5}	1.41×10^{-4}	1.83×10^{-4}	2.91×10^{-5}	4.42×10^{-5}
Ni^{ncc}	3.61×10^{-2}	7.37×10^{-1}	4.62×10^{-7}	2.10×10^{-3}	3.45×10^{-1}	1.44×10^{-7}
Cu	2.51×10^{-2}	1.32×10^{-1}	3.22×10^{-7}	1.46×10^{-3}	6.18×10^{-2}	1.01×10^{-7}

* Cancer risk (*R*) and hazard quotient (*HQ*) are unitless parameters

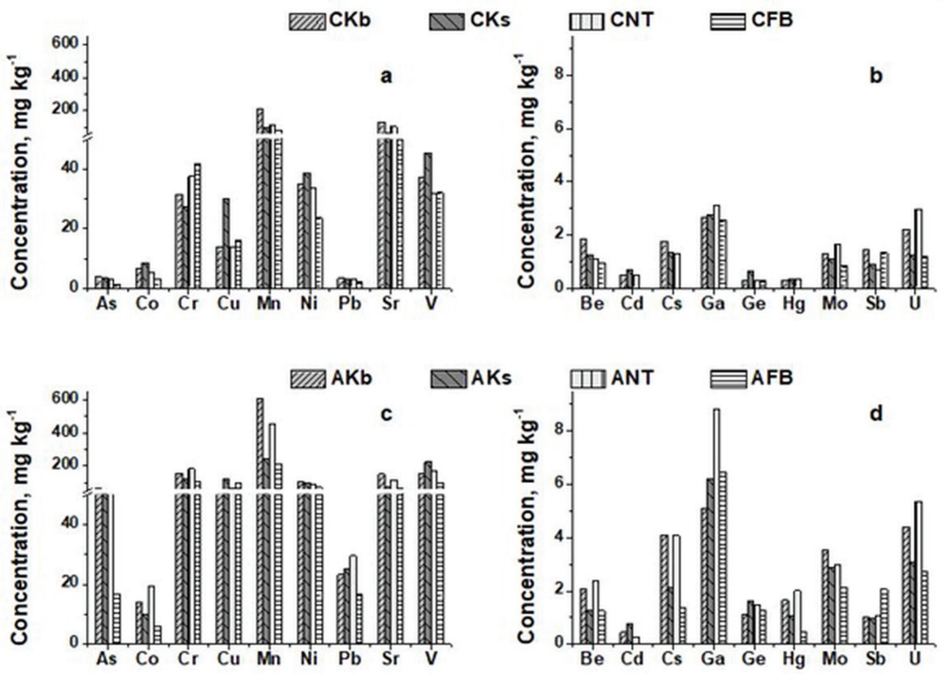

Fig. S-1. As, Co, Cr, Cu, Mn, Ni, Pb, Sr and V content in coals (a) and in fly ash samples (c); Be, Cd, Cs, Ga, Ge, Hg, Mo, Sb, U in coals (b) and in fly ash samples (d)

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